RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

July 1967



U.D.C. 547 : 547.022

ORIENTATION OF NUCLEOPHILIC ATTACK AT AN ACTIVATED DOUBLE BOND

A.N. Nesmeyanov, M.I. Rybinskaya, and L.V. Rybin

CONTENTS

I. Introduction 453

II. Mechanism of nucleophilic reactions of an ethylenic bond activated by electron-acceptor groups 453

III. Orientation of nucleophilic attack at the double bond of the X–CH=CH–Y system 455

I. INTRODUCTION

An explanation for the regularities in cyanoethylation and condensation with $\alpha\beta$-unsaturated carbonyl-containing compounds (a particular type of which is known as the Michael condensation) has been sought frequently since the time they were discovered up to the present (see earlier reviews [1-4]). The investigators were interested in a simple and cheap path of synthesis for compounds of the most varied types, many of which became available even on an industrial scale.

The main condition for the successful use of ethylene compounds in these reactions is the presence of electron-acceptor groups which activate the double bond. However, the problems of a detailed study of the influence of electron-acceptor groups on the condensation from a quantitative standpoint received attention comparatively recently. The influence on the mechanism and rate of reaction of the introduction in series with the alkene bond of additional electron-acceptor groups and of their nature has also been little studied, although even now it is clear that this influence is undoubtedly great, as the example of tetracyanoethylene has shown. The latter, as is well known, not only reacts readily with nucleophilic reagents, forming addition and substitution products, but is also the strongest of the known π-acids, capable of giving a stable anion-radical, isolated in the form of salts with various cations [5,6].

In the present brief review an attempt is made to generalise some of the properties of $\alpha\beta$-substituted ethylene systems in which the double bond is under the inconsistent action of two electron-acceptor groups. Such systems can be symmetrical (identical electron-acceptor groups) or unsymmetrical (different groups), the interest being greatest in unsaturated compounds with electron-acceptor groups conjugated with the double bond. An explanation of the regularity in the direction of the attack of the nucleophilic agent for unsymmetrical $\alpha\beta$-diactivated ethylenes is also a subject of this review.

These problems are mainly considered by the example of the compounds RCOCH=CHX, where X is CN, CO_2R, NO_2, SO_2Ar, COAr, etc. In connection with this in the present review the preparation and reactivity of compounds of this type will receive most attention.

II. MECHANISM OF NUCLEOPHILIC REACTIONS OF AN ETHYLENIC BOND ACTIVATED BY ELECTRON-ACCEPTOR GROUPS

The mechanism of the reaction of an activated double bond with nucleophilic reagents was predicted theoretically by Ingold [7] and confirmed experimentally by several authors [8-14]. According to this mechanism the rate-determining stage is the addition of the nucleophilic reagent to the β-carbon atom of the double bond relative to the electron-acceptor substituent, which can be written in general form:

$$X{-}CH{=}CH_2 + Z^- \underset{}{\overset{\text{slow}}{\rightleftharpoons}} X{-}\bar{C}H{-}CH_2{-}Z \overset{+H^+\ \text{fast}}{\rightleftharpoons} XCH_2CH_2Z.$$

The reaction rate is given by the equation:

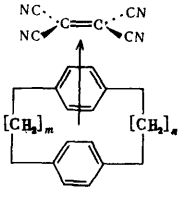
$$\frac{-d[XCH=CH_2]}{dt} = k[XCH{=}CH_2][Z^-].$$

The reactivity of monoactivated ethylenes with nucleophilic reagents is usually linked with the polarisation of the double bond[15] in these compounds, or, what is the same thing, with the presence of an appreciable positive charge on the β carbon atom of the double bond. From this standpoint the high reactivity (see Table 1) of the $\alpha\beta$-substituted† ethylenes of the *trans*-series is astonishing since the double bond in these compounds should be polarised comparatively weakly, as can be judged from the low intensity of the absorption band of the double bond in the infrared spectrum and the high intensity in the Raman spectrum[16].

The available information on the kinetics of the reaction of monosubstituted and $\alpha\beta$-disubstituted ethylenes, although meagre, allows some comparisons to be drawn. Table 1 gives data on the kinetics of the addition of methanol to an activated double bond, which show that the reaction rate is much greater than that for disubstituted ethylenes.

In this connection it is desirable to consider the molecule diagrams calculated by Shvarts[20] by the molecular orbital method for five cyano-substituted ethylenes. Table 2 gives some data from these calculations.

In examining these diagrams the positive charges on the ethylenic carbon atoms and the values of the energies of the lower vacant orbitals must be compared. Clearly the double bond is most polarised in the unsymmetrical compounds *1* and *2* (see Table 2). In these instances a considerable positive charge is concentrated on the β-carbon atoms in relation to the electron-acceptor groups. In compounds *3* and *5* there is no polarisation of the double bond (there is a small positive charge on both ethylene carbon atoms), but the level of the first vacant orbital lies considerably below that for *1* and *2*. This difference appears distinctly in the disubstituted alkenes *2* and *3*, the first of which is characterised by a strongly polarised double bond with the maximal value of the positive charge on all five cyano-substituents of the ethylenes and a higher level of the energy of the lower vacant orbital of the last four. An especially low energy level was calculated for tetracyanoethylene, in which it is close to the energy of the atomic orbital. Hence it can be seen that the accumulation of cyano-groups around the double bond lowers the energy of the first vacant orbital. This agrees well with the ability of tetracyanoethylene to form π-complexes and to give radical-anions by accepting one electron[5,6]. We note that π-π-complexes of tetracyanoethylene with *para*-cyclophanes are so stable that they could be isolated in the crystalline state[22].



orange for $m = n = 4$; red for $m = n = 6$, red-black for $m = 3$, $n = 4$.

Rather stable π-complexes are also formed by $\alpha\beta$-disubstituted ethylenes. According to Merrifield and Phillips[23], who studied complexes of maleic anhydride and *p*-quinone with pyrene (CH_2Cl_2, 22°) spectrophotometrically, the equilibrium constants for the formation of the complexes are 17.6 and 14.4 respectively. For tetracyanoethylene with the same π-base the constant is 29.5.

At the same time α- and $\alpha\alpha$-substituted ethylenes should show a very weak tendency to π-complex formation. Actually, even methylenemalononitrile forms a very weak complex with anthracene (benzene, 23°), the equilibrium constant for the formation of the complex being close to zero[24].

Unfortunately, the necessary quantitative data on the reactions of these compounds with nucleophilic reagents do not exist at present, so strict comparison with calculated data is impossible. Such comparisons would be especially interesting for methylenemalononitrile and fumarodinitrile. However, the difference in the positive charges and energy levels of the first vacant orbitals for the two types of substituted ethylenes (α and $\alpha\alpha$, or $\alpha\beta$ and $\alpha\alpha\beta\beta$) suggests that their reactions with nucleophilic reagents may have some differences in mechanism.

A possible hypothesis is that a not inconsiderable part (possibly the main part) in the mechanism of the $\alpha\beta$- and $\alpha\alpha\beta\beta$-substituted double bond is played by the ability to form π-complexes which subsequently rearrange into σ-complexes and then into the final product.

The correctness of this suggestion is confirmed by a series of experimental results. Actually tetracyanoethylene[5,6], tricyanovinyl chloride[25], dicyanobis(ethoxycarbonyl)ethylene[26], maleic anhydride[23], and esters of fumaric acid[27-29] have been separately shown to be capable of

TABLE 1. Data on the reaction kinetics for the addition of methanol to an activated double bond.

Alkene	K_{25}, litre mole^{-1} min^{-1}	Activation parameters
trans-$C_6H_5COCH{=}CHCN$[17]	425 (25°)	ΔE=13.5±1.3 kcal mole^{-1} ΔS=−11 e.u.
trans-$C_6H_5COCH{=}CHCOC_6H_5$[18]	182 (25°)	
$CH_2{=}CHCN$[13]	0.722 (25°)	ΔE=18.7 kcal mole^{-1} ΔS=−7.2 e.u.
$CH_2{=}CHCOCH_3$[19]	23.3 (19°)	

TABLE 2. Calculation of the molecular orbitals of cyano-substituted ethylenes*

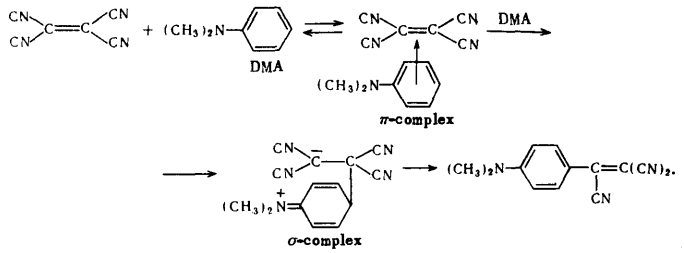
No.	Skeleton and charges on the carbon atoms of the double bond**	Energy of the lowest vacant orbital	Order of the ethylenic bond
1	−0.016 / +0.106	α−0.487β	1.886
2	−0.024 / +0.184	α−0.382β	1.802
3	+0.056 / +0.056	α−0.241β	1.784
4	+0.030 / +0.106	α−0.148β	1.704
5	+0.062 / +0.062	α−0.058β	1.638

* This table gives data calculated using Pullman and Pullman's parameters[21]

** The black circles denote CN groups, the lines C–H bonds.

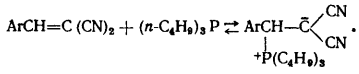
† In speaking of substituted ethylenes we will be thinking of ethylenes containing electron-acceptor substituents as well as the double bond.

forming π-complexes and of reacting with nucleophilic reagents. Rappoport and coworkers [30] have experimentally confirmed the formation of a π-complex which is an intermediate in the reaction of tetracyanoethylene with dimethylaniline. On investigating this reaction spectrophotometrically they found the rapid and reversible formation of a π-complex (K_{equil} = 15 litre mole^{-1}), which, they think, is converted into a σ-complex and then into the final product. This can be represented schematically:



Here it should be noted that a very low activation energy (5.7 kcal mole^{-1}) is found for the π-complex → σ-complex stage. Foster and Hanson suggested a similar mechanism for the reaction of tetracyanoethylene with indole [31].

On the other hand, of the α- and $\alpha\alpha$-substituted ethylenes, as noted above, even methylenemalononitrile forms a weak complex. In this connection it is interesting to consider the reaction of arylmethylenemalononitriles with tributylphosphine. In a spectrophotometric investigation of the kinetics of these reactions Rappoport and Gertler [32] observed the direct conversion of these compounds into an addition compound, having, according to the infrared spectra, the structure of a bipolar ion, which corresponds to the σ-complex:

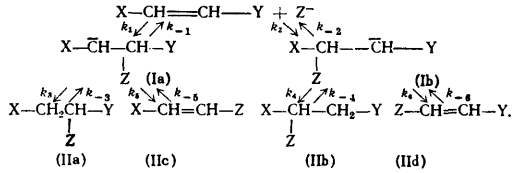


It was found that the addition product readily dissociates into the initial components. The authors did not observe any intermediate products within the sensitivity limits of the method.

Hence, on the basis of the above evidence it seems logical to suggest that the observed increase in reaction rate with methanol for $\alpha\beta$-disubstituted ethylenes in comparison with monosubstituted ones (see Table 1) can be due to the reaction with the disubstituted ethylenes proceeding through the intermediate formation of a π-complex.

III. ORIENTATION OF NUCLEOPHILIC ATTACK AT THE DOUBLE BOND OF THE X–CH=CH–Y SYSTEM

When ethylenes unsymmetrically substituted at each side react with nucleophilic reagents the orientation of the nucleophilic attack must be determined. The scheme of reaction of nucleophilic reagents with compounds of the type XCH=CH–Y, where X and Y are electron-acceptor groups, can be represented in the general form as follows:



In this, there are different probabilities of the formation of two carbanions (Ia) and (Ib). Kinetic investigations of reactions of this type undertaken by various authors [18] and by us [17,33] agree with these suggestions‡.

The stabilisation path of these carbanions will depend on several factors and above all on the nature of X and Y, on the nature of the nucleophilic substance, and on the surrounding medium. The stabilisation directions most frequently realised are§: (1) the addition of a proton or any positive species, as a result of which addition products (IIa) and (IIb) are formed; (2) ejection of an anion or neutral molecule and formation of substitution products (IIc) and (IId); (3) hydrolytic breakdown when the nucleophilic reagent is the OH^- ion. Naturally, the first stabilisation path of carbanions (Ia) and (Ib) predominates in systems where X and Y are electron-acceptor groups incapable of readily leaving in the form of anions (for example, RCO–, COOR). On the other hand, for X and Y which are easily removed in the form of stable anions (NO_2, halogens) the second path is possible. Naturally, for some examples of systems which we will consider mixed stabilisation of carbanions can occur (for example, where X is a group readily leaving as an anion and Y is not.

Let us consider additions and their energetic profile (Fig. 1), that is, that part of the general scheme by which products (IIa) and (IIb) are formed. According to the theory of the transition state, the ratio of the amounts of two kinetically controlled reaction products (P) formed from a single initial substance depends solely on the difference between the free energy levels of the two transition states and is not connected with the free energy level of the principal state (it is suggested that the reaction includes

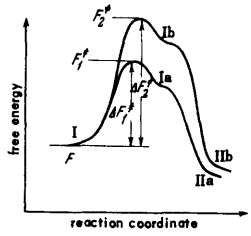
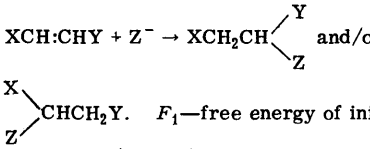


Fig. 1. Energy profile of the reaction:



and/or

F_1—free energy of initial state I; $F_1^{\neq}$ and $F_2^{\neq}$—free energies of transition states leading to the carbanions (Ia) and (Ib).

‡ The kinetic data also do not contradict the intermediate formation of a π-complex.

§ In the present work we shall consider only some of the possible stabilisation paths. For a detailed discussion of this problem see the paper of Patai and Rappoport [34].

the same kinetic expressions for the formation of both products)

$$P = \frac{k_1}{k_2} = e^{\frac{F_1^{\neq} - F_2^{\neq}}{RT}}.$$

In our particular instance the direction of attack of the nucleophile will be determined by the ratio k_1/k_2, and evidently to form a judgement about it the transition states leading to the carbanions (Ia) and (Ib) must be considered and an attempt made to evaluate their relative free energies $F_1^{\neq}$ and $F_2^{\neq}$. According to Hammond's hypothesis [35] the transition states can suggest by their structure the final products of a given stage, that is, the carbanions (Ia) and (Ib)¶ in our example and in the first rough approximation can be limited to comparison of the relative stability of the carbanions themselves, $X\overline{C}H-CHYZ$ (Ia) and $XZCH-\overline{C}HY$ (Ib) and this, in turn, for lack of other data, has to be judged from dissociation constants or from the rate constants for deuterium exchange of substituted methanes $X-CH_3$ and $Y-CH_3$. Here it is suggested that the stability of the anions depends primarily on the capability of the group directly adjoining the anionic centre to delocalisation of the negative charge. Such an approach is of course a considerable simplification, above all because it starts from these assumptions: the transition states which are formed either by the addition of negatively charged species to the double bond, or as a result of the dissociation of C–H bonds in saturated hydrocarbons, can be comparable in their structure†, that is:

$$X-CH=CH-Y+Z^- \rightleftarrows X-\overset{|}{\underset{Z}{\overline{C}H}}-CH-Y \rightleftarrows X-\overset{|}{\underset{Z}{CH_2}}-Y.$$

Moreover, this approach makes no allowance whatsoever for the fact that steric factors for groups ZYCH in (Ia) and ZXCH in (Ib) and solvents (especially strongly solvating anions) can have a significant influence on the formation of carbanions. Furthermore, the possibility of interaction between the groups themselves which enter into the carbanion and the formation of cyclic transition states can be of great importance. However, this approach can be useful to a certain extent since it is valid for many reactions, which will be considered below.

It is noteworthy that for most substitutions where the heterolysis of the C–X or C–Y bond in the stabilisation of carbanions (Ia) and (Ib)—with the formation of the products (IIc) and (IId)—takes place very readily (where the group leaving is a halogen or NO_2), the energy profile can relate solely to what has been discussed. However, a more complex example is presented by substitutions in which the heterolysis of the C–X(Y) bond proceeds slowly. Fig. 2 shows the generalised picture of the energy profile for such reactions.

There are several experimental facts which agree with the above ideas on the orientation of attack by a nucleophile at an ethylenic double bond activated at each side. We will restrict discussion mainly to those instances for which the dissociation constants of the corresponding substituted methanes or the rates of their deutero-exchange are known.

¶ According to the results of most of the kinetic investigations, the addition of nucleophilic reagents at an activated double bond leading to the formation of carbanions is the limiting stage of the process [7–14]. The rapid second stage of protonation proceeds in practice with a low activation energy [36].

† Possibly a more complete introduction to the transition state in these examples can be given by a study of the secondary α-isotopic effect [37,38].

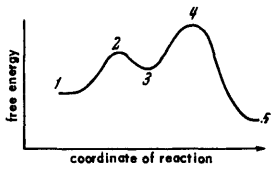


Fig. 2. Energy profile of the reaction: XCH=CHY + Z^- → XCH=CHZ and/or ZCH=CHY where the heterolysis of the C–X(Y) bond is slow.
1) Initial state; 2) transition state leading to carbanion 3; 4) transition state of heterolysis of the C–X(Y) bond; 5) final state.

On comparing the dissociation constants of nitromethane ($K_{CH_3NO_2} = 6 \times 10^{-11}$) [39] and acetic acid ($K_{CH_3CO_2H} = 10^{-24}$) [39] (see Table 3), it can be predicted that β-nitroacrylic acid will add on nucleophilic reagents in the following manner:

$$NO_2CH=CHCOOH+HZ \rightarrow NO_2\underset{Z}{\overset{|}{CH_2}}CHCOOH.$$

In fact, Shechter and coworkers [42] have shown that this acid adds on methanol and water with the formation of products of this structure. It is important to note that the addition of methanol proceeds very easily even in the absence of basic catalysts.

On studying the deuterium exchange of *cis*- and *trans*-arylsulphonylacrylic acids in D_2O–NaOD medium by NMR spectra, Montanari and coworkers [43] found that the β-H is exchanged first, then the α-H, and addition products with deuterium oxide (III) and (IV) are formed:

$$ArSO_2CH=CHCOOH \rightarrow ArSO_2CD=CHCOOH \rightarrow ArSO_2CD=CDCOOH$$
$$\downarrow D_2O \qquad \downarrow D_2O$$
$$ArSO_2CD_2\underset{OD}{\overset{|}{C}}HCOOH \qquad ArSO_2CD_2\underset{OD}{\overset{|}{C}}DCOOH.$$
$$\text{(III) 20\%} \qquad \text{(IV) 80\%}$$

In H_2O–NaOH solution (III) exchanges all the deuterium atoms for hydrogen, but (IV) under the same conditions retains one deuterium atom, which rules out alternative structures for the β-hydroxy-acids in which after the exchange one or two deuterium atoms respectively should remain. Although in the sulphonyl-substituted methane series the dissociation constant is known only for dimethylsulphone ($K_{CH_3SO_2CH_3} = 10^{-23}$) [39] there will be no great error in taking the dissociation constant for $CH_3SO_2C_6H_5$ to be close to this value.

TABLE 3. Dissociation constants for substituted methanes.

Substituted methane	Dissociation constant of the C–H bond	Reference	Substituted methane	Dissociation constant of the C–H bond	Reference
CH_3NO_2	$6.1 \cdot 10^{-11}$	39	$(CF_3)_2CFH$	10^{-20}	40
CH_3COCH_2COOR	$2.1 \cdot 10^{-11}$	39	$CH_3SO_2CH_3$	10^{-23}	39
$(CF_3)_2CH$	10^{-11}	40	CH_3COOH *	10^{-24}	39
$CH_2(CN)_2$	$6.5 \cdot 10^{-12}$	39	$CH_3COOC_2H_5$	$10^{-24.5}$	39
$CH_2(COOC_2H_5)_2$	$5 \cdot 10^{-14}$	39	CH_3CN	10^{-25}	39
$C_6H_5COCH_3$	10^{-19}	41	CH_3CONH_2*	10^{-25}	39
CH_3COCH_3	10^{-20}	39	$CF_3(CF_2)_2CF_2H$	10^{-30}	40

* Here, naturally we refer to constants for dissociation with the formation of the anions $^-CH_2CO_2H$ and $^-CH_2CONH_2$ and not $CH_3CO_2^-$ and $CH_3C\overline{O}NH$.

Trichloromethylnitroethylene[3,3,3-trichloro-1-nitroprop-1-ene] also exhibits an extremely electrophilic double bond and with nucleophilic reagents it gives addition products [44-49] of the expected structure:

$$CCl_3CH{=}CHNO_2 + HZ \rightarrow CCl_3\underset{\displaystyle Z}{\underset{|}{C}}HCH_2NO_2$$

where HZ = amines, alcohols.

By the action of hydrogen chloride upon it, Dornow and coworkers [50] obtained an α-chloro-oxime, for the formation of which they proposed the following mechanism:

$$CCl_3CH{=}CHNO_2 + HCl \longrightarrow \underset{\displaystyle Cl}{\underset{|}{CCl_3}}CHCH_2NO_2 \longrightarrow$$

$$\longrightarrow CCl_3{-}\underset{\displaystyle Cl}{\underset{|}{C}}H{-}CH{=}\overset{+}{N}\begin{matrix}O^-\\ \diagup\\ \diagdown\\ OH\end{matrix} \xrightarrow{HCl} CCl_3CHCH{=}NOH.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Cl$$

Perfluoroalkylnitroethylenes react‡ in an analogous fashion [51,52]:

$$R_fCH{=}CHNO_2 + HZ \longrightarrow R_f\underset{\displaystyle Z}{\underset{|}{C}}HCH_2NO_2,$$

where $R_f = CF_3$, C_3F_7, and HZ = $CH_2(CO_2R)_2$, C_2H_5OH, p-$NH_2C_6H_4CO_2H$, CH_3NO_2, or RMgX.

By studying the addition of water and ammonia to β-trifluoromethylacrylic acid and its derivative (V), Walborsky and coworkers [53,54] explained their results by the ability to stabilise the neighbouring anionic centre in the transition state being less for the CF_3 group than for the CO_2H, CO_2R, or $CONH_2$ groups. McBee and coworkers carried out an analogous work [55]:

$$CF_3CH{=}CHCOOR + HZ \longrightarrow CF_3\underset{\displaystyle Z}{\underset{|}{C}}HCH_2COOR.$$

(V)

Knunyants and Cheburkov [56] and McBee and coworkers [57] found that the methyl ester of 3-methyl-4,4,4-trifluorocrotonic acid (VI) adds on nucleophilic reagents as follows:

$$\begin{matrix}F_3C\\ \diagup\\ H_3C\end{matrix}C{=}CHCOOCH_3 + HZ \longrightarrow \begin{matrix}F_3C\\ \diagup\\ H_3C\end{matrix}\underset{\displaystyle Z}{\underset{|}{C}}{-}CH_2COOCH_3.$$

(VI)

As Table 3 shows, the attachment of CF_3 groups sharply raises the acidity of the hydrogen atoms in the α-position. In accordance with this ethyl $\beta\beta$-bis(trifluoromethyl)acrylate (VII) reacts according to the scheme [58]:

$$\begin{matrix}F_3C\\ \diagup\\ F_3C\end{matrix}C{=}CHCOOR + HZ \longrightarrow \begin{matrix}F_3C\\ \diagup\\ F_3C\end{matrix}\underset{\displaystyle Z}{\underset{|}{C}}H{-}CHCOOR.$$

(VII)

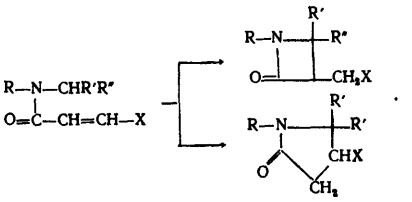
On determining the relative rate of formation of anions from deuterohaloforms, Hine and coworkers [59] found that in their ability to accelerate this reaction the halogens are arranged in the following order: I ~ Br > Cl > F. Slaugh and Bergman [60] came to similar conclusions in studying the kinetics of deuterium exchange in haloforms. This suggests that fluorine atoms stabilise neighbouring anionic centres worse than the other halogens. In this connection it is interesting to note that dichlorodifluoroethylene and chlorotrifluoroethylene add on nucleophilic reagents thus [61-63]:

$$CF_2{=}CCl_2 + HZ \rightarrow ZF_2C{-}CHCl_2$$
$$CF_2{=}CFCl + HZ \rightarrow ZF_2C{-}CHClF \quad .$$

The following results evidently also fit into the framework of the rule being considered [64]:

$$(AlkO)_2\overset{O}{\underset{}{P}}{-}CH{=}CHCOOR + H{-}P\overset{O}{\underset{(OAlk)_2}{}} \rightarrow ROCOCH_2CH\left[P\overset{O}{\underset{(OAlk)_2}{}}\right]_2.$$

Bose and coworkers [65] observed an interesting dependence of cyclisation upon the nature of substituent X in β-substituted acrylamides. They found that in cyclisation instead of the γ-lactams usually obtained, β-lactams are formed when X = CO_2R or p-$NO_2C_6H_4$:



The most extensive study of the orientation of the addition of nucleophilic reagents was made for the RCOCH=CHX system, where X represents an electron-acceptor group; therefore we will consider these examples in somewhat greater detail. It is noteworthy that there is a general method of making most of these compounds, based on the reaction known as β-ketovinylation§.

β-Ketovinylation can be effected in two ways, which differ in principle. The first is based on nucleophilic substitutions, mainly in β-chlorovinyl ketones¶ and in β-acylvinyltrimethylammonium salts. In the second, which has been comparatively little developed, nucleophilic addition to the triple bond of ethynyl ketones is employed [73-75]:

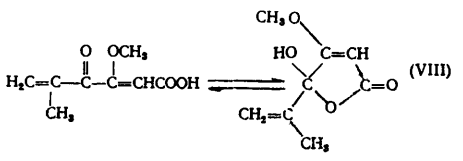
$$\begin{matrix}RCOCH{=}CHCl & [\text{or } \overset{+}{N}(CH_3)_3] & \xrightarrow{X^-}\\ RCOC{\equiv}CH & \xrightarrow{HX} & \end{matrix} RCOCH{=}CHX \ .$$

Note that as the present authors have shown in various papers it is best to use β-acylvinyltrimethylammonium salts for the ketovinylation of anions [76-80].

The chemistry of the β-acylacrylic acids† started to develop extremely rapidly after it had been observed that antibiotic action was exhibited by a series of compounds containing the grouping

$$-CO{-}\underset{|}{C}{=}C{-}COOH,$$

especially penicillic acid (VIII): [154]



(VIII)

‡ Andreades [40] gives $K = 10^{-30}$ for $CF_3[CF_2]_5CF_2H$. Evidently it can be assumed that the dissociation constants of CF_3CH_3 and $C_3F_7CH_3$ will be even smaller.

§ The term ketovinylation implies the introduction of the residue RCOCH=CH into the molecule. This term was proposed by Kochetkov [66].

¶ The chemistry of the β-chlorovinyl ketones has been presented in several reviews [66-71] and in a book [72].

† Preparation described elsewhere [81-153].

Since many authors thought that the antibiotic action of these compounds is based on the ability of easily adding on the active SH–, and possibly >NH, groups of bacterial enzymes, the β-acylacrylic acids and their derivatives were studied intensively in pharmacology. They were actually shown to be active against a series of gram-positive and gram-negative bacteria[93,95,144,155-159] and in some instances they showed fungicidal activity[94]. The nucleophilic reactions of the β-acylacrylic acids take place very readily and were investigated for a wide range of nucleophilic reagents. On comparison of the dissociation constants of acetophenone ($K_{C_6H_5COCH_3} = 10^{-19}$) [41] and of acetic acid, its amide, and esters ($K_{CH_3CO_2H} = 10^{-24}$, $K_{CH_3CONH_2} = 10^{-25}$, and $K_{CH_3CO_2R} = 10^{-24.5}$), [39] it can be suggested that addition products of the following structure are formed:

$$RCOCH{=}CHCOOR' + HZ \rightarrow RCOCH_2\underset{\displaystyle Z}{\underset{|}{C}}HCOOR\ .$$

Actually in most of the investigations‡ it was found that as a result of the reaction of the β-acylacrylic acids or their derivatives with nucleophilic reagents, α-substituted β-acylpropionic acids are formed. For example, even in the first work on the investigation of the properties of β-benzoylacrylic acid[168] it was shown that it readily adds on water, sodium cyanide, ammonia, aniline, hydrogen halides§, and that the general scheme of reaction can be represented as above. Sodium sulphite also adds on similarly[92,170].

Cromwell and coworkers[171,172] studied the reaction of methyl β-benzoylacrylate with primary and secondary amines:

$$C_6H_5COCH{=}CHCOOCH_3 + HNR_1R_2 \rightarrow C_6H_5COCH_2\underset{\displaystyle NR_1R_2}{\underset{|}{C}}HCOOCH_3.$$

The study of the various conversions of the reaction products and above all their reduction to α-amino-γ-phenylbutyric acids, showed that amines add on in the α position to the methoxycarbonyl group.

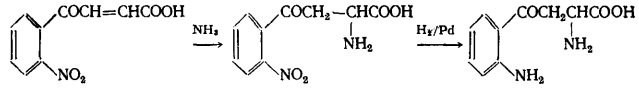
The reaction of β-aroylacrylic acids with ammonia proceeds in a similar manner[149,152,168,173]. The structure of the addition product of β-benzoylacrylic acid and ammonia:

$$ArCOCH{=}CHCOOH + NH_3 \rightarrow ArCOCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH$$

was shown by the yield of the known β-benzoyl-α-hydroxypropionic acid under the action of nitrous acid:

$$C_6H_5COCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH \xrightarrow{HNO_2} C_6H_5COCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCOON\ .$$

The ability of β-aroylacrylic acids to add on ammonia was used in several studies to make *dl*-kynurenine and some of its derivatives[81,149-153]:



It is known that *l*-kynurenine—a natural α-amino-acid—plays an important part in the genetic formation of pigments in insects[174] and is also the main product of the metabolism of tryptophan in the organism of mammals and micro-organisms[174,175]. Kynurenine was first synthesised by Butenandt[176,177], who also established its structure.

It was shown that β-benzoylacrylamide also readily adds on aniline[178]:

$$C_6H_5COCH{=}CHCONH_2 + NH_2C_6H_5 \rightarrow C_6H_5COCH_2\underset{\displaystyle NHC_6H_5}{\underset{|}{C}}HCONH_2.$$

Bougault and Chabrier[179] investigated the reaction of β-benzoylacrylic acid with thiols and found that the orientation of nucleophilic attack is here the same as for amines

$$C_6H_5COCH{=}CHCOOH + RSH \rightarrow C_6H_5COCH_2\underset{\displaystyle SR}{\underset{|}{C}}HCOOH.$$

Additions of cysteine can also be classified as this type of reaction[95]. Reactions of β-aroylacrylic acids with alcohols have been somewhat less studied. Here reference can be made to the work of Lutz and Scott[180,181] and also to Rice's earlier paper[182], where it was assumed that methanol adds on in the α position to the carboxyl group:

$$ArCOCH{=}CHCOOH + CH_3OH \longrightarrow ArCOCH_2\underset{\displaystyle OCH_3}{\underset{|}{C}}HCOOH.$$

It was found[166,168] that in acid medium water adds on to β-benzoylacrylic acid with the formation of β-benzoyl-α-hydroxypropionic acid:

$$C_6H_5COCH{=}CHCOOH + H_2O \xrightarrow[H^+]{} C_6H_5COCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCOOH\ .$$

At the same time aqueous alkali solutions bring about hydrolytic splitting of the double bond[85,167,168,183,184]:

$$C_6H_5COCH{=}CHCOOH + H_2O \xrightarrow[OH^-]{} C_6H_5COCH_3 + CHOCOOH\ .$$

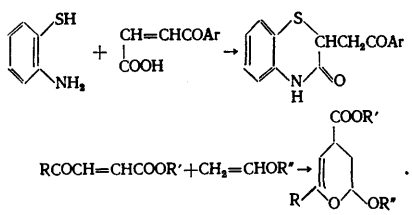
According to the generally accepted mechanism of similar reactions[185-189] the rate-limiting stage of the reaction is the addition of hydroxide ion to the double bond, as a result of which a carbanion (IX) is formed. The formation of acetophenone thus demonstrates that here the usual direction of nucleophilic attack is retained:

$$C_6H_5COCH{=}CHCOOR + OH^- \longrightarrow C_6H_5C\bar{O}CH\underset{\displaystyle OH}{\underset{|}{C}}HCOOR \rightleftarrows$$

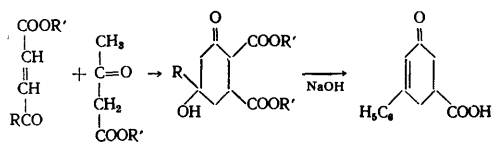
(IX)

$$\rightleftarrows C_6H_5COCH_2\underset{\displaystyle O^-}{\underset{|}{C}}HCOOR \longrightarrow C_6H_5C\bar{O}CH_2 + CHOCOOR.$$
$$\qquad\qquad\qquad

is known, and for many of these it is natural to postulate initial addition at the α-carbon atom of the double bond [193-194], for example:

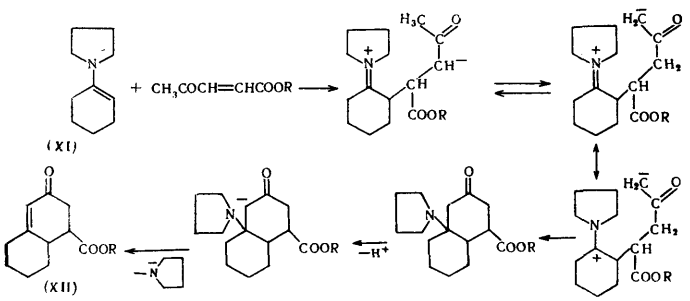


Julia and Bonnet [190] proposed to use the condensation of β-acylacrylic acids (or esters) with acetoacetic ester in the presence of basic catalysts for the synthesis of substituted cyclohexenones. It was shown, by the example of β-benzoylacrylic ester, that the reaction proceeds through an intermediate cyclic addition product (X), which under the action of alkali leads to a 3-substituted 5-carboxycyclohex-2-en-1-one. The ester of this acid is readily dehydrogenated into an ester of 3-hydroxy-5-phenylbenzoic acid, which also confirms its structure:

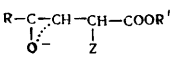


(X)

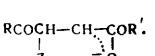
The diethylamide of acetoacetic ester reacts analogously [190]. In a brief communication Stork and Landesman [195] described the reaction of ethyl β-acetylacrylic acid with an enamine (XI), as a result of which a bicyclic product (XII) was isolated:



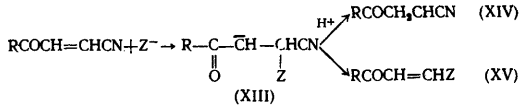
Hence all the known reactions of β-acylacrylic acids with nucleophilic reagents are characterised on the one hand by the ease with which they take place (apparently connected with the marked electron impoverishment of the ethylene bond in these compounds) and on the other by the invariable direction of attack by the nucleophile, which is probably explained by the stability of the carbanion of type



which is formed being greater than that of the carbanion



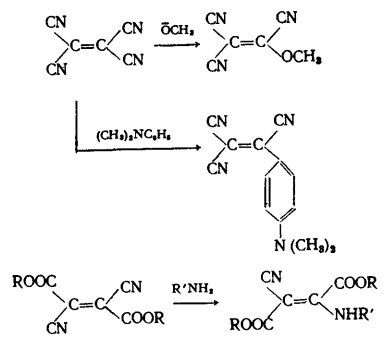
For β-cyanovinyl ketones [76] (the nitriles of β-acylacrylic acids) the expected direction of attack by the nucleophilic reagent:



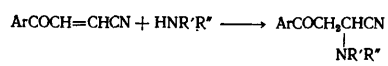
(XIII)

is the same as for the β-acylacrylic acids.

Let us remember that ($K_{C_6H_5COCH_3} = 10^{-19}$) [41] and ($K_{CH_3CN} = 10^{-25}$). [39] Actually in all the instances studied only one reaction product was observed in the reaction medium and this product contained the nucleophilic moiety in the β position to the carbonyl group, as was confirmed by thin-layer chromatography. However, unlike the β-acylacrylic acids, the intermediate carbanion (XIII) which is formed in attack by the nucleophile Z^- can be stabilised in two ways, giving addition product (XIV) as a result of protonation (Fig. 1 can represent the energy profile) and the substitution product (XV) as a result of possible heterolysis of the C–CN bond (energetic profile of Fig. 2). It is noteworthy that replacement of the CN group at an activated double bond has been observed repeatedly in the reactions of tetracyano-1,2-diethoxycarbonylethylene [5,196] and 1,2-dicyano-1,2-diethoxycarbonylethylene [197] with certain nucleophilic reagents:

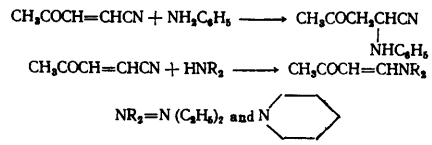


Nesmeyanov and Rybinskaya [178,198] showed that the reaction of β-cyanovinyl ketones with amines (primary and secondary) takes place very readily on simple mixing of the reagents in an appropriate solvent, as for β-acylacrylic acids. In this way aryl β-cyanovinyl ketones give an addition product in high yield. The method can serve as a preparative path for the synthesis of α-amino-γ-ketonitriles·

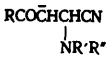


The structure of these compounds was shown by hydrolysis, which yielded known α-amino-β-benzoylpropionic acids.

However, methyl β-cyanovinyl ketone gives an addition product only with aniline [178], and the reaction is slower than for the aryl β-cyanovinyl ketones. Substitution products are formed with diethylamine and piperidine [198]:

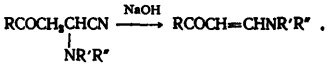


The latter is evidently explained by aliphatic amines being stronger bases than aniline, so that the equilibrium is more displaced towards the intermediate carbanion (XVI),

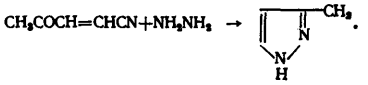


(XVI)

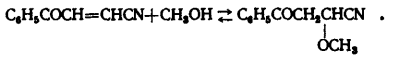
as a result of which the possibility of heterolysis of the C–CN bond is increased. It is therefore natural that the action of bases stronger than the amines (for example, alkalis) on the addition products should result in the loss of a molecule of hydrogen cyanide [178,198]:



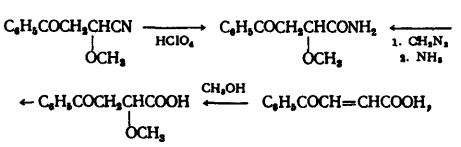
It is interesting to note that β-cyanovinyl methyl ketone, like β-chlorovinyl methyl ketone [199], gives 3-methylpyrazole with hydrazine:



Nesmeyanov and coworkers [17] showed that in the presence of basic catalysts *cis*- and *trans*-β-cyanovinyl phenyl ketones [200] add on methanol to form β-benzoyl-α-methoxypropionitrile:



This was hydrolysed by 70% perchloric acid to give the β-benzoyl-α-methoxypropionamide:

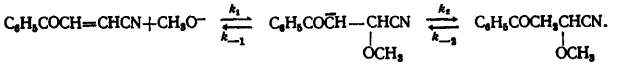


which was obtained by counter-synthesis from β-benzoylacrylic acid. Consequently the direction of the addition of methanol to β-cyanovinyl phenyl ketone is the same as to β-benzoylacrylic acid. The addition of methanol to *cis*- and *trans*-β-cyanovinyl phenyl ketones seemed a convenient method for the investigation of kinetics and mechanism [17]. Spectrophotometric studies of the kinetics showed that the reaction is reversible, but the equilibrium is strongly displaced to the side of the addition product and the equilibrium position is almost independent of the pH of the medium but dependent upon temperature (at 10° there is 90% addition, at 25°, 85%). It was found that the reaction is of first order in both *cis*- and *trans*-β-cyanovinyl phenyl ketones and first order in methoxide ion¶.

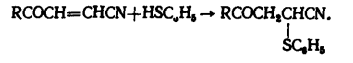
From a comparison of the second-order rate constants at 25°, k_1, *trans* = 425 litre mole^{-1} min^{-1} and k_1, *cis* = 260 litre mole^{-1} min^{-1} it is evident that there is a not very marked relation between the reaction rate and the geometrical isomerism in the β-cyanovinyl phenyl ketones.

¶ See Table 1 for the activation parameters.

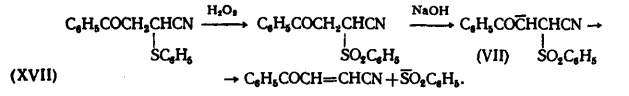
The experimental results agree with the reaction mechanism, which postulates a slow attack by the methoxide anion in the first stage with subsequent rapid protonation of the carbanion formed:



Alkyl and aryl β-cyanovinyl ketones add on thiophenol, the reaction being accelerated by the presence of bases, as a result of which β-acyl-α-phenylmercaptopropionitriles are formed in high yield [201]:

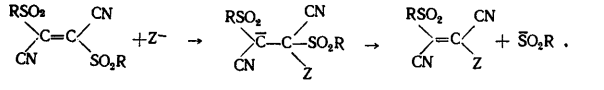


The structure was shown by the hydrolysis into the known β-aroyl-α-phenylmercaptopropionic acids. The β-acyl-α-phenylmercaptopropionitriles are oxidised by peroxide to the corresponding sulphones, which are more stable than the initial phenylmercapto-derivatives. It is interesting that when alkali acts on the latter there is an elimination of benzene sulphinic acid, which is evidently evidence that the heterolysis of the C–$SO_2C_6H_5$ bond in the carbanion (XVII) formed as intermediate is easier than the heterolysis of the C–CN bond:

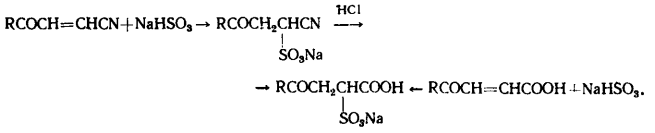


(XVII)

Probably it is for the same reason that when 1,2-dicyano-1,2-disulphonylethylene reacts with nucleophilic reagents a sulphonyl group and not a nitrile group is replaced [202]:

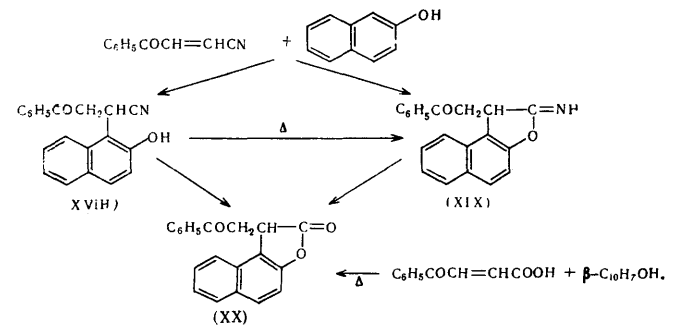


Aryl β-cyanovinyl ketones also add on sodium hydrogen sulphite very readily in aqueous alcoholic medium [178]. When the addition products are boiled with concentrated hydrochloric acid the monosodium salts of β-aroyl-α-carboxyethanesulphonic acids are formed, which can be obtained by direct synthesis from β-aroylacrylic acids [92,170]:

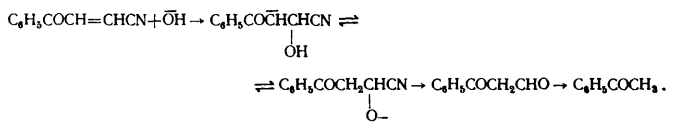


β-Cyanovinyl phenyl ketones react with 2-naphthol in the presence of catalytic quantities of calcium hydroxide [198]. When the reaction is carried out in 10 : 1 water–dioxan mixture in the cold in the presence of calcium hydroxide, β-benzoyl-α-(2-hydroxynaphthyl)propionitrile (XVIII) is formed. However, the same reaction at room temperature in 1 : 9 water–dioxan mixture with addition of catalytic amounts of calcium oxide gives a cyclic addition product, the imine of 1-*H*-1-phenacylnaphtho[2,1-*b*]furan-2-one (XIX). On hydrolysis with hydrochloric acid, (XVIII) and (XIX) are converted into 1-*H*-1-phenacylnaphtho[2,1-*b*]furan-2-one

(XX), which was also obtained by fusion of β-benzoylacrylic acid with 2-naphthol:

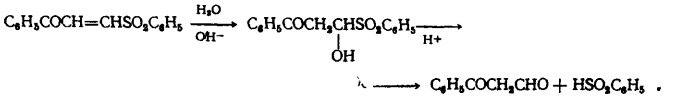


As might be expected, under the action of aqueous alkali β-cyanovinyl phenyl ketones decompose with the formation of acetophenone[78]:

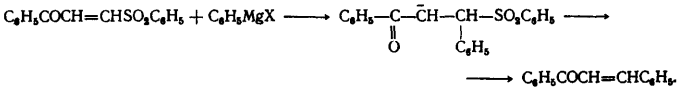


The addition of nucleophilic species in the β position to the carbonyl group is also characteristic for the αβ-unsaturated ketosulphones[73-75,80,203,204] $RCOCH{=}CHSO_2C_6H_5$ ($K_{C_6H_5COCH_3} = 10^{-19}$ and $K_{CH_3SO_2CH_3} = 10^{-23}$).[39,41] As already noted, there is a possibility of heterolysis of the C–SO_2R bond from the β position to a negatively charged atom in the intermediate carbanion. Therefore for αβ-unsaturated ketosulphones the formation of addition and substitution products is to be expected. However, the reactions of β-benzoylvinyl sulphone have only been investigated for a limited number of examples.

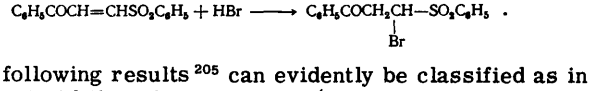
Kohler and Larsen[204] found that the addition of water is catalysed by bases. The addition product obtained decomposes into benzoylacetaldehyde and benzenesulphinic acid:



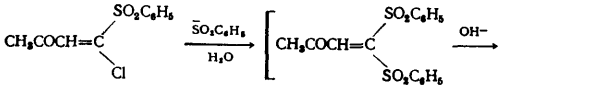
In the reaction with a Grignard reagent the main product is a chalcone[204]:

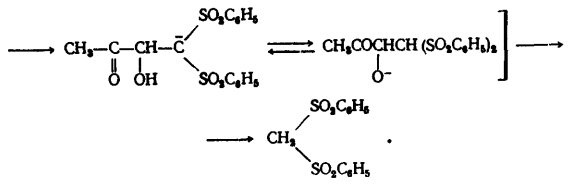


The same authors found that the addition product of hydrogen bromide has the structure of 2-benzoyl-1-bromoethyl phenyl sulphone[204]:

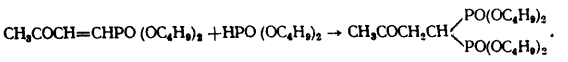


The following results[205] can evidently be classified as in agreement with the rule stated above (note that $K_{CH_2(SO_2CH_3)_2} = 10^{-14}$):[39]



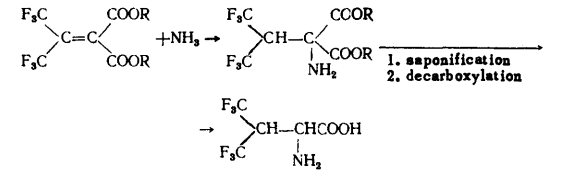


Note also the work of Kreutzkamp and Schindler[206], who showed that dibutyl 2-acetylvinylphosphonate adds on dibutyl phosphite to form tetrabutyl 2-acetylethane-1,1-diphosphonate:

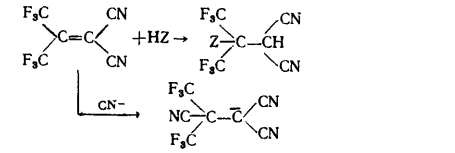


Hence the examples mentioned can serve as illustrations of the position stated above: that the direction of nucleophilic attack in XCH=CHY systems can be judged by comparison of the dissociation constants of the corresponding substituted methanes.

However, the above approach does not always fit the experimental facts. For example, it is inapplicable to ethylenic systems which contain several bulky substituents at the double bond, capable of delocalisation of the neighbouring anionic centre, mainly owing to the conjugation effect. As Ch'en and coworkers[207] showed, the reverse of the expected direction of attack of the nucleophile occurs for hexafluoroprop-2-ylidenemalonic ester with ammonia ($K_{(CF_3)_2CH_2} \simeq 10^{-20}$†, $K_{CH_2(CO_2R)_2} = 10^{-14}$).

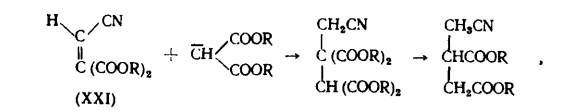


The structure of this product was convincingly demonstrated by conversion into hexafluorovaline, which was known already. At the same time, nucleophilic reagents add on in the expected direction to 1,1-dicyano-2,2-bis-(trifluoromethyl)ethylene, in which the ethoxycarbonyl groups have been replaced by more compact CN groups ($K_{CH_2(CN)_2} = 10^{-12}$).[39] As Middleton has shown[208] 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene reacts with aniline, water, and cyanide ion as follows:



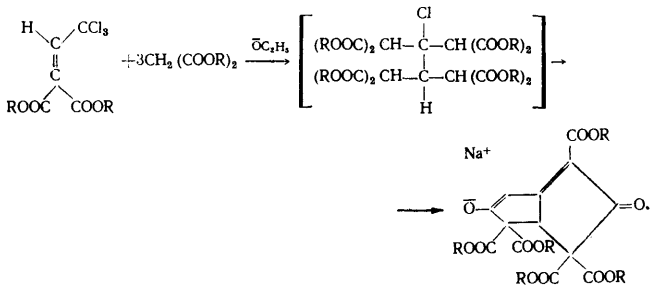
where Z = OH or NHC_6H_5.

Uchibayashi's results[209] also do not fit within the framework of the proposed hypothesis. He studied the reaction of cyanomethylenemalonic ester (XXI) with sodiomalonic ester ($K_{CH_3CN} = 10^{-25}$ and $K_{CH_2(CO_2R)_2} = 10^{-14}$):[39]

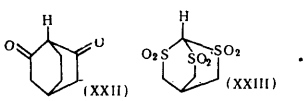


† Andreades[40] gives $K = 10^{-20}$ for $(CF_3)_2CFH$; it can be assumed that $K_{(CF_3)_2CH_2}$ will be even less.

However, the replacement in this example of the cyano-group by the CCl_3 group‡, which is considerably less capable of stabilising a negative charge, leads to a product with the expected orientation of attack by a nucleophile[210-215]:

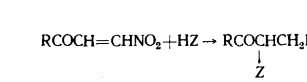


These examples show the great importance of secondary steric effects for the type of reaction being investigated[216]. Actually, if the electron-acceptor substituents, which delocalise the negative charge mainly by a conjugation effect, cannot occupy a planar position in the transitional complex owing to interference with the sides of other groups, then the stabilisation of the anionic centre of such substituents is much worse, which can also lead to orientation of the attack of the nucleophile opposite to what is expected. Naturally, secondary spatial effects do not play a large part for groups which stabilise the anionic centre mainly by an induction effect (such as $CHal_3$, SO_2R, etc.). Probably for these very reasons bicyclo[2,2,2]octane-2,6-dione (XXII) is devoid of acidic properties[217], although it is a 1,3-diketone, whereas the trisulphone (XXIII) exhibits high acidity[218]:



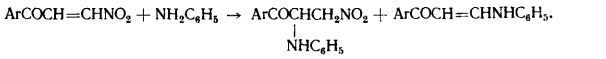
It is noteworthy that the addition of the bulky anion of malonic ester to the carbon atom of cyanomethylenemalonic ester (XXI), which is already carrying two carboxyl groups[209], shows that primary steric effects play such a small part in this type of reaction[216]. The minor part played by these effects is also demonstrated by the example already given of the addition of amines to esters of β-trifluoromethylacrylic (V), β-trifluoromethylcrotonic (VI), and ββ-bis-(trifluoromethyl)acrylic (VII) acids. Whereas introduction of a CH_3 group into the β position of the first of the esters mentioned has no effect on the orientation in the addition, replacement of the methyl group by CF_3 in the second leads to a change in the direction of nucleophilic attack. Hence the orientation of nucleophilic addition is mainly due to electronic influences, not steric.

It was stated earlier that the approach to the problem of the orientation of nucleophilic attack from the position of a determination of the stability of carbanions from the dissociation constants of the corresponding substituted methanes is a crude simplification in many respects. Thus, in clear contradiction to this there is the example of the reactions of aryl β-nitrovinyl ketones. Although a comparison of $K_{CH_3NO_2} = 6.1 \times 10^{-11}$ and $K_{C_6H_5COCH_3} = 10^{-19}$ suggests that the direction of attack of nucleophilic reagents can be represented as follows:



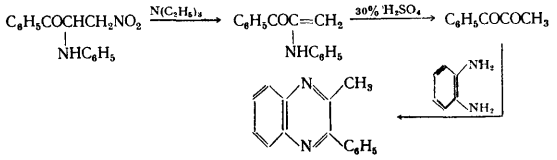
in reality, in addition to the products of the expected direction, products of the reverse orientation (and sometimes solely of the reverse orientation) are formed; it can be noted that for methanol[33,78] and aniline[219] both products belong to the kinetically controllable type.

Our own studies have repeatedly shown enhanced electrophilic nature of the ethylenic bond in these compounds. It was established that the reaction of aryl β-nitrovinyl ketones with aniline is exothermic[219]. As a result a mixture of the aryl α-anilino-β-nitroethyl ketone and the β-anilinovinyl aryl ketone is formed and the ratio of the products in the mixture depends on the nature of the substituent in the benzene ring:



As Table 4 shows, the introduction of electronegative substituents (*p*-NO_2, *p*-Br) facilitates attack by the nucleophilic reagent at the β-carbon atom, and of electron donor ones (*p*-CH_3) at the α position.

Unfortunately, the dissociation constants of acetophenones substituted in the nucleus have not been determined. However, it is known that their enolisation, which is catalytically based, varies in the order H < *p*-Hal < *p*-NO_2.[220] The products liberated are kinetically controllable and cannot be interconverted. Thus under the action of bases α-anilino-β-nitroethyl phenyl ketone loses nitric acid, as a result of which α-anilinovinyl phenyl ketone is formed, the structure of which is shown by hydrolysis to methyl phenyl diketone:



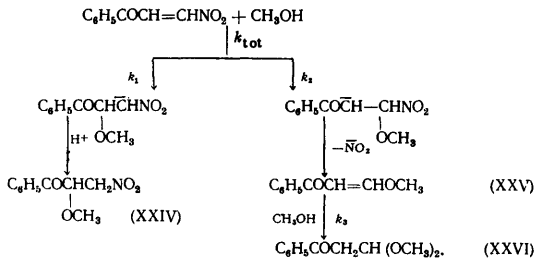
The dual direction of attack of the nucleophile was also observed by the example of the reaction of *trans*-phenyl

TABLE 4. Proportions of the products of the reaction of aryl 2-nitrovinyl ketones with aniline.

Ar	Proportions of the products of the reaction, mole %	
	aryl 1-anilino-2-nitroethyl ketone	aryl 2-anilinovinyl ketone
p-$CH_3C_6H_4$	> 95	< 5
C_6H_5	92	8
p-BrC_6H_4	60	40
p-$NO_2C_6H_4$	0	100

‡ Even if in this reaction chlorine atoms are first replaced by malonic ester residues, then this would have little effect on the capability of the $-CCl[CH(CO_2R)_2]_2$ group to stabilise the neighbouring anionic centre in comparison with the CCl_3 group.

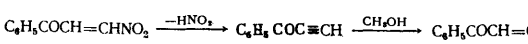
β-nitrovinyl ketone with methanol[78]. The reaction can be represented as follows:



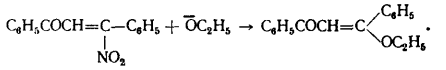
It takes place very readily and does not require a basic catalyst. Kinetic studies[33] showed that the reaction is pseudounimolecular in *trans*-phenyl β-nitrovinyl ketone and its overall rate (k_{tot}) considerably exceeds the rate of addition of methanol to other αβ-disubstituted ethylenes (see Table 5). It appeared that the reaction of β-nitrovinyl phenyl ketone proceeds irreversibly in both directions.

Moreover, it was found that the rate of formation of α-methoxy-β-nitroethyl phenyl ketone (XXIV) (α orientation), ($k_1 = 2.05 \times 10^{-3}$ min^{-1}) is only twice the rate of formation of β-methoxyvinyl phenyl ketone (XXV) (β orientation), ($k_2 = 0.92 \times 10^{-3}$ min^{-1}). Conversion of (XXV) into benzoylacetaldehyde dimethylacetal (XXVI) took place much more slowly ($k_3 = 9.1 \times 10^{-5}$ min^{-1}).

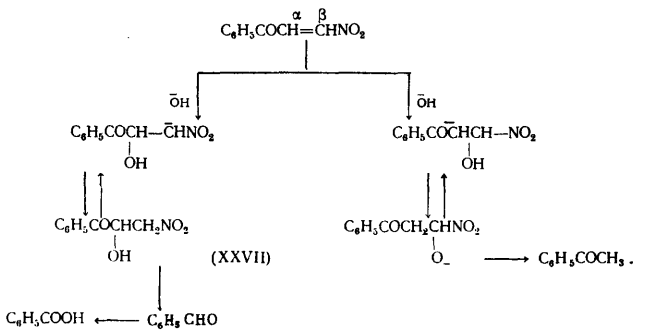
It was shown that the formation of β-methoxyvinyl phenyl ketone (XXV) is not connected with the elimination–addition mechanism which presupposes the intermediate formation of ethynyl phenyl ketone, since the ultraviolet absorption of the latter in standard buffer solution did not change in 24 h. After this period β-nitrovinyl phenyl ketone is almost completely converted into (XXIV) and (XXVI), and consequently the mechanism shown below does not take place:



The alternative mechanism of α elimination (HNO_2) with subsequent reaction of the carbene formed with methanol also seems improbable, since Smith and Davis[221] have shown that β-nitrobenzalacetophenone (which does not have an α-H close to the NO_2 group) reacts with the ethoxide ion to give β-ethoxybenzalacetophenone:



In the hydrolytic decomposition of β-nitrovinyl phenyl ketone the main products isolated were benzaldehyde and benzoic acid (products of α orientation of the OH^- ion), and there were traces of acetophenone (β orientation):[78]

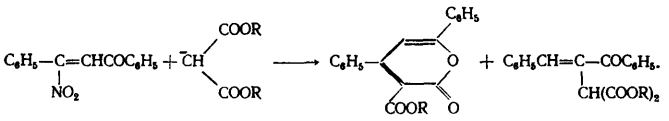


Here it is suggested that an intermediate α-hydroxy-ketone (XXVII) is formed, which on breaking down by a type of retrobenzoin decomposition[222-224], is capable of giving benzaldehyde.

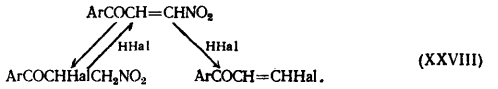
TABLE 5. Data on the kinetics of reactions with methanol of *trans*-αβ-disubstituted alkenes in standard buffer solution (0.0024 M CH_3CO_2H–0.0024 M CH_3CO_2Na) at 25°.

Alkene	k, min^{-1}	Ref.
$C_6H_5COCH=CHNO_2$	2.98×10^{-3}	33
$C_6H_5COCH=CHCOC_6H_5$	2.0×10^{-5}	18
$C_6H_5COCH=CHCN$	1.8×10^{-5}	17

A dual direction of attack by a nucleophile was also observed by Smith and Davis[221] in the example of the reaction of β-nitrobenzalacetophenone with sodiomalonic ester:



Aryl β-nitrovinyl ketones add on hydrogen chloride and bromide to form mainly aryl α-halo-β-nitroethyl ketones (XXVIII):[225]

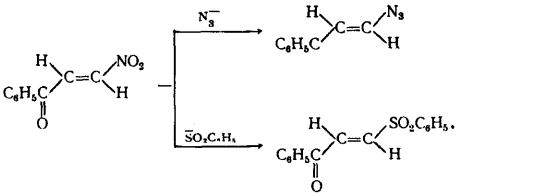


(XXVIII)

Among the products of the reaction of β-nitrovinyl phenyl ketone with hydrogen chloride, *trans*-β-chlorovinyl phenyl ketone was observed. The formation of these products confirms the possibility of dual orientation of the attacking reagent.

Note that when these hydrogen halides are passed for a long time into a solution of aryl β-nitrovinyl ketones the reaction is complex and leads to the formation of isoxazoles.

However, when *trans*-β-nitrovinyl phenyl ketone reacts with sodium azide or sodium benzenesulphinate[226] in aqueous alcoholic medium only products of replacement of the nitro-group which retain the *trans*-configuration are formed:



Hence the above examples of the reaction of the aryl β-nitrovinyl ketones contradict the orientation rule. Evidently these contradictions are due to several factors, which are not taken into account in the simplified approach to the orientation problem. Of such factors mention must first be made of the mutual influence of the groups entering the carbanion. The fact that these groups have an important influence is to some extent confirmed by the rather great sensitivity of the results of the reactions to the nature of the attacking nucleophile (compare the reactions with CH_3OH and $NH_2C_6H_5$ with those with N_3^- and $\overline{SO}_2C_6H_5$). The explanation of these anomalies is best provided by the hypothesis of the intermediate formation of π-complexes, the rearrangement of which into carbanions

is influenced by the nature of the groups entering into the carbanions. A noteworthy point is that the orientation rule is invalid for nitro-compounds in which the nitro-groups are replaced. It should be noted that, as already demonstrated[227], an anomalous course of reaction is also observed for ββ-bis(trifluoromethyl)nitroethylene; $K_{CH_3NO_2} = 10^{-11}$, $K_{(CF_3)_2CFH} = 10^{-20}$: [39,40]

$$F_3C\diagdown\!\!\diagup C{=}CHNO_2 + Z^- \rightarrow F_3C\diagdown\!\!\diagup C{=}CHZ$$

The nitro-group is known to be very easy to remove in nucleophilic substitution. Possibly its removal starts even before the π-complex is completely rearranged into the carbanion.

Furthermore, the influence of solvation can be of some significance and should be especially great for a solvent which strongly solvates anions (protonic solvents). The role of the solvent appears particularly clearly in the ionisation of $\geq$C–H acids activated by electron-acceptor groups. For example, nitromethane in aqueous medium with OH^- ions reacts 10^6 times more slowly than phenol, but in dimethylformamide proton transfer for both these acids is diffusion-controlled[228].

The decrease in the rate of ionisation of $\geq$C–H acids in proton-containing solvents is connected with the reconstruction of the solvate sheath, due to a change in the electronic structure on going from a neutral molecule to a mesomeric anion, unlike –OH or $\diagdown$N–H acids where there is no significant rearrangement of the electronic structure[228].

If it is assumed that this hypothesis is correct for the formation of anions by the ionisation of $\geq$C–H acids, then evidently it can be taken that solvation can also have considerable influence in the formation of carbanions by the addition of a nucleophilic reagent to a carbon–carbon double bond.

Naturally in αβ-disubstituted ethylenes different electron-acceptor groupings at the two ends of the ethylenic bond will be solvated differently. It can therefore be expected that the rate of formation of carbanions from these ethylenes will also show the influence of effects due to the rearrangement of the solvate sheaths. The difference in these effects can lead to some levelling of the rates of formation of the carbanions, in both the α and the β directions. Possibly such influence of the solvent will show particularly strongly in the reactions of substituted nitroethylenes.

In conclusion we must note that the problem of the orientation of nucleophilic attack at the double bond in XCH=CHY systems is too complex for it to be fully covered in the present review. Moreover, unfortunately this problem has not been studied systematically and with a purposeful direction. For this reason the present review only attempts to consider certain aspects of the problem.

1. E.D. Bergman, D. Ginsburg, and R. Pappo, in "Organic Reactions" (Edited by R. Adams) (Translated into Russian), Inostr. Lit., Moscow, 1963, Vol. 10, p. 181.
2. A.P. Terent'ev and A.N. Kost, "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), Goskhimizdat, Moscow, 1952, Vol. 2, p. 47.
3. H.A. Bruson, "Organic Reactions" (Edited by R. Adams), Wiley, New York, 1949, Vol. 5, p. 79.
4. O. Bayer, Angew. Chem., 61, 229 (1949).
5. T.L. Cairns and B.C. McKusick, Angew. Chem., 73, 520 (1961).
6. J. Remond, Uspekhi Khim., 31, 1257 (1962) [Translated from Rev. Prod. chim., 63, 407 (1960)].
7. C.K. Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1959, p. 553.
8. M.J. Kamlet and D.J. Glower, J. Amer. Chem. Soc., 78, 4556 (1956).
9. J. Hine and L.A. Kaplan, J. Amer. Chem. Soc., 82, 2915 (1960).
10. I. Okata, M. Okano, Y. Turuja, and Y. Tabushi, J. Amer. Chem. Soc., 78, 5426 (1956).
11. R. Oda and T. Shono, J. Chem. Soc. Japan, 78, 1683 (1957).
12. U. Schmidt and H. Kubitzek, Chem. Ber., 93, 866 (1960).
13. Ben-Ami Feit and A. Zilkha, J. Org. Chem., 28, 406 (1963).
14. Ben-Ami Feit, J. Sinnreich, and A. Zilkha, J. Org. Chem., 28, 3245 (1963).
15. C.K. Ingold, Ref. 7, p. 542.
16. L.J. Bellamy, "The Infra-Red Spectra of Complex Molecules" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 59.
17. A.N. Nesmeyanov, L.V. Rybin, and M.I. Rybinskaya, Zhur. Org. Khim., 2, 985 (1966).
18. T.I. Crowell, G.C. Helsley, R.E. Lutz, and W.L. Scott, J. Amer. Chem. Soc., 85, 443 (1963).
19. N. Ferry and F.J. McQuillin, J. Chem. Soc., 103 (1962).
20. B.N. Shvarts, Izv. Akad. Nauk Beloruss. SSR, Ser. Fiz.-Tekh. Nauk, 86 (1964).
21. B. Pullman and A. Pullman, Rev. Mod. Phys., 32, 428 (1960).
22. D.J. Cram and R.H. Bauer, J. Amer. Chem. Soc., 81, 5972 (1959).
23. R.E. Merrifield and W.D. Phillips, J. Amer. Chem. Soc., 80, 2778 (1958).
24. W.P. Tyler, D.W. Beesing, and S.J. Averill, Analyt. Chem., 26, 674 (1954).
25. C.L. Dickinson, D.W. Wiley, and B.C. McKusick, J. Amer. Chem. Soc., 82, 6132 (1960).
26. K. Kudo, Bull. Chem. Soc. Japan, 35, 1490, 1730 (1962).
27. C.F. Koelsch, J. Amer. Chem. Soc., 65, 437 (1943).
28. M.C. Kloetzel, J. Amer. Chem. Soc., 70, 3571 (1948).
29. A.N. Pudovik, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 926 (1952).
30. Z. Rappoport, J. Chem. Soc., 4498 (1963).
31. R. Foster and P. Hanson, Tetrahedron, 21, 255 (1965).
32. Z. Rappoport and S. Gertler, J. Chem. Soc., 1360 (1964).
33. A.N. Nesmeyanov, L.V. Rybin, and M.I. Rybinskaya, Zhur. Org. Khim., 2, 991 (1966).
34. S. Patai and Z. Rappoport, J. Chem. Soc., 377 (1962).
35. G.S. Hammond, J. Amer. Chem. Soc., 77, 334 (1955).
36. M. Eigen, Pure Appl. Chem., 6, 97 (1963).
37. A. Streitwieser, R.H. Jagow, R.C. Fahey, and S. Suzuki, J. Amer. Chem. Soc., 80, 2326 (1956).
38. E.A. Halevi, in "Progress in Physical Organic Chemistry" (Edited by S.G. Cohen, A. Streitwieser, Jnr., and R.W. Taft), Interscience, New York, 1963, Vol. 1, p. 109.
39. R.W. Pearson and R.L. Dillon, J. Amer. Chem. Soc., 75, 2439 (1953).
40. S. Andreades, J. Amer. Chem. Soc., 86, 2003 (1964).
41. R.E. Dessy, J. Amer. Chem. Soc., 84, 2899 (1962).
42. H. Shechter, F. Conrad, A.L. Daulton, and R. Kaplan, J. Amer. Chem. Soc., 74, 3052 (1952).
43. H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddey, Boll. Sci. Fac. Chim. Ind. Bologna, 21, 259 (1963).
44. H. Irving and H.I. Fuller, J. Chem. Soc., 1989 (1948).

45. F. Brower and H. Burkett, J. Amer. Chem. Soc., 75, 1082 (1953).
46. I. Thompson, E. Louloudes, R. Fulmer, F. Evans, and H. Burkett, J. Amer. Chem. Soc., 75, 5006 (1953).
47. H. Burkett, G. Nelson, and W. Wright, J. Amer. Chem. Soc., 80, 5812 (19 8).
48. F. I. Carroll, H. M. Dickson, and M. E. Wall, J. Org. Chem., 30, 33 (1965).
49. J. Colonge and G. Lartigau, Bull. Soc. chim. France, 738 (1965).
50. A. Dornow, H. D. Jordan, and A. Müller, Chem. Ber., 94, 67 (1961).
51. D. J. Cook, O. R. Pierce, and E. T. McBee, J. Amer. Chem. Soc., 76, 83 (1954).
52. U. S. P. 2 997 505 (22nd August 1961); Chem. Abs., 56, 320[e] (1962).
53. H. M. Walborsky and M. Schwarz, J. Amer. Chem. Soc., 75, 3241 (1953).
54. H. M. Walborsky and M. E. Baum, J. Org. Chem., 21, 538 (1956).
55. E. T. McBee, O. R. Pierce, and W. Smith, J. Amer. Chem. Soc., 76, 3722 (1954).
56. I. L. Knunyants and Yu. A. Cheburkov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1057 (1961).
57. E. T. McBee, Y. S. Kim, and H. P. Bralndlin, J. Amer. Chem. Soc., 84, 3154 (1962).
58. I. L. Knunyants and Yu. A. Cheburkov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1516, 2162 (1960).
59. J. Hine, N. W. Burske, M. Hine, and P. B. Langford, J. Amer. Chem. Soc., 79, 1406 (1957).
60. L. H. Slaugh and E. Bergman, J. Org. Chem., 26, 3158 (1961).
61. J. H. Simons (Editor), "Fluorine Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1953, p. 400.
62. J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, J. Amer. Chem. Soc., 70, 1550 (1948).
63. J. Lichtenberger and R. E. Rusch, Bull. Soc. chim. France, 254 (1962).
64. A. N. Pudovik and R. G. Kuzovleva, Zhur. Obshch. Khim., 35, 354 (1965).
65. A. K. Bose, M. S. Manhas, and N. J. Noboken, Angew. Chem., 75, 1026 (1963).
66. N. K. Kochetkov, Uspekhi Khim., 24, 32 (1955).
67. N. K. Kochetkov, Chem. Tech. (Berlin), 7, 518 (1955).
68. N. K. Kochetkov, J. prakt. Chem., 12, 336 (1961).
69. N. K. Kochetkov, L. I. Kudryashov, and B. P. Gottich, Tetrahedron, 12, 63 (1961).
70. A. N. Nesmeyanov and N. K. Kochetkov, Uch. Zap. Moskov. Gos. Univ., No. 175, 85 (1956).
71. N. Sugiyama and G. Inouye, Yuki Gosei Kagaku Kyokai Shi, 19, 373 (1961).
72. A. N. Nesmeyanov, "Izbrannye Trudy" (Selected Works), Izd. Akad. Nauk SSSR, Moscow, 1959, Vol. 3, pp. 7–214.
73. E. P. Kohler and G. R. Barrett, J. Amer. Chem. Soc., 46, 748 (1924).
74. K. Bowden, E. A. Braude, and E. R. H. Jones, J. Chem. Soc., 945 (1946).
75. C. J. Cavallito, J. Amer. Chem. Soc., 47, 4159 (1955).
76. A. N. Nesmeyanov and M. I. Rybinskaya, Dokl. Akad. Nauk SSSR, 115, 315 (1957).
77. A. N. Nesmeyanov and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 816 (1962).
78. M. I. Rybinskaya, L. V. Rybin, and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 899 (1963).
79. A. N. Nesmeyanov and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1764 (1966).
80. M. I. Rybinskaya and A. N. Nesmeyanov, Zhur. Org. Khim., 2, 978 (1966).
81. A. N. Nesmeyanov, M. I. Rybinskaya, and L. V. Rybin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1292 (1961).
82. M. Goldman and E. I. Becker, Nature, 170, 35 (1952).
83. L. Steinbach and E. I. Becker, J. Amer. Chem. Soc., 76, 5808 (1954).
84. T. Sato and M. Ohto, Bull. Chem. Soc. Japan, 28, 480 (1955).
85. H. von Pechman, Ber., 15, 885 (1882).
86. S. Gabriel and J. Colman, Ber., 32, 395 (1899).
87. T. Koziniewski and L. Marchlewski, Chem. Zentr., II, 1190 (1906).
88. H. G. Oddy, J. Amer. Chem. Soc., 45, 2156 (1923).
89. G. P. Rice, J. Amer. Chem. Soc., 53, 3153 (1931).
90. K. P. Dave and K. S. Nargund, J. Univ. Bombay, 7, (3), 191 (1938); Chem. Abs., 33, 3779[i] (1939).
91. R. Pummerer and E. Buchta, Ber., 69, 1005 (1936).
92. M. T. Bogert and J. J. Ritter, J. Amer. Chem. Soc., 47, 526 (1925).
93. D. Papa, E. Schwenk, F. Villani, and E. Klingsberg, J. Amer. Chem. Soc., 70, 3356 (1948).
94. D. Papa and E. Schwenk, U. S. P. 2 562 208 (31st July 1951); Chem. Abs., 46, 2759[i] (1952).
95. F. H. Kirchner, J. H. Bailey, and C. J. Cavallito, J. Amer. Chem. Soc., 71, 1210 (1949).
96. W. Cocker and C. Lipman, J. Chem. Soc., 533 (1947).
97. W. Cocker and C. Lipman, J. Chem. Soc., 1519 (1950).
98. B. P. 588 108 (14th May 1947); Chem. Abs., 42, 329[c] (1948).
99. E. P. Kohler and D. W. Woodward, J Amer. Chem. Soc., 58, 1933 (1936).
100. W. Koga, J. Chem. Soc. Japan, Pure Chem. Sect., 77, 1276 (1956); Chem. Abs., 53, 5186[c] (1959).
101. W. Koga, Bull. Chem. Soc. Japan, 29, 725 (1956).
102. K. P. Barr, F. M. Dean, and H. D. Locksley, J. Chem. Soc., 2425 (1959).
103. H. G. A. Sattar, P. B. Sattar, V. V. Badiger, and N. S. Nargund, J. Karnatak. Univ., 3, No. 1, 66 (1958); Chem. Abs., 54, 5557[b] (1960).
104. G. Baddeley, G. Holt, and S. M. Makar, J. Chem. Soc., 3289 (1952).
105. G. Baddeley, S. M. Makar, and M. G. Ivinson, J. Chem. Soc., 3969 (1953).
106. B. J. Cramer, W. Schroeder, W. J. Moran, C. H. Nield, M. Edwards, C. I. Jarowski, and P. Puetzer, J. Amer. Pharmaceut. Assoc. (Sci. Edn.), 37, 439 (1948).
107. R. R. Burtner and J. M. Brown, J. Amer. Chem. Soc., 75, 2334 (1953).
108. R. H. Martin and P. Stoffyn, Bull. Soc. chim. belges, 59, 83 (1950).
109. P. Zambert and R. H. Martin, Bull. Soc. chim. belges, 61, 132 (1952).
110. R. R. Burtner and J. M. Brown, U. S. P. 2 610 210 (9th September 1952); Chem. Abs., 47, 5966[g] (1953).
111. S. M. Makar, H. F. Basslios, and A. Y. Salem, J. Chem. Soc., 2437 (1958).
112. A. E. Kretov and V. V. Litvinov, Zhur. Obshch. Khim., 31, 2880 (1961).
113. A. E. Kretov, V. V. Litvinov, and V. L. Dubina, Zhur. Obshch. Khim., 32, 1564 (1962).
114. C. C. Price, H. M. Shafer, M. F. Huber, and C. Bernstein, J. Org. Chem., 7, 517 (1942).
115. C. I. Jarowski, W. J. Moran, and B. J Cramer, J. Amer. Chem. Soc., 71, 944 (1949).
116. C. I. Jarowski and G. B. Hess, J. Amer. Chem. Soc., 71, 1711 (1949).
117. R. E. Lutz and R. J. Taylor, J Amer. Chem. Soc., 55, 1593 (1933).
118. H. J. Bestmann and H. Schulz, Angew. Chem., 73, 620 (1961).
119. H. J. Bestmann, F. Seng, and H. Schulz, Chem. Ber., 96, 465 (1963).

120. W. Koenigs and E. Wagstaffe, Ber., 26, 554 (1893).
121. A. W. Noltes and F. Koge, Rec. Trav. chim., 80, 1334 (1961).
122. Yu. A. Arbuzov and E. I. Klimova, Zhur. Obshch. Khim., 32, 3676 (1962).
123. H. B. Hill and W. S. Hendrixon, Ber., 23, 452 (1890)
124. H. B. Hill and W. Jennigs, Amer. Chem. J., 15, 159 (1893).
125. K. B. L. Mathur and H. S. Mehra, J. Chem. Soc., 2576 (1961).
126. H. M. Waltom, J. Org. Chem., 22, 308 (1957).
127. F. L. Breusch and H. Keskin, Arch. Biochem., 18, 305 (1948).
128. H. Keskin, Rev. Fac. Sci. Istanbul, 51a, 54 (1950); Chem. Abs., 45, 2904 (1951).
129. J. Ernest and M. Jelinkova, Coll. Czech. Chem. Comm., 24, 3341 (1959).
130. J. Bougault, Compt. rend., 146, 140 (1908).
131. J. Bougault, Ann. Chim. (France), [8], 15, 298 (1908).
132. J. Bougault, Compt. rend., 157, 377 (1913).
133. J. Bougault, Ann. Chim. (France), [8], 15, 491 (1908).
134. B. P. 678 183 (27th August 1952); Chem. Abs., 47, 6440[b] (1953).
135. U. S. P. 2 663 728 (22nd December 1953); Chem. Abs., 49, 10 364 (1955).
136. R. Quelet and J. Gavarret, Bull. Soc. chim. France, 1075 (1950).
137. D. S. Tarbell, J. Amer. Chem. Soc., 60, 215 (1938).
138. A. W. Ninehan and R. A. Raphael, J. Chem. Soc., 118 (1949).
139. H. Baer, M. Holden, and B. C. Segal, J. Biol. Chem., 162, 65 (1946).
140. W. Königs and E. Wagstaffe, Ber., 26, 555 (1893).
141. L. Wolf, Annalen, 264, 234 (1891).
142. A. Angeli and A. Chiussi, Ber., 25, 2206 (1892).
143. G. Schultz and O. Löw, Ber., 42, 577 (1909).
144. J. S. Mofatt, G. Newberry, and W. Webster, J. Chem. Soc., 451 (1946).
145. R. W. Wynn and A. H. Corwin, J. Org. Chem., 15, 203 (1950).
146. M. Pauly, R. Gilmour, and G. Will, Annalen, 403, 150 (1914).
147. M. Conrad and M. Guthzeit, Ber., 17, 2285 (1884).
148. L. M. Turton and L. F. Wiggins, J. Chem. Soc., 3500 (1950).
149. T. Sakan, J. Chem. Soc. Japan, 63, 1545 (1942).
150. M. Kotake, T. Sakan, and S. Senoh, J. Amer. Chem. Soc., 73, 1832 (1951).
151. S. Senoh and T. Sakan, J. Chem. Soc. Japan, Pure Chem. Sect., 74, 200 (1953).
152. S. Senoh and Y. Hayashi, J. Chem. Soc. Japan, Pure Chem. Sect., 75, 927 (1954).
153. H. F. Ginsburg, I. Lederman, and D. Papa, J. Amer. Chem. Soc., 75, 4587 (1953).
154. R. A. Raphael, Nature, 160, 261 (1947).
155. N. Hellström, Nature, 179, 589 (1957).
156. R. L. Worral, Med. World, 11 (January 1946).
157. J. S. Thomas, U. S. P. 2 532 579 (December 1950); Chem. Abs., 45, 1290 (1951).
158. S. Raymond, J. Amer. Chem. Soc., 72, 4304 (1950).
159. C. J. Cavallito and F. K. Kirchner, U. S. P. 2 863 910 (9th December 1958); Chem. Abs., 53, 8078[d] (1959).
160. J. Bougault and P. Chabrier, Compt. rend., 226, 1378 (1948).
161. J. Bougault and P. Chabrier, Compt. rend., 230, 212 (1950).
162. J. Bougault and P. Chabrier, Compt. rend., 237, 1420 (1953).
163. A. Quevauviller, J. W. Lonw [Louw? (Ed. of Translation)], and P. Chabrier, Ann. pharm. franç., 13, 111 (1955).
164. J. Bougault and P. Chabrier, Compt. rend., 228, 1952 (1949).
165. R. Moreau and G. Dumant, Compt. rend., 250, 2383 (1960).
166. R. Delaby, S. Danton, and P. Chabrier, Bull. Soc. chim. France, 2061 (1961).
167. R. Delaby, P. Chabrier, and S. Danton, Compt. rend., 232, 2326 (1951).
168. J. Bougault, Ann. Chim. (France), [8], 15, 491 (1908).
169. E. S. Gould, "Mechanism and Structure in Organic Chemistry", New York, 1960, p. 527.
170. J. Bougault, Ann. Chim. (France), [8], 15, 229 (1908).
171. N. H. Cromwell, P. L. Greger, and K. E. Cook, J. Amer. Chem. Soc., 78, 4412 (1956).
172. N. H. Cromwell and K. E. Cook, J. Org. Chem., 23, 1327 (1958).
173. M. M. Faser and R. A. Raphael, J. Chem. Soc., 2245 (1950).
174. "Perspectives in Organic Chemistry" (Edited by Sir Alexander Todd) (Translated into Russian), Inostr. Lit., Moscow, 1959, p. 341.
175. A. Butenandt, W. Weidel, R. Weichert, and W. von Derjugin, Z. phys. Chem., 279, 27 (1943).
176. A. Butenandt, W. Wiedel, and W. von Derjugin, Naturwiss., 30, 51 (1942).
177. A. Butenandt and G. Hallmann, Z. Naturforsch., 5b, 444 (1950).
178. A. N. Nesmeyanov, M. I. Rybinskaya, and L. V. Rybin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2152 (1961).
179. J. Bougault and P. Chabrier, Compt. rend., 224, 395 (1947).
180. G. W. Scott and R. E. Lutz, Proc. Virginia Acad. Sci., 2, 195 (1944); Chem. Abs., 36, 2259[7] (1942).
181. R. E. Lutz and G. W. Scott, J. Org. Chem., 13, 284 (1948).
182. G. P. Rice, J. Amer. Chem. Soc., 50, 229 (1928).
183. J. Bougault, Compt. rend., 147, 476 (1908).
184. J. Bougault, Compt. rend., 148, 1271 (1909).
185. S. Patai and Z. Rappoport, J. Chem. Soc., 383 (1962).
186. S. Patai and Z. Rappoport, J. Chem. Soc., 392 (1962).
187. R. Stewart, J. Amer. Chem. Soc., 74, 4531 (1952).
188. E. A. Walker and J. R. Yong, J. Chem. Soc., 2045 (1957).
189. T. J. Crowell and A. W. Francis, J. Amer. Chem. Soc., 83, 591 (1961).
190. S. Julia and Y. Bonnet, Compt. rend., 243, 2079 (1956).
191. E. P. Kohler and H. Eugelbrecht, J. Amer. Chem. Soc., 41, 764 (1919).
192. G. P. Rice, J. Amer. Chem. Soc., 45, 222 (1923).
193. F. K. Kirchner and E. J. Alexander, J. Amer. Chem. Soc., 81, 1721 (1959).
194. B. P. 733 805 (20th July 1955); Chem. Abs., 50, 7874[b] (1956).
195. G. Stork and H. K. Landesman, J. Amer. Chem. Soc., 78, 5129 (1956).
196. B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, J. Amer. Chem. Soc., 80, 2806 (1958).
197. K. Kudo, Bull. Chem. Soc. Japan, 35, 1490, 1730, 1842 (1962).
198. A. N. Nesmeyanov and M. I. Rybinskaya, Dokl. Akad. Nauk SSSR, 120, 793 (1958).
199. A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 350 (1950).
200. A. N. Nesmeyanov, M. I. Rybinskaya, L. V. Rybin, L. B. Senyavina, G. L. Slonimskii, and V. S. Papkov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1758 (1966).
201. A. N. Nesmeyanov, L V. Rybin, and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1451 (1961).
202. E. L. Martin, J. Amer. Chem. Soc., 85, 2449 (1963).
203. N. K. Kochetkov and V. N. Vinogradova, Zhur. Obshch. Khim., 27, 460 (1957).
204. E. P. Kohler and R. G. Larsen, J. Amer. Chem. Soc., 57, 1448 (1935).
205. A. N. Nesmeyanov, O. A. Reutov, and A. S. Gudkova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 260 (1961).
206. N. Kreutzkamp and H. Schindler, Chem. Ber., 92, 1696 (1959).
207. Ch'en Ch'in-yün, N. P. Gambaryan, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 133, 1113 (1960).

208. W. J. Middleton, J. Org. Chem., 30, 1402 (1965).
209. M. Uchibayashi, J. Pharm. Soc. Japan, 78, 853 (1958); Chem. Abs., 53, 331[d] (1959).
210. G. Schroeter, Annalen, 426, 1 (1922).
211. H. W. Wanzlick, Chem. Ber., 86, 269 (1953).
212. P. Yates and G. Bhat, Chem. and Ind., 1237 (1954).
213. H. Paul and J. Wendel, Chem. Tech. (Berlin), 8, 189 (1956); Chem. Abs., 51, 5713 (1957).
214. S. Tanaka, J. Amer. Chem. Soc., 80, 5264 (1958).
215. P. Yates, E. S. Hand, and G. B. French, J. Amer. Chem. Soc., 82, 6347 (1960).
216. "Progress in Stereochemistry" (Edited by W. Klyne and P. B. D. de la Mare) (Translated into Russian), Goskhimizdat, Moscow, 1961, Vol. 2, p. 527.
217. P. D. Bartlett and G. F. Woods, J. Amer. Chem. Soc., 62, 2933 (1940).
218. W. E. von Doering and L. K. Levy, J. Amer. Chem. Soc., 77, 509 (1955).
219. A. N. Nesmeyanov, M. I. Rybinskaya, and L. V. Rybin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1382 (1965).
220. V. G. Morgan and H. B. Watson, J. Chem. Soc., 1173 (1935).
221. L. I. Smith and B. K. Davis, J. Amer. Chem. Soc., 76, 5376 (1954).
222. E. Anderson and R. A. Jacobson, J. Amer. Chem. Soc., 45, 836 (1923).
223. J. S. Jenkins, J. Amer Chem. Soc., 53, 3115 (1931).
224. A. Weissberger, A. Döken, and W. Schwarz, Ber., 64B, 1200 (1931).
225. A. N. Nesmeyanov, L. V. Rybin, M. I. Rybinskaya, and S. D. Sokolov, "Khimiya Geterotsiklicheskikh Soedinenii" (Chemistry of Heterocyclic Compounds), 1967, in the press.
226. L. V. Rybin, Candidate's Thesis, Institute of Organoelemental Compounds, Moscow, 1965.
227. Ch'en Ch'in-yün, N. P. Gambaryan, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 133, 1113 (1960).
228. C. D. Ritchie and R. Uschold, J. Amer. Chem. Soc., 86, 4488 (1964).

Institute of Organoelemental Compounds,
Academy of Sciences of the USSR,
Moscow

U. D. C. 547.315.2'13 : 547.258.11-15 : 547.245 : 545.246

ETHYNYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

L. K. Luneva

CONTENTS

I. Introduction 467

II. Preparation of ethynyl derivatives of silicon, germanium, tin, and lead 468

1. Preparation of ethynyl derivatives from the alkali metal acetylides 468

2. Preparation of ethynyl compounds of silicon, germanium, tin, and lead through magnesium bromide derivatives of acetylenes 468

3. Other methods of obtaining ethynyl organoelemental compounds 469

III. Preparation of prop-2-ynyl derivatives of silicon, germanium, tin, and lead 469

IV. Chemical properties of ethynyl organoelemental compounds 470

V. Physical properties 472

VI. Organic polymers of silicon, germanium, and tin containing acetylenic groupings 474

I. INTRODUCTION

Many papers have been published on the synthesis and study of the properties of unsaturated organoelemental compounds of the elements of Group IV of the Mendeleev Periodic System. Practical interest in these compounds arose in connection with the need to create new types of polymers. The investigation of the structure and reactivity of such compounds is of great theoretical importance since there is a specific interaction between carbon–carbon multiple bonds and the elements, an interaction which brings about the appearance of anomalous properties.

There is special interest in the unsaturated derivatives of the elements of the carbon subgroup since it is in this very series, situated at the heart of the Periodic System, that we can expect both an analogy with the purely carbon compounds, and also a considerable difference connected with the electronic structure of the atoms of the Group IV elements. Vinyl and allyl derivatives of silicon, germanium, tin, and lead have been studied most fully. The absence of reliable methods for the preparation of the ethynyl derivatives until recently retarded investigation in this field. It was only in the nineteen-forties, with the development of the chemistry of acetylene, that the first information appeared on the synthesis of alkynylsilanes[1,2]; the more systematic investigation of the alkynylsilanes started much later[3].

The first communication on the preparation of organogermanium compounds containing an acetylenic bond was published in 1958.[4] The first organotin acetylene derivatives were obtained in 1954.[5] A large number of acetylene derivatives of silicon, germanium, and tin are now known.

The present review considers only the acetylene derivatives of silicon, germanium, tin, and lead having a triple bond in the α or β positions to the atom of the element. Organoelemental compounds with a triple bond in the α position show most markedly the mutual influence of the π-electrons of the triple bond and the electrons of the element atoms.

The prop-2-ynyl derivatives of the Group IVb elements (C≡C in the β position) are interesting because they allow the influence of the elements on the prop-1,2-dienyl–prop-2-ynyl isomerism to be studied. The prop-1,2-dienyl derivatives formed as a result of the isomerisation are electronic analogues of ethynyl compounds (sp-hybridisation) [sic (Ed. of Translation)]; the resulting intramolecular interaction with the atoms of the Group IV elements should give effects analogous to those found with ethynyl groups [sic (Ed. of Translation)]. Therefore the preparation and properties of prop-2-ynyl compounds will also be considered within the bounds of our review.

This review describes in succession the synthesis and the chemical and physical properties of the ethynyl and