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The Reactions of Hydrazones

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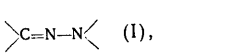
The chemical properties of organic compounds containing an open-chain hydrazono-group are surveyed systematically. A list of 412 references is included.

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I. INTRODUCTION

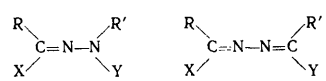
In the chemical literature hydrazones are not usually discussed as a separate class of organic compounds: most often they are regarded as derivatives of carbonyl compounds or of acids. The present review includes in the category of hydrazones all compounds whose molecules contain the triatomic fragment



(I),

not forming part of a heterocycle. However, the amino-nitrogen atom and/or the carbon atom may be included in a non-aromatic ring [1].

The close similarity of chemical and physical properties and the presence of a common functional group enable hydrazones (II) and azines (III) to be considered a single class of compounds:



(II) (III)

where R and R′ = H, Alk, Ar, Az, Ht†; Y = H, Alk, Ar, Ht, Az; X = H, Alk, Ar, Az, Ht, Hal, OR″, SR, CN, SO_2R, NO_2, NH.NR″R‴, NH.NHR″, N:NR″, COOR″, CO.NR″R‴. Several types of hydrazones have already been surveyed [2-51], and the electrochemical reduction of this class of compounds has been reviewed [52].

We have classified the numerous reactions undergone by hydrazones on the formal principle of the type of reactant.

II. REACTIONS OF HYDRAZONES WITH ELECTROPHILIC REAGENTS

Protonation

The distinguishing feature of the hydrazono-group is the presence of two nitrogen atoms—imino and amino—the valency electrons of which differ in their hybridisation (see formula II). The transition of a nitrogen atom from the sp^3 to the sp^2 state lowers its basicity. Amines possess more pronouncedly basic properties than do imines [2]. Conversion of an arylhydrazine into an arylhydrazone involves a substantial diminution in basicity [2,53-56]. Semicarbazones are less basic than semicarbazide by several orders of magnitude [56,57]. The basic character of azines (di-imines) is especially weak [2,44,49]: for example, acetone azine is 0.1% as basic as hydrazine [58]. Since the lone pair of electrons of the amino-nitrogen is delocalised in unsubstituted hydrazones as a result of conjugation with the π-system of the imino-bond [1], these compounds are also less basic than hydrazine: acetophenone hydrazone has $pK_a = 4.94$, whereas the value for hydrazine is 8.07. [59]

Increase in the electron-accepting character of R in (II) lowers the basic strength of hydrazones. This rule has been observed both with unsubstituted hydrazones [59] and with the phenyl-, [56] *p*-nitrophenyl-, [53,54] 2,4-dinitrophenyl-, [54,55] and nitroguanyl-hydrazones [60] of a large number of substituted benzaldehydes and aromatic ketones. A linear relation has been established between the Hammett constants of the substituents in the benzene ring of the carbonyl component and the pK_a value of the 2,4-dinitrophenylhydrazones [55]. The number of electron-accepting groups and their position in the benzaldehyde molecule affect the basicity of the phenylhydrazones [56].

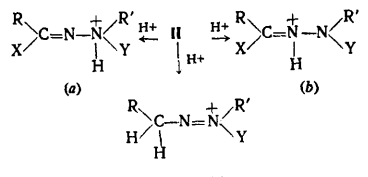
The substituent attached to the amino-nitrogen (R′ or Y in II) also has an effect. The basic character diminishes, for example, in the sequence unsubstituted hydrazones > > phenylhydrazones > *p*-nitrophenylhydrazones > 2,4-dinitrophenylhydrazones [1,2,10,45,48,53-56,59].

The introduction of electron-donor substituents into the hydrazone group will, of course, enhance the basicity, especially if the substituent is attached to the amine nitrogen. Dimethylhydrazones are stronger bases than unsubstituted hydrazones or phenylhydrazones [2]. Acetone *p*-nitrophenylhydrazone is a stronger base than the corresponding acetophenone derivative by a factor of 5. [54] The basic character of hydrazones is influenced not only by the nature of the substituents but also by the configuration of the molecule. Thus Vogel and Matter reported [61] that the *anti*-isomer of the *p*-tolylhydrazone of *p*-n-butylphenylglyoxylic acid has $pK = 6.6$, whereas the corresponding exponent for the *syn*-isomer is 5.1.

The hybridisation of the electrons of the amino-nitrogen atom varies with increase in the bulk of the substituents, depending on their nature [1], and sometimes approaches the

†Az = RCO = acyl; [Ht = heterocyclic group].

sp^2 state. As a consequence of this and the competitive influence of the substituents R, X and R', Y, hydrazones may undergo protonation either at the amine (*a*) or at the imine (*b*) nitrogen atom:



The more complicated case (*c*) is theoretically also possible, although it appears less probable.

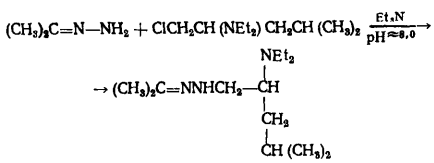
Semicarbazones are protonated at the carbamoyl group [57]. Dimethylhydrazones form quaternary salts on alkylation [62-64]; their protonation also takes place at the amino-nitrogen atom. The possibility of protonation at the imino-nitrogen is suggested by the insignificant change in basicity on passing from monoalkylhydrazones of aliphatic ketones to their *N*-acyl derivatives [65]. It is assumed that in 1,5-diarylformazans the amino-nitrogen of the hydrazone group is protonated.

Alkylation

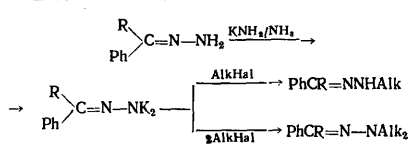
Unsubstituted hydrazones (II: R = Y = H) are converted by alkyl halides into azines of the same carbonyl compound [9,10,49]:

$$2\,PhCH{=}N{-}NH_2 + BrCH_2CH_3 \rightarrow PhCH{=}N{-}N{=}CHPh + CH_2{=}CH_2 + N_2H_4HBr$$

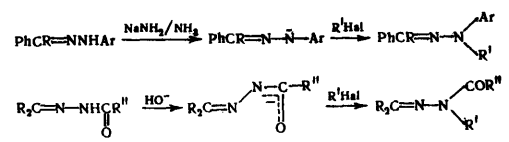
This reaction is accelerated in the presence of alcoholic alkali [66]. If, however, triethylamine in a buffer solution is used as the base, alkylation takes place at the amino-nitrogen atom [65]:



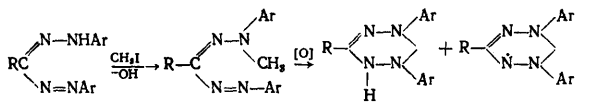
If an unsubstituted hydrazone is converted into a dianion by the action of potassamide in liquid ammonia, mono- or di-alkylhydrazones can be obtained depending on the quantity of alkyl halide taken [67]:



The less basic aryl- and acyl-hydrazones are usually alkylated after preliminary conversion into anions [2,9,10,45,49,68-70]. Conducting the reaction in liquid ammonia [69] generally gives high yields of alkylhydrazones:

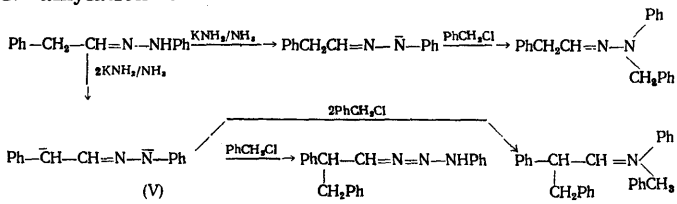


The alkylation of formazans, like that of arylhydrazones, involves the intermediate formation of anions [47,71], although in some cases the reaction is complicated by the formation of 1,2,5,6-tetrahydro-1,2,4,5-tetrazine derivatives and then of verdazyl(IV). [72] The formation of (IV) may become the main reaction, because of the great tendency of $N_{(1)}$-methylformazans to undergo autoxidation:



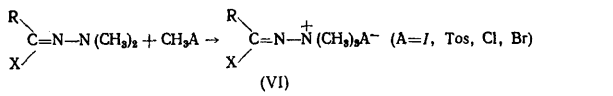
(IV)

Arylhydrazones of carbonyl compounds having an α-methine group, on treatment with excess of potassamide, form the dianion (V), which is more liable to *C*- than to *N*-alkylation [70]:



According to Grandberg et al. [73] arylhydrazones of aliphatic and alicyclic carbonyl compounds are alkylated by benzyl chloride and by dimethyl sulphate in boiling alcohol, after which they are converted into *N*-alkylindoles.

Dimethylhydrazones are easily converted into quaternary salts (VI) by the action of alkylhalides [62-64] and alkyl [arene]sulphonates [74]:

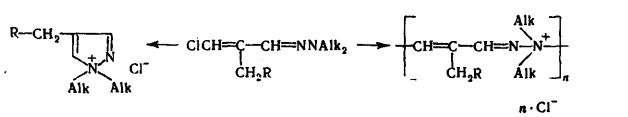


(VI)

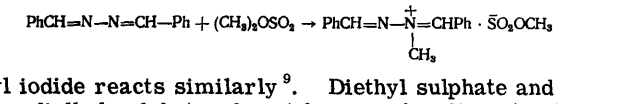
When α-bromoacetophenone is used, quaternary salts cannot be isolated from the dialkylhydrazones of aldehydes, evidently owing to their instability. In this case the products are a nitrile and an amino-ketone, resulting from rearrangement of an intermediate salt [75]:



Dialkylhydrazones of β-chlorovinyl-aldehydes are able to form polymeric quaternary salts [76]. Self-quaternisation with conversion into a 1,1-dialkylpyrazolium salt is also possible:



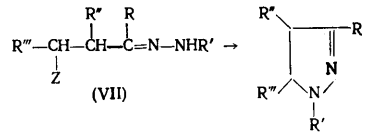
Benzaldehyde azine on treatment with dimethyl sulphate or ethyl iodide is converted into a saltlike product, whose structure is assumed [9,10,49] to correspond to a quaternary salt:



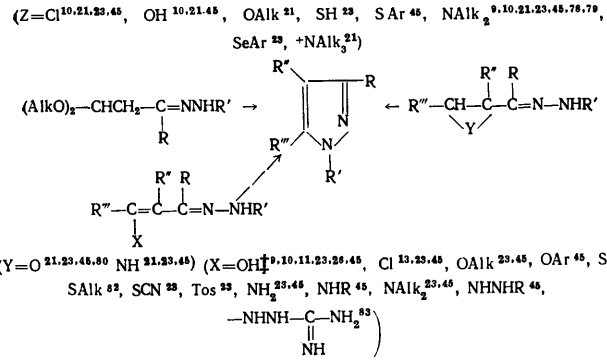
Ethyl iodide reacts similarly [9]. Diethyl sulphate and higher dialkyl sulphates do not form such salts. Aliphatic and alicyclic azines containing an α-methine group are converted by alkylating agents into a mixture of unsubstituted pyrazoline and an *N*-alkylpyrazoline [21,44,49,77].

Reactions involving the intramolecular alkylation of hydrazones with the formation of simple and fused heterocyclic systems are well known and have been widely studied [2,4,10,11,13,14,21,23,45,48,78,79]. The reaction mechanisms are largely obscure [21,23]: in parallel with an SN

mechanism[21,23,78] the possibility is discussed of initial elimination of HZ from (VII) with formation of a hydrazone of an unsaturated oxo-compound followed by intramolecular addition of the HN fragment of the hydrazono-group at the resulting C=C bond[21,23,79]. The reactions involved in intramolecular alkylation can be represented by the schemes

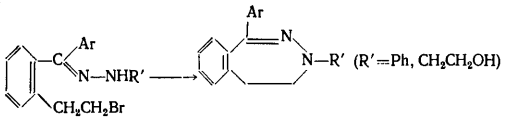


(VII)

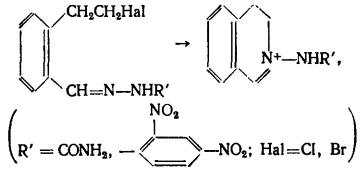


Here R″ and R‴ [10,84,85] and/or R and R′ [86] represent Alk, Ar, Ht, Az, a heterocyclic or a carbocylic fragment[87], a steroid residue[80], and possibly also nitroso[88] or arylazo[89,90].

Not only hydrazones of oxo-compounds having a reactive substituent in the β-position but also those in which the substituent is attached to a more remote carbon atom are capable of intramolecular alkylation. In particular, hydrazones of δ-halogeno-ketones are cyclised to diazepine derivatives by self-alkylation at the amino-nitrogen atom[91]:



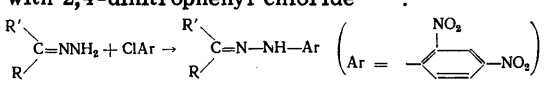
With increase in the electron-accepting properties of the substituent R′ attached to the amino-nitrogen atom the reaction centre may migrate, and self-alkylation involve the imino-nitrogen[35,45,92,93]:



The basic character of the imino-nitrogen diminishes more slowly than that of the amino-nitrogen under the influence of the acceptor substituent.

Arylation

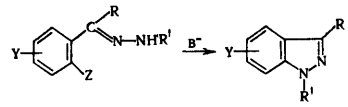
2,4-Dinitrophenylhydrazones of sterically hindered ketones are obtained by condensing unsubstituted hydrazones with 2,4-dinitrophenyl chloride[45,94]:



‡The monoenolic form of 1,3-dioxo-compounds.

This reaction was even recommended for the quantitative determination of unsaturated hydrazones[94]. Similar reactions can be used for the preparation of 2,4- and 2,6-dinitro- and the 3-R-2,4,6-trinitro-phenylhydrazones of benzophenone and fluorenone (R = H, Cl, CH_3).[95] Acetone azine reacts with picryl chloride in ethanol to form acetone 2,4,6-trinitrophenylhydrazone[45].

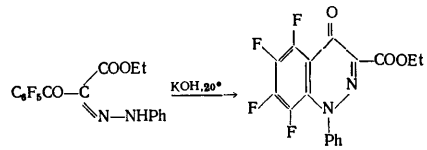
Monosubstituted and unsubstituted hydrazones of *ortho*-substituted benzaldehydes, acetophenones, and related compounds are converted by alkaline reagents into indazole derivatives (intramolecular arylation):[10,24,45,48,96-98]



(Z = Cl,[10,45] Br,[24,45] NO_2,[24,45,97] OH,[98] OAlk;[45,96] R = H, Alk, COOH, $CH_2C_6H_5$,[24,45] $COOC_2H_5$,[45] $COCH_3$,[97] R′ = H, Alk, Ph, *p*-$CH_3C_6H_4$, $Cl_XC_6H_{5-X}$,[24,45] 2,4-$C_6H_3(NO_2)_2$[45]).

Not only do hydrazones of 2,6-dinitrobenzaldehyde undergo this reaction, as assumed earlier[24], but also those of 2,4-di- and 2,4,6-tri-nitrobenzaldehydes[45] and pyridinealdehydes[98]. When Z = Hal, increasing the number of nitro-groups in the same ring increases the yield of indazole[24]. If the aryl ring contains a 2-chloro-substituent and a 6-nitro-group, the latter is the more readily replaced[45].

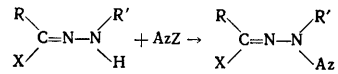
An example of intramolecular arylation with formation of a substituted cinnoline



has been reported[99].

Acylation

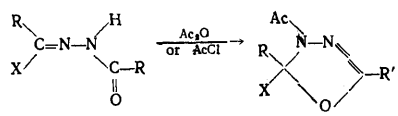
If Y = H in the hydrazone (II), acylation occurs in the usual way, and *N*-acylhydrazones (Y = Az) are formed[2,7,10,38,45,47,48,65,100-113]:



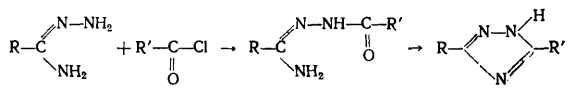
(R′ = H, Alk, Ar, Ht; Z=Cl,OEt, OAz).

Unsaturated hydrazones are converted smoothly into acylhydrazones[10,100]. Under the conditions of the Schotten-Baumann reaction many alkylhydrazones yield acetyl-, benzoyl-, and arenesulphonyl-alkylhydrazones[2,65]. Arylhydrazones are fairly easily acylated[45,48,101], but the resulting arylacylhydrazones tend to hydrolyse, and therefore the arylacylhydrazines and the oxo-compounds often separate instead of the acylated hydrazones[45]. A successful preparation requires an anhydrous solvent[45,102], and excess of the acylating agent or a catalyst (pyridine[102], zinc chloride[45,101]). 1,5-Diarylformazans are acylated with difficulty, and the yields of 1-acyl-1,5-diarylformazans are often low[47,103]. The acylation of phenylosazones is more successful[38]. Reaction between acylhydrazones

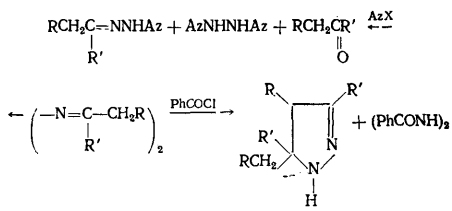
and acetic anhydride results most frequently in the formation of 1,3,4-oxadiazolines [104-107], although anomalies are observed [106]:



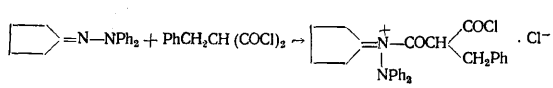
When arylhydrazones of quinones are acylated, the hydrazone form is fixed [108]. Amidrazones are acylated at the hydrazono-group [109,110], but reaction generally proceeds further with the formation of 1,2,4-triazole derivatives [45, 109-111]:



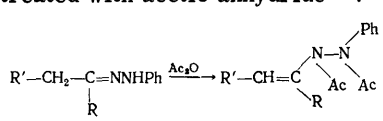
Azines, on treatment with acylating agents, are converted into acylhydrazones [49] or into mono- and di-acylhydrazines [49,112], and the methylene groups present undergo cyclisation into pyrazolines [44,113]:



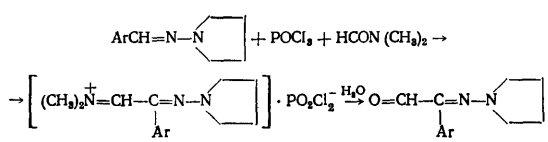
When the basicity of the amino-nitrogen atom is weakened considerably, the hydrazone may be acylated at the imino-nitrogen with the formation of a quaternary salt [114]:



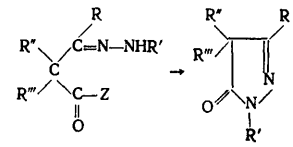
A product in which both nitrogen atoms of the hydrazone had been acylated was isolated when phenylhydrazones of aliphatic ketones, capable of conversion into alkenylhydrazines, were treated with acetic anhydride [115]:



Even disubstituted hydrazones of aldehydes do not form *C*-acyl derivatives under the usual conditions of acylation, and only in the Vilsmeier reaction are dialkylhydrazones of aromatic aldehydes converted into those of an arylglyoxal [116]:



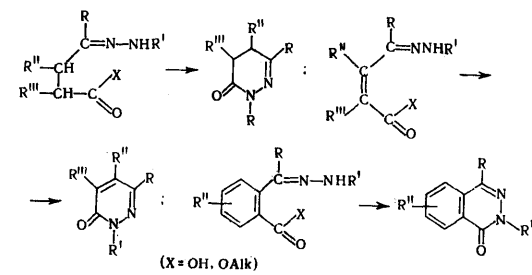
As in the case of alkylation, detailed studies have been made of intramolecular acylation with the formation of heterocyclic systems [2,9,10,23,45,83,99,114]. Hydrazones [23,45], alkylhydrazones [2,9,23,45], arylhydrazones [23,45,99], acylhydrazones [23,45], semicarbazones [23,45], thiosemicarbazones [23,45], selenocarbazones [117], and guanylhydrazones [83] of derivatives of β-keto-acids are cyclised to substituted pyrazolones:



(R′=H, Alk, Ar, Ht, —C(=O)—NH$_2$; Z=OH, OAlk, OAr, NH$_2$, NHR, NRR′, NHNHR, NHNH$_2$)

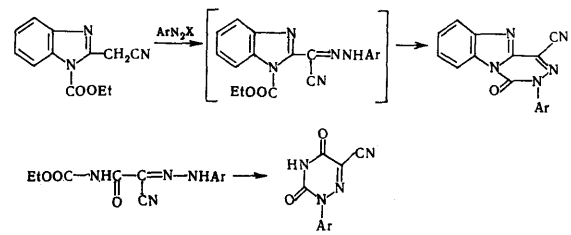
(S,Se)

Here R, R″, and R‴ may vary widely. Hydrazones of γ-keto-acids and their derivatives are cyclised to tetrahydro-3-oxopyridazines [9,10,25,26,45,46,118], and hydrazones of αβ-unsaturated γ-keto-acids to dihydro-3-oxopyridazines and tetrahydro-oxocinnolines [9,10,25,26,45,119-121]; however, hydrazones of *o*-formyl(or keto)benzoic acids are converted into dihydro-1-oxophthalazine derivatives [27,45,122]:

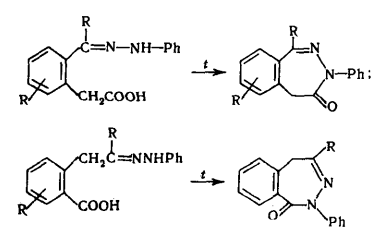


(X = OH, OAlk)

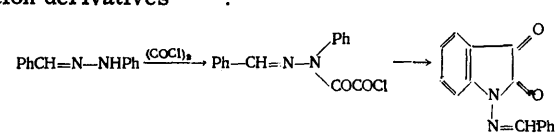
The hydrazone and carboxyl groups may be separated not only by a hydrocarbon chain but also by a fragment of a heterocycle [123] or by a carbamoyl group [124], when derivatives of tetrahydro-3,5-dioxo-1,2,4-triazine or its fused-ring analogues are formed:



Hydrazones of δ-keto-acids yield [91] substituted dihydro-3-oxoazepines:

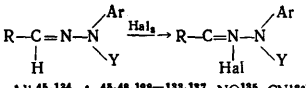


The acylation of phenylhydrazones with oxalyl chloride gives initially phenylacylhydrazones, and then *N*-aminoisation derivatives [45,125]:



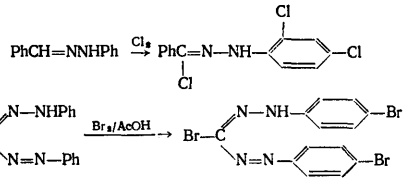
Halogenation

Halogens oxidise unsaturated hydrazones to azines [2,10,44,49] although substitutive halogenation is sometimes observed [126]. The action of halogens on arylhydrazones has been studied in greatest detail [45,48,127-137]. The hydrogen atom attached to the carbon of the hydrazone group (the methine hydrogen) in arylhydrazones of aldehydes can be replaced by a halogen atom [2,45,48,127-137]:

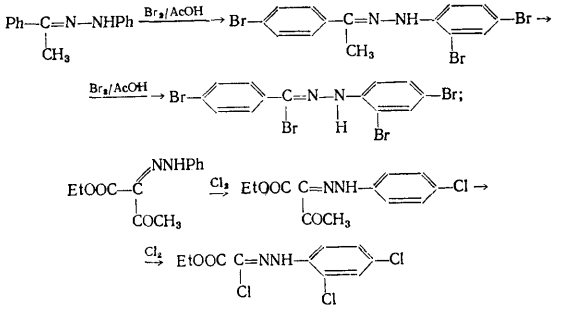


(R=Alk[45,134], Ar[45,48,128-133,137], NO_2[135], CN[136];
Y=H, CH_3; Ar=Ph, $(Hal)_nC_6H_{5-n}$, $(NO_2)_mC_6H_{5-m}$[45,48,129,130,133,134,137], Ht[128,131,133]).

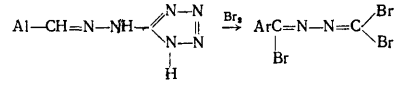
In phenylhydrazones substitution of the methine proton is accompanied by halogenation of the benzene ring attached to the amino-nitrogen atom [45,48,129], and halogens react similarly with 3*H*-formazans [43,138]:



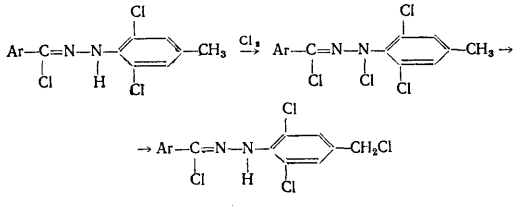
In arylhydrazones of ketones the ring is halogenated initially, after which the methyl or acetyl group may be replaced by halogen [45,48,129]:



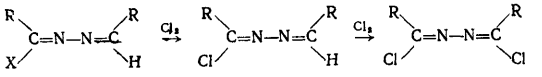
In the bromination of tetrazolylhydrazones replacement of the methine proton is accompanied by breakdown of the tetrazole ring [128]:



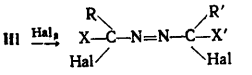
A kinetic study of the bromination of 2,4-dinitrophenylhydrazones of aliphatic aldehydes has shown that steric factors are more important than electronic factors in this series. The reason is that the *syn*-form, which does not react, must be converted into the reactive *anti*-form [134]. Arylhydrazones can undergo not only *C*- but also *N*-halogenation. The resulting derivatives are unstable, like all *N*-halogeno-compounds, and rearrange into more stable products (the Chattaway–Adamson rearrangement): [45,48,127,129]



Azines of aldehydes undergo substitution halogenation on treatment with halogens, with the stepwise replacement first of one and then the second hydrogen atom of the azine group [2,10,44,45,49,139]:

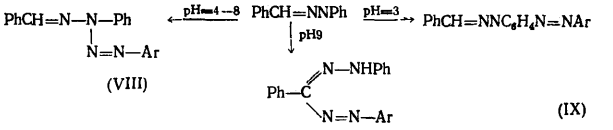


Under severe conditions of halogenation azines of the anthraquinone series undergo nitrile cleavage [139]. Azines of ketones do not undergo substitution, but add the halogen molecule at the 1,4-positions [2,10,11,44,48,140,141]:

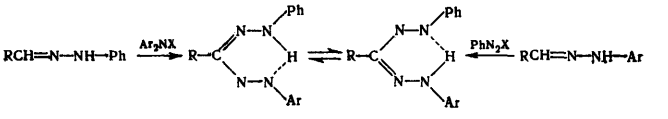


Reactions with Arenediazonium Salts

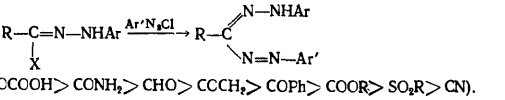
Phenylhydrazones of aldehydes react with arenediazonium salts to yield various products depending on the conditions [45,47,103,142]:



Production of the brightly coloured formazans (IX) has been the most thoroughly studied [2,11,31,38-40,47,48,71,103,137,143,144]. Arylhydrazones [47,103,117,143-146] and heterocyclic hydrazones [47,103,147-150] of aromatic [47,103,142,143,148,150], heterocyclic [47,103,143]; and aliphatic [144,147,149] aldehydes can be coupled, as well as arylhydrazones and arylosazones of sugars [38-40,47]. In general the isomeric forms of unsymmetrical formazans cannot be isolated, since they exist in equilibrium [47,103,143,145] and the two possible routes for the preparation yield the same product [145]:

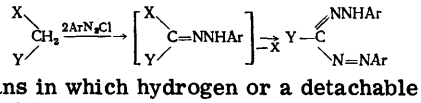


Among arylhydrazones of ketones only those in which the hydrazone carbon atom is combined with an easily eliminated group are able to undergo this reaction [47,103,144]:

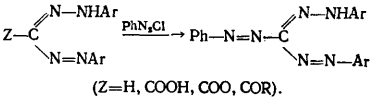


(X=COOH> H> CCCOOH> $CONH_2$> CHO> $CCCH_3$> COPh> COOR> SO_2R> CN).

Formazans are often produced by the action of diazonium salts on compounds containing an active methylene group (in the presence of a labile activating group) or a methyl group, since the rate of the second coupling (with the hydrazone formed as intermediate) far exceeds that of the first coupling [47,144]. In compounds containing an active methylene group one of the activating groups (listed above) is split off [47,144,151-155]:

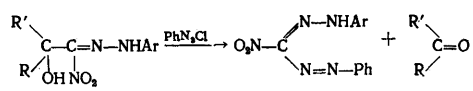


Formazans in which hydrogen or a detachable group is combined with the carbon atom react with diazonium salts analogously to arylhydrazones of aldehydes [47,108]:



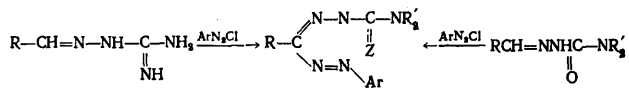
(Z=H, COOH, COO, COR).

Arylhydrazones of general formula (X) also yield formazans by eliminating a molecule of a carbonyl compound[144]:



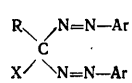
(X)

It has been reported[83,103] that analogues of formazans, the so called guanazyls, have been prepared from guanylhydrazones; among semicarbazones only $N_{(4)}N_{(4)}$-disubstituted derivatives yield such products, whereas acyl- and thioacyl-hydrazones do not react with arenediazonium salts[156].



(a) Z=NH, R'=H, (b) Z=O, R'=Ar.

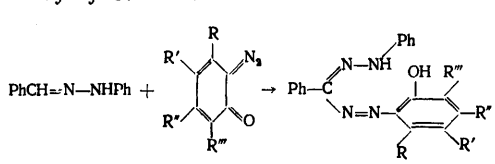
Since disubstituted hydrazones of aldehydes and $N_{(5)}$-alkylated formazans do not undergo the reaction, it was supposed that the formation of formazans involved tetrazens (VIII) as intermediates[47,103,142,148,157]. It has been shown recently, however, that the intermediate compounds are bisarylazo-derivatives (XI)



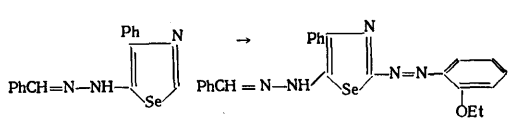
(XI)

(X=H, COOH, COOR, etc.)

In alkaline medium they isomerise rapidly into formazans (IX).[48,72,158,159] The possibility of direct substitution of the hydrogen atom in arylhydrazones of aldehydes by an arylazo-group has also been discussed[116,142]. The probability of this mechanism is supported, in our opinion, by the coupling[160] of arenediazonium salts with 1-aryl-2-pyrazolines, which are cyclic analogues of hydrazones. Diazoquinone derivatives react similarly to arenediazonium salts with arylhydrazones[161,162]:

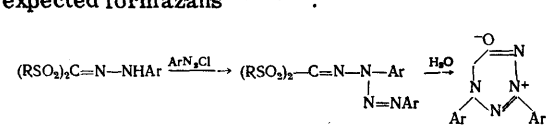


However, not all hydrazones can be converted into formazans. Thus compound (XII) is obtained from 5-benzylidenehydrazino-4-phenylselenazole and diazotised *o*-phenetidine[117]:

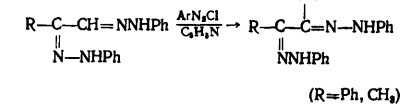


(XII)

Although arylhydrazones of bisalkylsulphonylformaldehydes split off the sulphonyl group, 1,3-diaryltetrazol-5-ones, which exist in the betaine form, are produced instead of the expected formazans[31,163,164]:



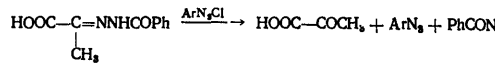
Phenylosazones of monosubstituted glyoxals are converted into phenylosazones of α-diketones[45,47,165,166], *C*-arylation occurring instead of azo-coupling:



(R=Ph, CH_3)

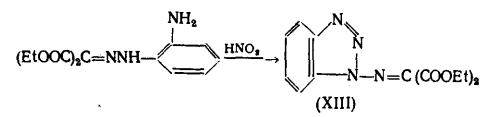
Nevertheless, formazans (azaformazans) are formed smoothly from arylosazones of sugars[38,39,47].

Acylhydrazones yield aryl azides, amides of the corresponding acids, and carbonyl compounds[167]:



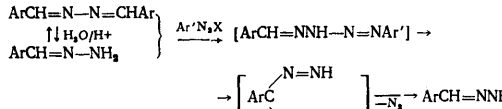
This reaction is assumed[167] to involve the intermediate formation of tetrazens, and support for this view will be found in Refs. 45 and 168.

The ability of *o*-aminophenylhydrazones to undergo intramolecular azo-coupling at the amino-nitrogen atom has been used recently by Campbell and Rees[169] to prepare derivatives of benzo-1,2,3-triazol-1-amine (XIII):



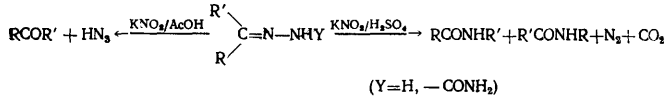
(XIII)

Azines and unsubstituted hydrazones (into which the former are initially hydrolysed under the reaction conditions) of aromatic aldehydes react with arenediazonium salts in acetic-acid solution to give arylhydrazones of the aldehydes[170]:



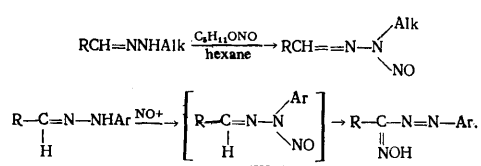
Nitrosation

In acetic-acid solution the nitrite ion decomposes hydrazones and semicarbazones with formation of an oxo-compound and an azide ion[2,171], but in concentrated sulphuric acid the Schmidt rearrangement occurs to the corresponding acid amide[2,172,173]:



(Y=H, $-CONH_2$)

Monoalkylhydrazones of aldehydes are nitrosated by nitrous acid and its esters to relatively stable *N*-nitroso-derivatives[2], whereas the monoarylhydrazones are rapidly converted by nitrosating agents into arylazo-aldoximes (nitrosazones), which are oxime analogues of formazans[2,45,48,174]:

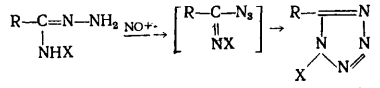


(XIV) (XV)

The formation of arylazo-aldoximes (XV) involves intermediate formation of the compound (XIV).[2,45,48,174-176]

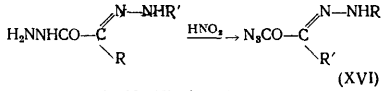
Bulky *ortho*-substituents in aromatic arylhydrazones prevent both nitrosation and the formation of arylazo-aldoximes [174].

Amidrazones, hydrazidines, and α-hydroxyamino-hydrazones, on treatment with nitrosating agents, are cyclised into tetrazoles via a stage of azido-derivatives [10,31,110,177-179]:



(X=H, NHR', OR", R'=H, Ph, 2,4-$C_6H_3(NO_2)_2$, R"=H, Alk, Ar).

When the hydrazone molecule contains an amine or a hydrazide group (not attached to the hydrazone group), attack by the nitrite ion takes place firstly at the former groups, not at the hydrazone fragment [45,170,180,181]:

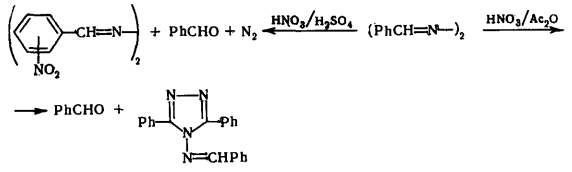


(XVI)

(R=H, Alk, Ar; R'=H, Ar).

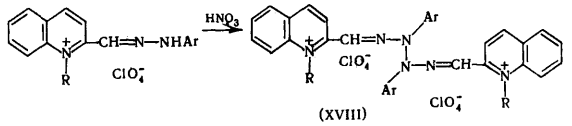
Nitration

On treatment with nitric acid in sulphuric acid, benzaldehyde azine undergoes oxidative cleavage and is partly nitrated, with formation of the azines of *p*- and *o*-nitrobenzaldehydes; when the reaction is conducted in acetic anhydride, only benzaldehyde and 4-benzylideneamino-3,5-diphenyl-1,2,4-triazole (XVII) are formed [182]:



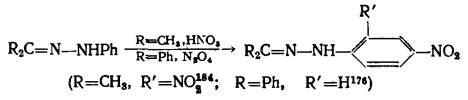
(XVII)

Aldehyde arylhydrazones are evidently more liable to be oxidised than to be nitrated by nitric acid. Thus arylhydrazones of 1-substituted 2-formylquinolinium perchlorates are easily oxidised to dimeric products (XVIII):[183]



(XVIII)

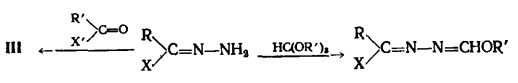
Under mild conditions phenylhydrazones of ketones are nitrated in the aniline ring by nitric acid [184] or by oxides of nitrogen [176]:



(R=CH_3, R'=NO_2 [184]; R=Ph, R'=H [176])

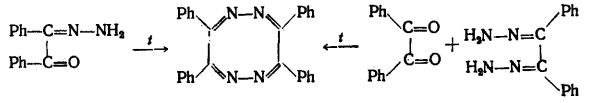
Reactions with Carbonyl Compounds

Carbonyl compounds react at the amino-nitrogen in unsubstituted hydrazones, and convert them into azines, a reaction very frequently used for the preparation of unsymmetrical azines [2,9,10,44,49,109,185,186]:

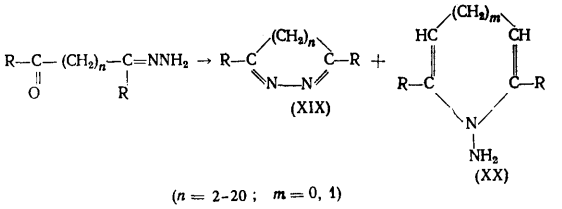


Dihydrazones of cyclohexane-1,3-dione [187] and the 1-hydrazone 2-methylphenylhydrazones of α-dicarbonyl compounds [188] react similarly. Unsubstituted amidrazones are converted into amino-azines [110]. The carbonyl compounds can be replaced by their acetals [10,44,49]. Ortho-esters give α-alkoxy-azines with hydrazones [45,189].

Monohydrazones of α-diketones when heated form an eight-membered heterocycle [190], which can be obtained also from the α-diketone together with its dihydrazone [191]:



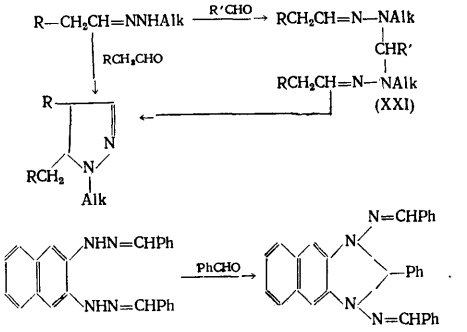
However, this reaction is not general [192]. Monohydrazones of β-dicarbonyl compounds are converted into pyrazoles (see subsection on alkylation). Monohydrazones of γ–ω-dicarbonyl compounds are able to yield either polyazines or heterocyclic compounds of the type (XIX), [2,10,25,49,193] as well as compounds of type (XX) (derivatives of *N*-aminopyrrole and *N*-aminodihydropyridine respectively) [10]:



(XIX) (XX)

(n = 2-20; m = 0, 1)

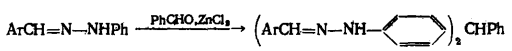
The higher electron density on the amino-nitrogen atom in monoalkylhydrazones facilitates electrophilic attack by oxo-compounds at this atom, and the reaction products are geminal dihydrazones (XXI); [2,9,10,194,195] in the aromatic series a similar reaction has been reported for a vicinal naphthylenedihydrazone of benzaldehyde [45,196]:



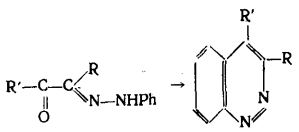
Compounds of type (XXI) are highly reactive: anhydrides of carboxylic acids acylate them to acylhydrazones [100], alkylhydrazines convert them into the corresponding hydrazones [194], and in the presence of excess of the aldehyde they are transformed into pyrazolines [194] (when Alk = H in (XXI), aldehydes yield azines [100]). It is supposed [194] that compounds (XXI) are formed as intermediates in the conversion of alkylhydrazines [194,197] or alkylhydrazones and aldehydes [194,197,198] into pyrazolines. Ioffe et al. have shown [198] that a pyrazoline is formed very easily from an aldehyde and its alkylhydrazone, but in the cross condensation of aldehydes with monoalkylhydrazones of other aldehydes and ketones the process is complicated by transhydrazonation, which occurs widely among hydrazones [199-212].

Arylhydrazones are more liable to transhydrazonation on reaction with carbonyl compounds, although phenylhydrazones form products of the triphenylmethane type,

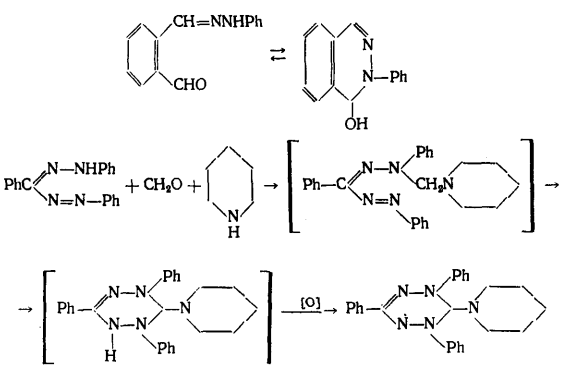
involving condensation at the *para*-position; the reaction is catalysed by zinc chloride and by acids[45]:



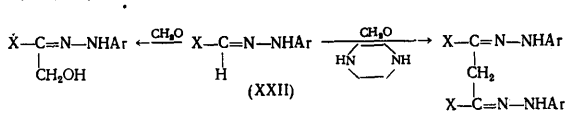
The phenyl ring is involved also in the intramolecular cyclocondensation of monophenylhydrazones of α-dicarbonyl compounds, which leads to the formation of cinnoline derivatives[26]:



The amino-group of arylhydrazones is also capable of condensation with carbonyl compounds. Phthaldehyde monophenylhydrazone exists in equilibrium with 1,2-dihydro-1-hydroxy-2-phenylphthalazine[27]; and 1,3,5-triphenylformazan reacts with formaldehyde and piperidine to give 1,3,5-triphenyl-5-piperidinomethylformazan, which under the reaction conditions cyclises into a 1,2,3,4-tetrahydrotetrazine derivative, and this oxidises spontaneously to verdazyl[213]:

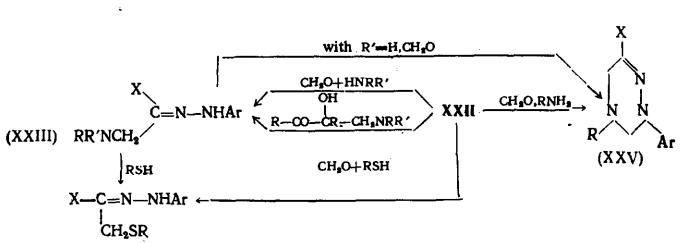


Oxo-compound arylhydrazones of type (XXII) (X = Az, NO_2, N:NAr, Ht, sometimes Ar) behave as if they contain a mobile hydrogen atom, and form arylhydrazones of α-hydroxy-ketones or bisarylhydrazones of 1,3-diketones[2, 10, 26, 45, 157, 214, 215]:



If the phenyl group in (XXII) contains an *ortho*-carbonyl group, intramolecular cyclocondensation may occur, leading ultimately to cinnoline derivatives[26].

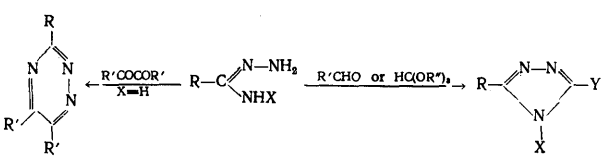
As compounds (XXII) (including 3*H*-formazans[157]) contain a mobile hydrogen atom, they undergo the Mannich reaction[45, 215-219], being converted into (XXIII), and with formaldehyde in the presence of thiols they yield (XXIV):[219]



A case of detachment of an acetyl group has been reported in the preparation of Mannich bases of the type (XXIII) from 2,3,4-trioxopentane 3-phenylhydrazone, formaldehyde, and piperidine[220]. The dialkylamino-group in (XXIII) is quite mobile, and can be substituted by the action of secondary amines, compounds containing a reactive hydrogen atom[218], and thiols[219] (including benzenethiols[220]), which helps to explain certain anomalies observed when these reactions are carried out[215]. The activity of (XXII) in the Mannich reaction is extremely high: they displace the dialkylaminomethyl group from Mannich acyloin bases[217].

When R′ = H in (XXIII), the *syn*-forms are able to condense with a further aldehyde molecule to 2,4,6-trisubstituted 2,3,4,5-tetrahydro-1,2,4-triazines (XXV).[221] Hahn showed[222-225] that the same products are formed by the reaction of hydrazones of type (XXII) with formaldehyde and primary amines. The formation of 1,2,4-triazine derivatives (XXV) from hydrazones of type (XXII) is a variety of the Mannich reaction, is quite general in character[222-226], and can be termed the Mannich–Hahn reaction.

Amidrazones and hydrazidines are also cyclised to 1,2,4-triazine derivatives on reaction with α-dioxo-compounds[110, 227-230], and into 1,2,4-triazole derivatives on treatment with aldehydes, acetals, or orthoesters[28, 45, 110, 231-233]:

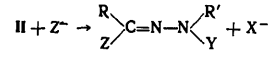


(X=H, Alk, Ar, NHR; Y=R′ or OR″).

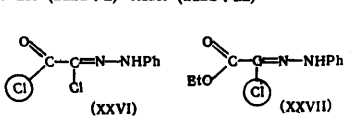
III. REACTIONS OF HYDRAZONES WITH NUCLEOPHILIC REAGENTS

1. Substitutions at the Carbon Atom of the Hydrazone Group

Substitution occurs readily at the carbon atom attached to the hydrazono-group if the substituent X in the general formula (II) for a hydrazone is chlorine, hydroxyl, nitrile, an *NN*-dialkylaminoarylazo-group, etc.[2, 31, 32, 45-47, 123, 130, 134, 138, 143, 179, 187, 189, 234-251] (see Table):



A chlorine atom attached to the hydrazone carbon atom is less reactive than one attached to a carbonyl carbon but more reactive than an ethoxy-group; and the circled chlorine atoms in (XXVI) and (XXVII)

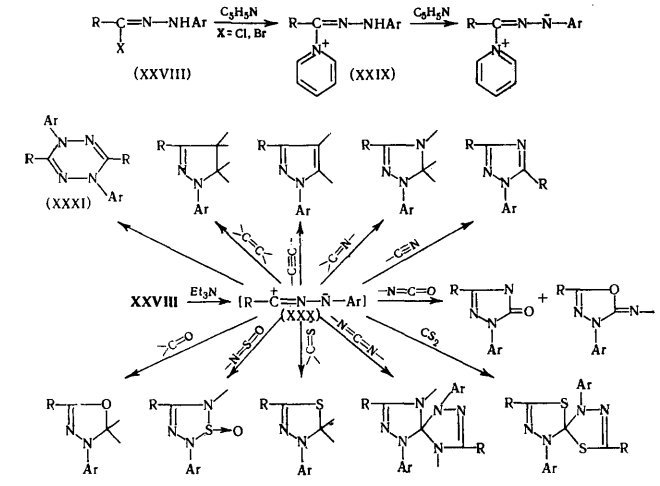


are replaced by the action of the azide ion[237, 239, 243].

There are also cases in which the products of nucleophilic substitution of hydrazones then undergo cyclisation[23, 31, 45, 131, 243-248]. Azines also undergo S_N reactions readily if X = Hal, CN, NO_2, etc. in (III),[22, 29, 31, 128, 138, 167, 189, 249-251] but cyclisation is then observed considerably more frequently[22, 29, 31, 32, 45, 133, 250, 251].

2. Reactions of Halogenated Hydrazones with Tertiary Amines

Halogeno-hydrazones (XXVIII) are able to react with tertiary amines by the usual mechanism of nucleophilic substitution to give a quaternary salt (XXIX),[45] but more frequently XH is eliminated with the formation of the extremely reactive "nitrilimine" (XXX), one of the most thoroughly studied 1,3-dipolar reagents[2,31-35,45,252,253]:



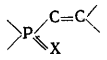
X	Z	Ref.	X	Z	Ref.
— Cl	— OH[a]	45,234	Br	— OH[a]	130, 133, 134 240, 241
	— OAc	45		— OAlk	45, 234
	— OAlk	45,234		— NHAr	128, 134
	— SH[a]	144			
	— SR	47		— NH_2	45
	— NH_2	2, 45, 47, 138		— $NHNH_2$	134, 179, 236
	— NHAlk	45, 138		— NHNHAr	47, 137
	— NHAr	2		— N_3	134, 236
	— $NAlk_2$	45, 138, 237 258	— NH_2	— NHAlk	189, 241
	— $NHNH_2$	31, 32, 45, 237		— $NAlk_2$	241
	— $NHNHR^b$	47, 143		— $NHNAlk_2$	240
	— N_3	31, 167, 239			
	— CN	45	— NHAlk	— OH[a]	189
	— I	47	— OAlk	— N_3	45
— $NHNAlk_2$	— NHAlk	241		— NH_2	194
	— OH[a]	45		— NHAlk	189, 242
	— SH	47			
	— CN	46		— NHAr	242
	— NHPh	2		— $NAlk_2$	189
— CN	— NHR	250		— $NHNHAr^b$	45
— OH[c]	— $NHNHR^b$	143		— NAlkAr	189
			— N = N — Ar	— OH	230

[a] Under the reaction conditions rearranges into a hydrazide (thiohydrazide).
[b] Very easily oxidised to formazan[47,143].
[c] The hydrazide of the acid is used.

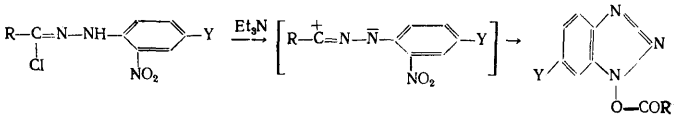
A nitrilimine cannot be isolated in individual form, since it either dimerises to a dihydrotetrazine (XXXI)[31-35,45,252-255] or, in the presence of an unsaturated compound in the reaction medium, undergoes 1,3-dipolar cycloaddition with the formation of various five-membered heterocyclic systems. The mechanism of the latter type of reaction has been discussed many times in the literature[253,256,257], and a multicentre cyclic transition state is the most probable. 3-Halogenated formazans can also serve as source of nitrilimines[31-35,45,252,253]. Various types of ethylenic compounds (including cyclic and heterocyclic), alkenylamines, alkynes, nitriles, azomethines, isocyanates, aldehydes, thioaldehydes, carbon disulphide, and carbodi-imines have been used as dipolar reagents[31-35,45,252-263]. The enhancement of the electron-accepting properties of the substituents R and Ar in (XXX) diminishes its reactivity towards addition at the double bond and increases the probability of dimerisation[268].

A nitrilimine adds more easily at a C=C than at a C≡N[264] or a C≡C[259] bond, but reacts less actively with a >C=N fragment[260]. In pent-1-en-4-yn-3-ones the nitrilimine reacts with the multiple bond having fewer substituents[261]. Cycloaddition is a stereospecific reaction: the most highly substituted carbon atom of the ethylenic or acetylenic group becomes position 5 of the pyrazoline or pyrazole ring[262].

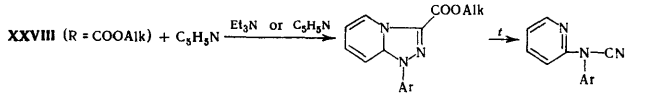
The cyclic products formed by the reaction of (XXX) with aldehyde oximes and azines rapidly undergo further reaction, splitting off a molecule of water in the first case and cleaving at the N–N bond in the second, to give substituted triazoles as final products[268]. Vinyl derivatives of quinquevalent phosphorus, containing the group



undergo the usual type of 1,3-dipolar cycloaddition with nitrilimine[264], whereas $\alpha\beta$-unsaturated phosphonites and phosphines react by a mechanism of 3 + 3 addition[265]. Acylhydrazones, as well as semicarbazones and α-halogeno-aldehydes, are converted by tertiary amines into oxadiazole derivatives[2,266]. If the aryl ring in (XXVIII) contains an *o*-nitro-group, the resulting nitrilimine rearranges rapidly into a 1-acyloxybenzotriazole[267,268]:



Pyridine, quinoline, and isoquinoline can also act as dipolarophilic agents in reactions with hydrazones of type (XXVIII) in which R = COOAlk, but at high temperatures the products rearrange into heterocyclic *N*-arylcyanamides[269,270]:

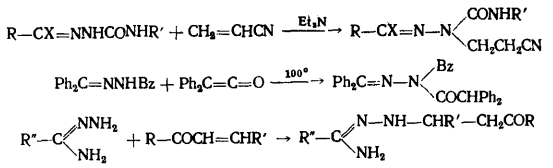


IV. ADDITION REACTIONS

1. Addition of Hydrazones at Multiple Bonds

Unsubstituted and monosubstituted hydrazones of aldehydes and ketones, as well as disubstituted hydrazones of aldehydes, contain a mobile hydrogen atom, and therefore are able to undergo the Michaelis reaction[2-7,9-12,21,23,24,25,271-281]. Addition can take place at azo[45,282-284], ethylenic[2-7,9-12,21,23,45,271,272,285,287], acetylenic[9,10,23,24,45,286] azomethine[45,100,103,180,181,209,273-277], nitrile[2-7,9-12,23,45,278-281], and carbonyl[27] groups, the amino-proton being more mobile than the hydrogen atom attached to carbon.

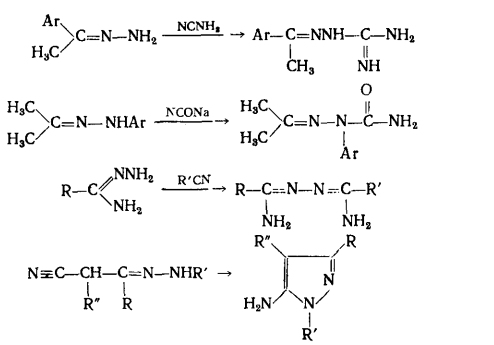
The reaction between semicarbazones and acrylonitrile is catalysed by tertiary amines[271]; benzophenone benzoylhydrazone reacts with diphenylketen in hot (100°C) xylene[287]; whereas amidrazones (amino-hydrazones) add to the ethylenic bond in vinyl ketones already at room temperature[272]:



The cyclisation of hydrazones of $\alpha\beta$-unsaturated carbonyl compounds, which occurs by a mechanism of intramolecular nucleophilic addition[23], is the most widely developed method for obtaining pyrazolines. The ease of ring closure depends on the nature of the substituents in carbonyl and hydrazine residues, and it occurs either when the hydrazones are formed or when they are heated in solution, often in the presence of acids[21,23]. The capacity for cyclisation diminishes with increase in the electron-accepting character of R′. Addition of the N–H group of hydrazones to an acetylenic bond has been observed mainly in cases of intramolecular cyclisation with the formation of pyrazoles[2-7,9-12,23,45]. Unsubstituted hydrazones[273], alkyl-, aryl-, and acyl-hydrazones[45,273,274], 1,5-diarylformazans[47,103], and substituted amidrazones[275,276] are easily added at the C=N bond of alkyl, aryl, and acyl isocyanates and isothiocyanates to give *N*-substituted semicarbazones and thiosemicarbazones respectively.

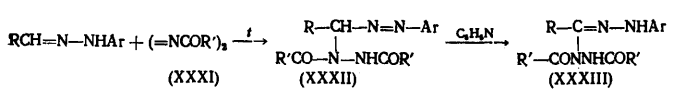
An example has also been reported of the preparation of a pyrazoline by the intramolecular nucleophilic addition of a hydrazone at the C=N bond of an azomethine[277], and an example of the addition of an unsubstituted hydrazone at a C=N bond of an azine[100].

The NH group of a hydrazone adds also to a C≡N bond, although with greater difficulty than at an ethylenic bond[271]. Acetophenone hydrazone and cyanamide in boiling alcohol yield the guanylhydrazone of this ketone[278], and $N_{(2)}$-arylsemicarbazones are obtained from sodium cyanate and arylhydrazones[45]:



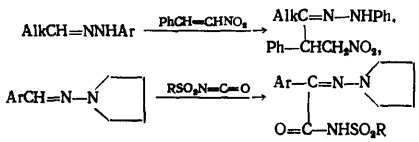
Amidrazones add to mono- and di-nitriles in the presence of triethylaluminium[279]. The intramolecular addition characteristic of hydrazones of α-cyano-carbonyl compounds provides a method for preparing aminopyrazoles[2-7,9-12,23,45,280,281].

The nature of the reaction products obtained from arylhydrazones and azo-acyls (XXXI) has been discussed many times. It is now considered that an azo-hydrazine (XXXII) is formed, which under the reaction conditions sometimes—and then only partly—rearranges into the hydrazidine (XXXIII); but (XXXII) easily passes into (XXXIII) on dissolution in pyridine[45,282-285]:

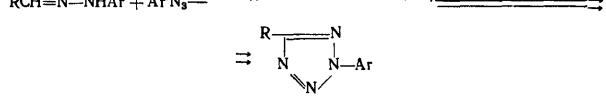


The ability of hydrazones to add to a C=O bond has been discussed above (Section II, subsection on reactions with carbonyl compounds).

Hydrazones are able to add to ethylenic[286], acetylenic[287], and azomethine[209] bonds by means of the =C–H fragment, but few examples of these reactions have been reported hitherto:



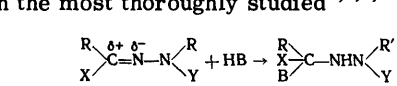
The reaction of aldehyde hydrazones with azides in the presence of sodium alkoxides leads to the formation of 2,5-diaryltetrazoles[31,45,288,289]. If the reaction is conducted under milder conditions, however, it is possible to isolate intermediate addition products—1,4,6-trisubstituted 1,2,3,5,6-penta-azahexa-2,4-dienes—which on further heating are cyclised to the tetrazoles[45,167,288]. Hence the first stage involves addition to the 1,3-dipolar reagent, and the second stage intramolecular azo-coupling:



Unsubstituted hydrazones, in the form of an anion, add to toluene-*p*-sulphonyl azide, but the products are unstable, and decompose into a diazo-compound, nitrogen, and toluene-*p*-sulphonamide[290,291].

2. Addition at the C=N Bond of the Hydrazone Group

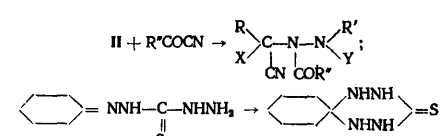
Reactions involving the addition of nucleophilic reagents have been the most thoroughly studied[1,2,9,10,32,44,45,48,49,292-314]:



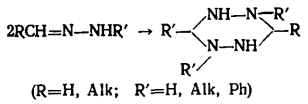
(B=—CN [2,10,32,44,45,48,49,292-294], —NHN=CRX[100], —NHNHR″[295], —OR″[1,296], —SR″[297], —P(O)(R″$_2$)[298-300], —HCR′NO$_2$[301,302], —R″ (R″MgX, R″Li)[2,9,10,44,45,292,303-308]).

In azines both azomethine fragments are capable of addition[2,9,10,44,49].

Hydrocyanic acid adds relatively easily to unsaturated hydrazones[10,45], alkylhydrazones[292], arylhydrazones[2,45,48], semicarbazones[2,10,45,292], and azines[2,32,44,49,292] of aliphatic and alicyclic aldehydes and ketones, which are converted into α-cyano-substituted hydrazines. Acetone cyanohydrin can be used instead of hydrocyanic acid[293]. α-Ketonitriles behave similarly to hydrocyanic acid, adding at the azomethine bond of arylhydrazones of aliphatic aldehydes and ketones to form acylated α-cyano-substituted hydrazines[45,294]:

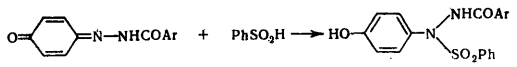


Hydrazines[295] and hydrazones[100] are able to add to the C=N bond of hydrazones. The transhydrazonation of hydrazones by hydrazines evidently also involves an intermediate stage of addition. The dimerisation of unsaturated hydrazones of aliphatic aldehydes[45,309] and of monoalkylhydrazones[32,310,311] and phenylhydrazones[312] of formaldehyde to 1,3,4,6-tetrasubstituted hexahydro-1,2,4,5-tetrazines is due to the addition of the NH group of one hydrazone molecule at the C=N bond of another molecule:



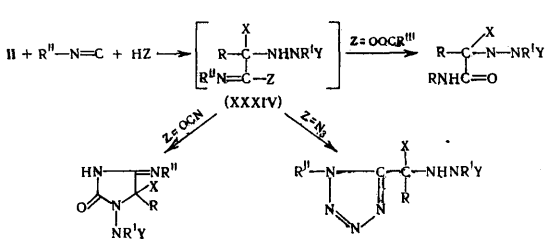
(R=H, Alk; R'=H, Alk, Ph)

The hydroxy-groups of cellulose react with the thiosemicarbazone of formaldehyde[296], and hydrogen sulphide with its azine[297]. Ring–chain tautomerism of 2'-hydroxyethylhydrazones also involves addition of a hydroxyl at the azomethine bond (Ioffe and Potekhin, Dorman—see Ref. 1 for literature). Dialkyl(and aryl)phosphines[298,299], dialkyl hydrogen phosphines[300], and nitroalkanes[301,302] add normally to hydrazones. Arenesulphinic acids and to mono(benzoylhydrazones) of *p*-benzoquinone at the 1,6-substituents[45]:

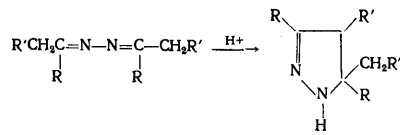


Mixed organomagnesium compounds react with unsaturated hydrazones, alkyl-, aryl-, and dialkyl-hydrazones, and azines of aldehydes to form hydrazines. This involves alkylation (or arylation) of the carbon atom in the hydrazone group[2,9,10,44,45,292,303–305]. The reaction is complicated by several secondary and consecutive processes, such as cleavage of the N–N bond, reduction, and rearrangements[2,45,304–308]. Organolithium compounds add somewhat more readily at the azomethine bond of hydrazones, and the yields of hydrazines are higher[304]. Strengthening the electron-accepting properties of the aryl group in dimethylhydrazones of substituted benzaldehydes favours the addition of an organolithium compound.

In the presence of acids isocyanides react with acetylhydrazones and azines to form an addition product (XXXIV),[2,31,313,314] which tends to rearrange or cyclise (Ugi's reaction):

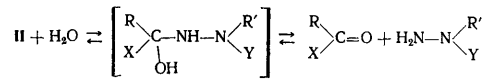


Less study has been made of reactions in which electrophilic addition takes place at the C=N bond in hydrazones. The aldol type of condensation in the presence of acid catalysts must be included among such reactions. Thus azines of carbonyl compounds containing an α-methine group cyclise to pyrazolines under the influence of acidic reagents[2,9,10,21,23,44,49,105,113,315,316]:



A kinetic study of the formation of 1-*cis*-3'-phenylpropenyl-5-phenylpyrazole in the pyrolysis of the azine of cinnamaldehyde has shown that this reaction is intramolecular[317], and so can indeed be included in the present type.

Hydrolysis. Being a weak nucleophilic reagent, the water molecule adds with difficulty at the C=N bond of hydrazones. The resulting *gem*-hydrazino-alcohols are unstable and decompose into the hydrazine and the carbonyl compound, or else lose the molecule of water and are converted back to the hydrazone, so that a dynamic equilibrium is established that under normal conditions is almost entirely displaced to the left:



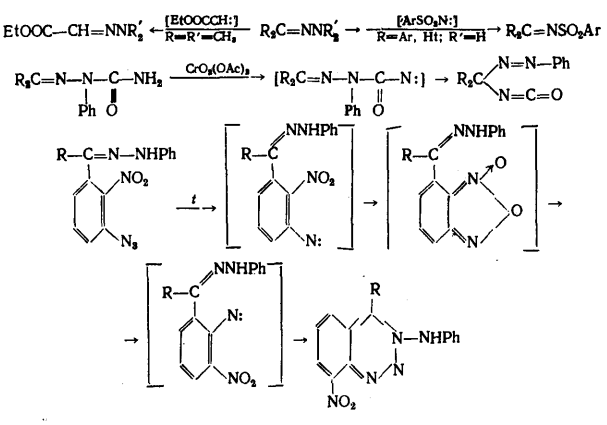
Alkaline[2,45,48] and especially acid catalysis[2,9,10,41,45,48,101,209,292] facilitates considerably the hydrolytic cleavage of hydrazones. The hydrolytic stability of these compounds is very greatly dependent on the nature of the substituents[2,45,48]: quaternary salts of hydrazones are most easily hydrolysed[9,10,49], followed by unsubstituted hydrazones[45] and alkyl- and acyl-hydrazones[2,9,10,49,292]. Arylhydrazones are more difficult to hydrolyse than are semicarbazones. Increasing the number of electron-accepting groups in the phenylhydrazone molecule improves its stability to acid hydrolysis[45,48]: for example, acetone 2,4-dinitrophenylhydrazone remains unchanged under conditions such that the phenylhydrazone is completely hydrolysed[45]. Arylhydrazones of α-keto-acids and α-dicarbonyl compounds possess improved stability. Arylosazones of sugars readily eliminate an arylhydrazine when boiled in acid medium[35,45]. Whereas the rates of hydrolysis of stereoisomeric oximes differ substantially, those of the stereoisomeric hydrazones of *p*-methoxybenzophenone differ insignificantly[318]. Almost all types of hydrazones and azines can be cleaved hydrolytically to the carbonyl compound, but if in (II) the substituent X = Hal, AlkO, ArO, NO_2, CN (see Section III, 2), ArN:N (formazans)[319], a hydrazide (a tautomeric form of a hydroxy-hydrazone: X = OH) is formed initially, and is then hydrolysed to the carboxylic acid and the hydrazine.

The hydrazone group is hydrolysed with greater difficulty than ester[10,38,45] and acylamino[10,45] groups. If these are present in a hydrazone molecule (X = COOR, OAr, NHAz, CONHR), they can be hydrolysed without the hydrazone fragment being affected.

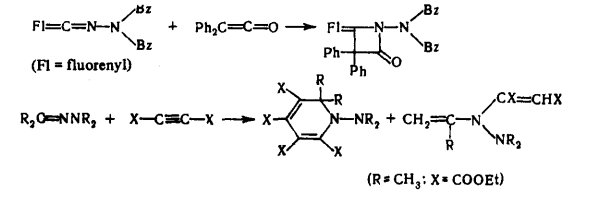
3. Cycloaddition

In contrast to alkenes and azomethines, which form three-membered rings with carbenes and nitrens[11,320], hydrazones are cleaved by these reagents. A carbene displaces the residue of the carbonyl compound[321,322],

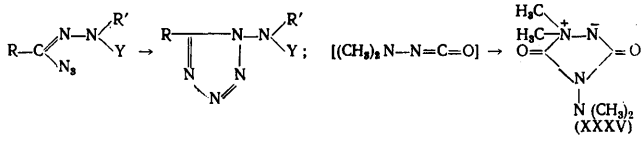
and a nitren the hydrazone fragment[323]; examples of 1,1-cycloaddition to hydrazones are not yet known. If a nitren is formed directly in the hydrazone molecule, the reaction is complicated by rearrangement[324,325]:



The possibility of 1,2-cycloaddition with hydrazones is shown by the reaction of aromatic diacylhydrazones with ketens[262]. Hydrazones do not react by 1,2-cycloaddition with acetylenic derivatives, perhaps owing to the instability of the ring: either linear 1 : 1 adducts are formed, or a second acetylenic molecule is involved to yield a cyclic 1 : 2 adduct[326]:

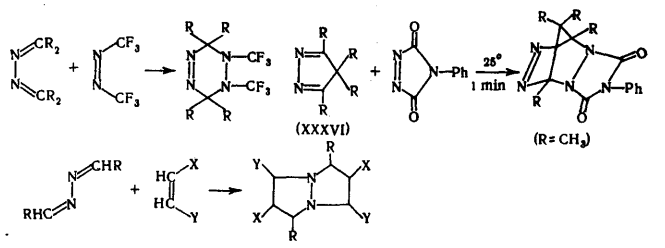


Reactions involving the 1,3-cycloaddition of hydrazones and azines to nitrilimine have been discussed above (Section III, 2). The formation of tetrazole derivatives from azido-hydrazones and azido-azines (very often at the instant of formation)[31,174] and the dimerisation of the dimethylhydrazone of carbon dioxide (dimethylamine isocyanate) into an ylid (XXXV)[327]



must be included in this type of reactions.

Examples of hydrazones functioning as dienophiles in the Diels–Alder reaction could not be found. A very attractive idea was to use azines as dienes, but the investigations showed[28,44,49,328] that only in very rare cases[329] could azines undergo 1,4-cycloaddition: usually they behave as "criss-cross" bis-1,3-dipolar reagents and form 1 : 2 adducts that are derivatives of tetrahydropyrazolo[1,2-*a*]pyrazole[28,44,328,330–333]. Aromatic and aliphatic aldazines and ketazines, and azines of perfluorinated carbonyl compounds react with alkylated alkene derivatives of acrylic, maleic, hydrocyanic, cyanic, and thiocyanic acids, and with alkyl, aryl, and acyl isocyanates, in conformity with this scheme of "criss-cross" addition[28,44,49,328,330–333]:

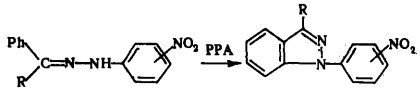


Such behaviour of azines towards dienophiles must evidently be explained by the non-coplanarity of azine molecules[1,334] and by steric hindrance to formation of the S-*cis*-form. The cyclic azine (XXXVI) very readily undergoes the Diels–Alder reaction[335].

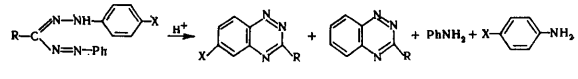
V. CATALYTIC CONVERSIONS

Action of Acids

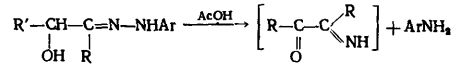
Several reactions of hydrazones in the presence of acids have already been discussed. The conversion of arylhydrazones of carbonyl compounds into indoles, known as the Fischer–Arbuzov reaction, also takes place under the influence of acids and acidic reagents[2,15–19,45,336]. Information on the catalysts used in this reaction will be found in Refs. 16–19. The formation of pyrroles from azines (the Piloty reaction) is a form of the Fischer–Arbuzov reaction[2,16–19,49]. The process involved in the formation of products of non-indole type under conditions for the synthesis of indoles has been termed an "anomalous Fischer–Arbuzov reaction".[16–19,337–341] Nitrophenylhydrazones of acetophenones, benzaldehyde, and aromatic ketones are cyclised into indazoles under the influence of polyphosphoric acid (PPA):[24,342–344]



Formazans are converted by strong acids into benzo-1,2,4-triazines and anilines[45,47,103,143,345]. Phenazine derivatives have been isolated as secondary products. Unsymmetrical formazans yield two benzo-1,2,4-triazines:

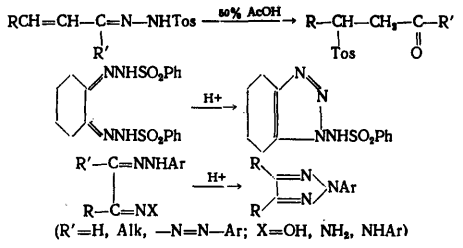


Heating arylhydrazones of α-hydroxy-carbonyl compounds in acetic acid results in fission of the nitrogen–nitrogen bond with formation of an unstable α-iminoketone, formed as intermediate in the preparation of osazones from α-hydroxy-carbonyl compounds and hydrazines[346,347]:

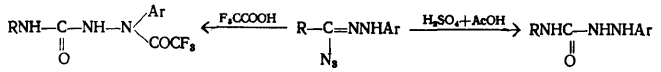


Toluene-*p*-sulphonylhydrazones of αβ-unsaturated ketones are converted in hot 50% acetic acid into good

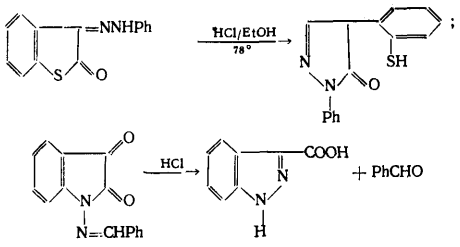
yields of β-tosylated ketones[348], whereas bisbenzenesulphonylhydrazones of α-diketones in acid medium form 1-substituted 1,2,3-triazoles[349]:



Formazan osazones[38,39], bisarylhydrazones, and hydrazone oximes of α-dicarbonyl compounds cyclise under these conditions to give 2-substituted 1,2,3-triazoles[20,28,88,350]. α-Azido-hydrazones in acid medium undergo rearrangement into 1,4-disubstituted semicarbazides (Curtius type of rearrangement)[236]:

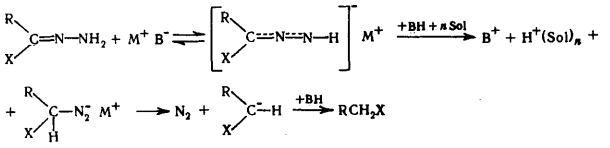


Several hydrazones of heterocyclic aldehydes and ketones, as well as hydrazones containing a heterocyclic radical, are able to rearrange under the influence of acids to form a new heterocyclic system, most often a pyrazole ring[25,45,351] (recyclisation):



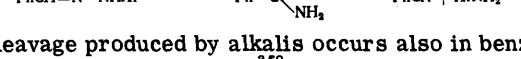
Action of Bases

Strong alkalis (potassium hydroxide and alkoxides) convert unsubstituted hydrazones and semicarbazones into saturated hydrocarbons (Wolff–Kishner reductions)[2,10,11,36,37,352–354]:

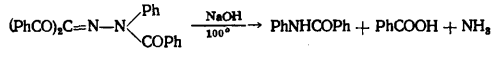


(B=OH$^-$, RO$^-$, $CH_3SOCH_2^-$; Sol = ROH, dimethyl sulphoxide)

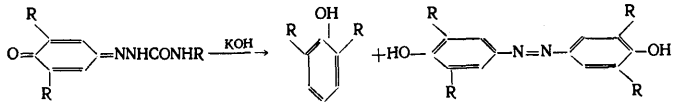
Azines undergo complicated changes in the presence of strong bases, evidently through an intermediate stage of nitrile cleavage. Thus under the influence of potassium t-butoxide in boiling xylene benzaldehyde azine gives a mixture of products, mainly 3,5-diphenyl- and 1-benzyl-3,5-diphenyl-1,2,4-triazoles together with benzoic acid[355]. Boiling arylhydrazones of aromatic aldehydes in the presence of potassamide or sodamide in xylene or benzene leads to the formation of amides[11,45,50,356–358] (the Robev rearrangement), which under the reaction conditions may decompose into an arylamine and a nitrile. This reaction involves an intermediate stage of homolytic cleavage of the nitrogen–nitrogen bond[357,358]:



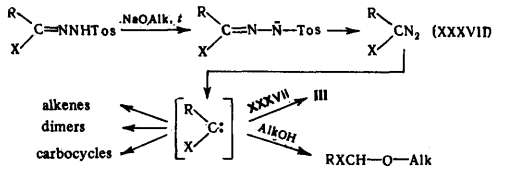
Such cleavage produced by alkalis occurs also in benzoylphenylhydrazones of quinones[359] or aromatic ketones[360]:



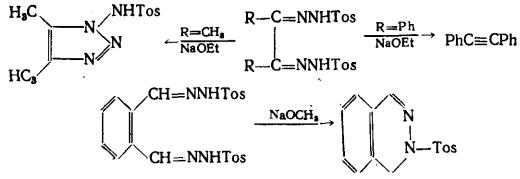
Semicarbazones of quinones decompose in hot alkali into phenols[361,362], and azophenols have been isolated as by-products[362]:



Diazo-compounds are formed by the hot alkaline cleavage of toluene-p-sulphonylhydrazones of aliphatic, mono-, di-, and tri-cyclic, aromatic, and steroid aldehydes and ketones[11,320,363]. They are not usually separated from the hydrazones, but are converted *in situ* into carbenes[10,11,321,363–372]. Decomposition of the dry sodium salts of toluene-p-sulphonylhydrazones gives similar results[365,370,371]:

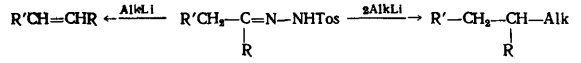


Toluene-p-sulphonylhydrazones of $\alpha\beta$-unsaturated ketones behave similarly on alkaline decomposition in protic solvents[372], whereas in an aprotic medium cyclopropenes are formed[373]. Depending on the nature of the groups in the carbonyl component, bistoluene-p-sulphonylhydrazones of α-dicarbonyl compounds form either alkynes or 1,2,3-triazole derivatives[363]:



The alkaline cleavage of the corresponding dihydrazone of phthaldehyde also yields a heterocycle, not a dicarbene[374].

The action of a lithium alkyl on toluene-p-sulphonylhydrazones of carbonyl compounds containing an α-methine group provides a convenient method for obtaining alkenes[375,376] and dienes[377] that are particularly inaccessible, e.g. in the terpene or steroid series. The abnormally high content of *cis*-alkenes in the products is evidently due to the fact that intermediate formation of a carbene is not involved[378]. Toluene-p-sulphonylhydrazones of $\alpha\beta$-unsaturated ketones are converted by butyllithium or sodium hydride into pyrazoles[372]. The use of excess of a lithium alkyl yields the alkylated hydrocarbon without the formation of alkenes[379]:



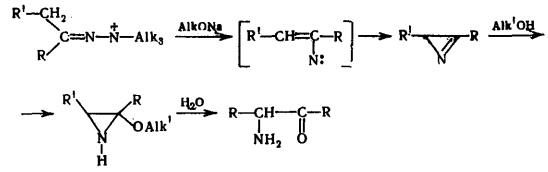
Under the influence of alkalis quaternary hydrazonium salts of aldehydes undergo amino–nitrile cleavage with rupture of the nitrogen–nitrogen bond[2,11,49,51,63,74–76,380–383]:

$$RCH{=}N{-}\overset{+}{N}Alk_3 \xrightarrow{OH^-} RCN + Alk_3N$$

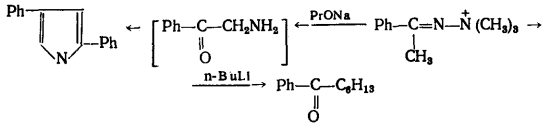
This is a general reaction for cyclic and acyclic hydrazonium salts[51] containing the fragment

$$-CH{=}N{-}\overset{+}{N}\lessgtr .$$

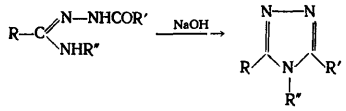
Quaternary salts of disubstituted hydrazones of ketones containing an α-methine group are cleaved by alkalis to α-amino-ketones[2,8,62,384–386]. The intermediate nitren isomerises into an azirine, which adds a molecule of an alcohol to form the alkoxyaziridine, and this is converted by water into the amino-ketone[62,384–386]:



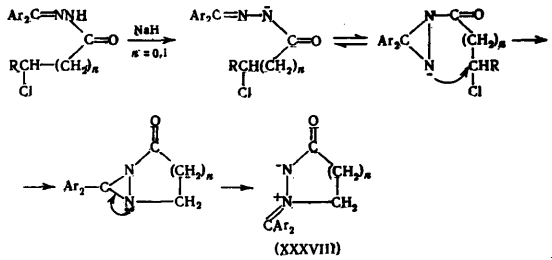
Acetophenone trimethylhydrazonium iodide is converted by an alkoxide into 2,4-diphenylpyrrole[386], and n-butyllithium yields 1-phenylheptanone[387]:



In the presence of alkalis or acids dihydrazones and oxime hydrazones of α-dicarbonyl compounds are cyclised to 1,2,3-triazole derivatives[28,45], whereas acylated amidrazones in alkaline medium are cyclised to 1,2,4-triazole derivatives[22,28,388]:



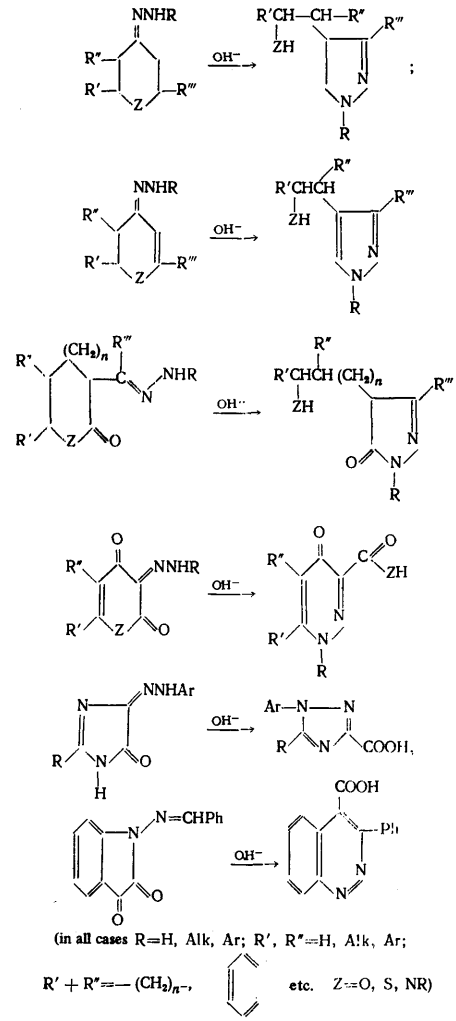
Acylhydrazones of aromatic ketones, obtained from hydrazides of α- and β-chloro-carboxylic acids by the action of bases such as sodium hydride, form cyclic ylides (XXXVIII),[389] most probably by the following series of reactions:



(XXXVIII)

Hydrazones of certain heterocyclic ketones undergo rearrangement with formation of a different heterocyclic system[9,10,23,25–27,45,49,390–396], more often in alkaline than in acid solutions. Monosubstituted and unsubstituted hydrazones of flavanones[45,390,391] chromones and thiochromones[45], 3-acylchromones[392], pyrones[23,45,49], α-acyl-γ-lactones[23,45] and thiolactones[45,393], and 3-acylindoles[49,394] when heated in alkaline medium rearrange to derivatives of pyrazole, pyrazoline, or pyrazolone.

Hydrazones of α-acyl- and α-oxo-δ-lactones[26,27,45,395] are converted into pyridazones (cinnolines), and 5-arylhydrazones of unsubstituted, 2-alkylated, and 2-arylated imidazoline-4,5-diones into 1-aryl-5-R-1,2,4-triazole-3-carboxylic acids[396]. Hydrazones that are derivatives of *N*-amines of nitrogenous heterocycles also tend to undergo such rearrangements[26,45,125]. A common feature of these reactions is rupture of the Z–C bond in the heterocycle with nucleophilic attack on the amino-nitrogen atom of the hydrazono-group and formation of a carbon–nitrogen bond in a new heterocycle:



(in all cases R=H, Alk, Ar; R′, R″=H, Alk, Ar; R′ + R″ = —(CH$_2$)$_n$—, etc. Z=O, S, NR)

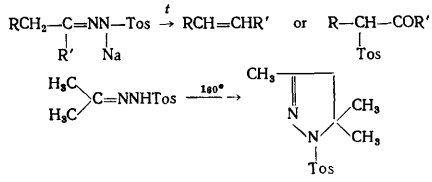
Pyrolysis

Heating to 200–300°C aryl-, diaryl-, and acyl-arylhydrazones of aldehydes, sometimes also of ketones[397], often in the presence of transition-metal chlorides, leads to heterolytic cleavage of the nitrogen–nitrogen bond with formation of a nitrile and an arylamine[2,10,45,50,101]:

$$RCH{=}NNHR'Y \xrightarrow{200-300^\circ} RCN + R'NHY$$

Alkylhydrazones of aldehydes are also capable of nitrile cleavage, but the reaction occurs with greater difficulty[50,197]. Trialkylhydrazonium salts of aldehydes of type (VI) are cleaved considerably more easily[50,51].

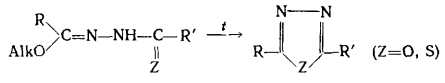
In the case of bisarylhydrazones of 1,4-diketones heating leads to the formation of *N*-arylpyrroles[17]. Pyrolysis of the sodium derivatives of toluene-*p*-sulphonylhydrazones is one method for generating carbenes[320,398,399], whose further transformation depends on the structure of the carbonyl component, mostly yielding alkenes[398], sometimes ketones containing a *p*-tolylsulphonyl group[399]:



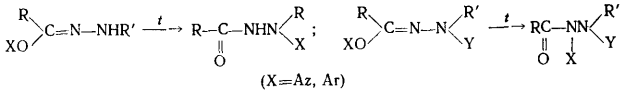
Pyrolysis of acetone toluene-*p*-sulphonylhydrazone is "anomalous" and leads to the formation of 3,5,5-trimethyl-1-*p*-tolylsulphonyl-Δ^2-pyrazoline[400]. Thus the products are analogous in structure to those obtained by the catalytic decomposition of acetone phenylhydrazone[339]. Derivatives of Δ^2-pyrazoline are formed also by pyrolysis of the perchlorate of acetophenone dimethylhydrazone[101].

When acylhydrazones, including semicarbazones and thiosemicarbazones, are boiled in solvents or are heated above their melting points, azines are formed[44]. The pyrolysis of aromatic azines at temperatures around 300°C passes through a stage in which diazo-compounds are formed[2,11] and then carbenes[338,401], yielding stilbene derivatives[2,10,44,49,402], but cyclopropane derivatives when alkenes are present[332]. Aliphatic azines decompose analogously, but the possibility of isomerisation into azo-compounds produces conditions under which various alkanes can be formed[44,49,403].

Amidrazones, acylamidrazones, and hydrazidines are cyclised at 150–200°C to 1,2,4-triazole derivatives[2,28,110,404], but dihydrazones and oxime hydrazones of α-diketones form 1,2,3-triazole derivatives[20,28,405]. Acyl- and thioacyl-hydrazones, including semi- and thiosemi-carbazones, of α-alkoxy-carbonyl compounds (acylhydrazones of esters) are cyclised at high temperature to oxadiazoles or thiadiazoles[10,316,406]:



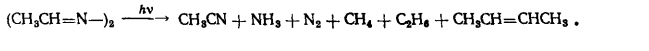
Arylhydrazones and disubstituted hydrazones of α-acyloxy- and sometimes α-aryloxy-carbonyl compounds (arylhydrazones of acid anhydrides or esters), however, undergo a Chapman rearrangement under these conditions[31,45,407]:



(X=Az, Ar)

Photolysis

When benzaldehyde phenylhydrazone is illuminated, the nitrogen–nitrogen bond is broken with the formation of benzonitrile, aniline, and benzaldehyde, the last produced from its imine[408]. Diazo-compounds[409] and then carbenes[369] are intermediates in the photolysis of toluene-*p*-sulphonylhydrazones, but the products obtained are different from those from the alkaline or thermal decomposition of this group of hydrazones[369,409,410]. Thus photolysis of the sodium salt of the toluene-*p*-sulphonylhydrazone of nortricyclanone yields 3-nortricyclyl *p*-tolyl sulphone, whereas its pyrolysis gives 4-ethynylcyclopentene[410]. The photolysis of aromatic azines involves rupture of both nitrogen–nitrogen and carbon–nitrogen bonds with the formation of aryl cyanides, *cis*- and *trans*-stilbenes, and aromatic imines, which are hydrolysed to aldehydes[2,44,411]. In aliphatic azines the cleavage of carbon–carbon bonds in the carbonyl component is also observed[44,49,412]:



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