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THE CYCLOPROPENYL CATION

I. A. D'yakonov and R. R. Kostikov

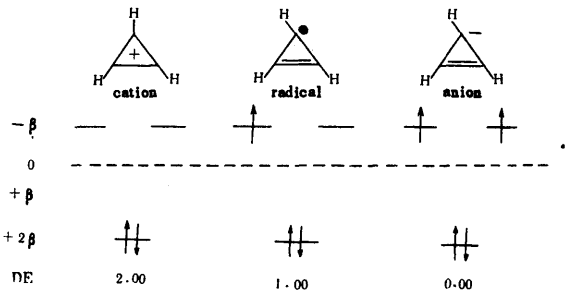
CONTENTS

1. The cyclopropenyl cation 557
2. Cyclopropenyl cations containing aryl and alkyl substituents 558
3. Reactions of cyclopropenyl cations with water, alcohols, and other nucleophilic reagents 558
4. Aromatic substitutions involving the cations 560
5. Reactions of cyclopropenyl cations with compounds containing an active methylene group 561
6. Methods of preparing cyclopropenyl cations 561

1. THE CYCLOPROPENYL CATION

A considerable amount of work has now been published on the three-membered analogue of the tropylium cation—the aromatic cyclopropenyl cation—and the present paper gives a brief survey of the literature on the preparation and the electrophilic character of this cation. A recent review[1] of the reactions of the cyclopropenyl cation and allied compounds paid very little attention to this question.

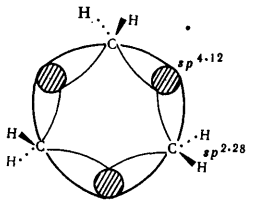
According to Hückel's rule, a planar monocyclic system having trigonal hybridisation of the carbon atoms and containing $4n + 2$ π-electrons possesses a filled electronic configuration and enhanced stability[2]. The simplest system satisfying Hückel's aromaticity conditions with $n = 0$ is the cyclopropenyl cation.



The accompanying diagram shows the molecular levels and the delocalisation energies (DE) for the cyclopropenyl cation, radical, and anion calculated by the LCAO-MO method[3]. The above scheme shows that the cation possesses the maximum delocalisation energy, while the anion has DE = 0 and is in a triplet state. Consequently these species can be arranged in the sequence—cation > radical > anion—of diminishing stability. For the cyclopropenyl cation DE = 2β, which is somewhat lower than the delocalisation energy of the tropylium cation (2.99β),[3] but considerably exceeds that for the allyl cation (0.8β).[4] Nevertheless, in spite of the considerable delocalisation energy, the cyclopropenyl cation itself has not yet been obtained, and several authors[1] cast doubt on the possibility of its existence. The strongest destabilising influence on the cation is exerted by the angular strain of the three-carbon ring. It is usually considered that the energy of the angular strain in cyclopropane is 27.6 kcal mole^{-1},[5] and for cyclopropene an estimate of 55 kcal mole^{-1} has been made[6]. This energy would increase still more in the cation, probably to 74 kcal mole^{-1} [1,7] as a consequence of the change in the valency state of the carbon atoms on formation of the cation from cyclopropene.

Baeyer's theory of angular strain has been discussed by Walsh[8] and also by Coulson and Moffit[9]. They reached

the conclusion that a satisfactory description of the state of the bonds in cyclopropane can be obtained only on the assumption that the type of hybridisation of the atomic orbitals of the ring carbon atoms is other than sp^3:



Coulson and Moffit calculated that the atomic orbitals involved in the formation of C–H bonds have $sp^{2.28}$ hybridisation.

It must be noted here that, in calculating the energies of strain in cyclopropane and cyclopropene from their heats of combustion or heats of hydrogenation compared with those of unstrained cycloalkanes, these workers took no account of the change in valency state of the carbon atoms on passing from unstrained to strained rings. Actually, however, such transfer of a carbon atom is accompanied by a change in its valency state from the first to the second in cyclopropane, and to the second and the third in cyclopropene. We have attempted to allow for these changes [10] by using in the calculation values of the C–H bond energies in ethylene and acetylene [11], and have thus obtained higher values for the energies of strain in cyclopropane and cyclopropene than had been accepted hitherto (48.6 and 87 compared with 27.6 and 55 kcal mole^{-1} respectively). It is quite obvious that the energy of strain for the cyclopropenyl cation, too, will be greater than the value calculated previously (102.5 instead of 74 kcal). Results obtained by Wiberg et al. on the heats of dissociation of propene and cyclopropene into a hydride ion and the corresponding carbonium ions are consistent with these calculations. They show [6] that the cyclopropenyl cation is only 10 kcal more stable than the allyl cation. Such a small difference can be explained by the presence of a high energy of strain in the cyclopropenyl cation, which brings its delocalisation energy close to that for the allyl cation.

Another cause of the instability of the cyclopropenyl cation may be electrostatic repulsion between positively charged carbon atoms of the three-membered ring. It must be regarded as proved that, in this cation just as in the tropylium cation, the positive charge is uniformly distributed among all the ring carbon atoms. X-Ray examination of triphenylcyclopropenyl perchlorate [12] has shown that the interatomic distances in the C–C bonds of the three-membered ring all have the same value of 1.37 Å. Hence it follows that the charge in this compound is uniformly distributed among the three carbon atoms forming the ring.

2. CYCLOPROPENYL CATIONS CONTAINING ARYL AND ALKYL SUBSTITUENTS

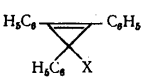
Manatt and Roberts [13] calculated the delocalisation energies of the mono-, di-, and tri-phenylcyclopropenyl cations by the simple Hückel molecular-orbital method. Table 1 gives the values calculated by these [13] and other authors [3,7,14,15] for the total and excess delocalisation energies of these cations. The latter parameter represents the difference between the total delocalisation energy of a given cation DE and the delocalisation energy of the cyclopropenyl cation itself ($DE_0 = 2.00$) together with the sum of the delocalisation energies of the phenyl groups (ΣDE_{ph}): $\Delta DE = DE - DE_0 - \Sigma DE_{ph}$.

TABLE 1. Total and excess delocalisation energies (in β-units) of phenylated cyclopropenyl cations.

No. of C_6H_5	DE	ΔDE	Ref.
0	2.00	—	3
1	4.39	0.39	13
	4.40	0.40	14
2	6.70	0.70	13
	6.78	0.78	7,14
3	9.19	1.19	13
	9.16	1.16	15

Table 1 shows that replacing a hydrogen atom in the cyclopropenyl cation by a phenyl radical increases both the total and the excess delocalisation energy of the ion. Breslow and his coworkers studied the influence of the number and nature of substituents on the ease of formation of cyclopropenyl cations [7,16,17], and found that their stability increases primarily with increasing degree of substitution. From this it followed that the cyclopropenyl cation itself will be the most unstable. It was further found that, with the same degree of substitution of the ring, electron-donor substituents have a more favourable effect than have electron-acceptor substituents on the formation of the cation. Dialkoxycyclopropenyl cations proved to be more stable than diaryloxycyclopropenyl cations [18–20].

The ease of formation of a cyclopropenyl cation from a cyclopropene derivative depends both on the ring substituents and on the nature of the anion which is eliminated. Thus in triphenylcyclopropenyl bromide, for example, the bromine is present as an anion, whereas in tetrabromocyclopropene all the bromine atoms are combined covalently [21]. A series of cyclopropene derivatives is now known in which a definite relationship can be observed between the nature of the atom of group X and the character of the C–X bond in compounds of the type



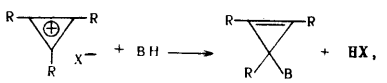
where X = H, OCH_3, CN, 2,4,5-$(NO_2)_3C_6H_2O^-$, Br^-, BF_4^-. In the first three of these compounds the C–X bond is found to be covalent, and in the latter three it was ionic. A similar series is known also for derivatives of the tropylium cation [22]. Vol'pin et al. [23] showed that the weakest acid whose anion forms an ionic compound with the tropylium cation is isocyanic acid HNCO ($K_a = 1.2 \times 10^{-4}$), while the strongest acid with which the same cation will give a covalent compound is benzoic acid ($K_a = 6.3 \times 10^{-5}$).

3. REACTIONS OF CYCLOPROPENYL CATIONS WITH WATER, ALCOHOLS, AND OTHER NUCLEOPHILIC REAGENTS

As follows from the preceding Section, a greater or smaller concentration of cationic charge on the carbon atoms of the three-membered ring is determined by the number and nature of the substituent groups. The more delocalised is the cationic charge on the substituent groups,

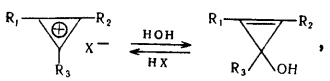
the greater its stability and the smaller the electrophilic activity. With less delocalisation of the charge, the electrophilic properties of the cation will be more strongly developed.

Just like the aromatic tropylium cation, the cyclopropenyl cation can take part in electrophilic substitution reactions, represented by the general equation



where R = Alk, Ar, or Hal; BH is a nucleophilic reagent, e.g. HOH, CH_3OH; and X = Br, BF_4, ClO_4.

The simplest reaction of this type is the hydrolysis of cyclopropenyl salts to the corresponding cyclopropenols. In this case the electrophilic cation attacks the nucleophilic water molecule. Breslow et al. have shown[7] that this can be regarded as an equilibrium:



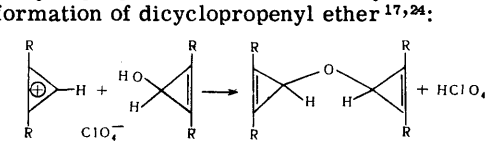
where HX is the conjugate acid. The equilibrium constant K_{R^+} is given by the equation

$$K_{R^+} = \frac{[C_3H_3OH]\cdot[H^+]}{[C_3H_3^+]}$$

where $[C_3H_3OH]$ and $[C_3H_3^+]$ are the concentrations of cyclopropenol and cyclopropenyl cation respectively. This constant can be more conveniently expressed in the form $pK_{R^+} = -\lg K_{R^+}$, which is numerically equal to the pH at which the cyclopropenyl salt is 50% converted into the cyclopropenol.

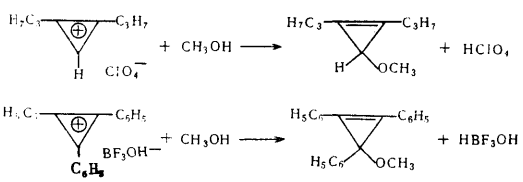
Table 2 lists experimental values of pK_{R^+} obtained by Breslow and his collaborators, and of ΔDE for the cyclopropenyl cations calculated by the LCAO-MO method. The latter represent the difference in delocalisation energy between the cation and the corresponding cyclopropenol. Table 2 clearly shows that ΔDE and pK_{R^+} are directly related. It is noteworthy also that, while the triphenylcyclopropenyl cation is stable at pH 3, the tripropylcyclopropenyl cation is stable even at pH 7. Hence it may be concluded that alkyl groups stabilise the cyclopropenyl cation better than do aromatic groups.

In the case of the above equilibrium hydrolysis of disubstituted cyclopropenyl salts, account must be taken of the possibility that the cation will undergo another, irreversible reaction, involving its hydrolysis product, dipropyl(or diphenyl)cyclopropenol. This secondary reaction results in the formation of dicyclopropenyl ether[17,24]:

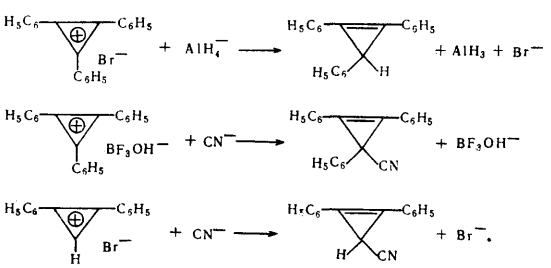


where R = C_3H_7, C_6H_5. Since the rate of the equilibrium reaction far exceeds that of the secondary reaction, the occurrence of the latter does not complicate study of the former: equilibrium is established before appreciable quantities of the dicyclopropenyl ether are able to accumulate in the reaction products.

Substitutions in which the cyclopropenyl cation acts as an electrophilic reagent take place also with alcohols. For example, dipropyl- and triphenyl-cyclopropenyl cations react with methanol to form respectively methoxydipropylcyclopropene[17] and methoxytriphenylcyclopropene[25]:



Like the tropylium cation the cyclopropenyl cation reacts also with lithium tetrahydroaluminate[26] and with potassium cyanide[16,25,27], the tetrahydroaluminate and cyanide anions acting as nucleophiles. The reaction products are in both cases covalently bound compounds. Examples of these reactions given below involve the tri- and di-phenylcyclopropenyl cations



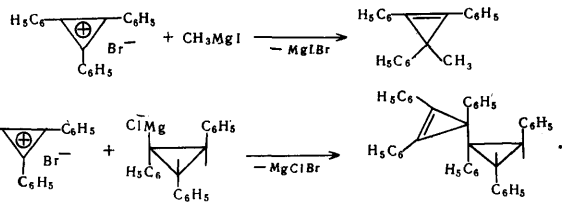
The electrophilic character of the cyclopropenyl ion is exhibited also in its ability to react with other typical nucleophilic reagents, such as organomagnesium and organolithium compounds. The triphenylcyclopropenyl cation reacts with methylmagnesium iodide and with *trans*-1,2,3-triphenylcyclopropylmagnesium chloride, to yield

TABLE 2. Influence of substituents on the position of the cation–cyclopropenol equilibrium.

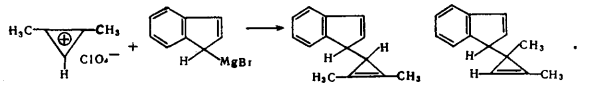
Substituted cyclopropenyl cation	ΔDE[a]	ΔDE[b]	pK_{R^+} ±0.05	Ref.
Unsubstituted	2.00	—	>0[c]	16
			−6.3[c]	17
Dipropyl	—	—	+2.68[d]	17
Tripropyl	—	—	+7.2[d]	17
Diphenyl	1.90	3.00	−0.67[e]	16
			+0.32[f]	16
Propyldiphenyl	—	—	+3.80[e]	17
Triphenyl	2.31	3.46	+3.1[d]	17
			+2.80[e]	7
			+3.18[f]	16
Diphenyl-*p*-methoxyphenyl	2.34	3.53	+4.00[e]	7
Phenyldi-*p*-methoxyphenyl	2.37	3.58	+5.16[d]	17
			+5.22[e]	7
Tri-*p*-methoxyphenyl	2.40	3.64	+6.50[d]	17
			+6.42[e]	7

(*a*) Calculated by the simple Hückel method.
(*b*) Calculated by the ω-technique.
(*c*) Values of pK_{R^+} for the unsubstituted cyclopropenyl cation obtained by extrapolating experimental values of pK_{R^+} for di- and tri-substituted cations.
(*d*) Equilibrium in 50% aqueous acetonitrile.
(*e*) Equilibrium in 23% aqueous alcohol.
(*f*) Equilibrium in water.

respectively methyl-1,2,3-triphenylcyclopropene and 1,2,3-triphenyl-(*trans*-1,2,3-triphenylcyclopropyl)cyclopropene [26]:

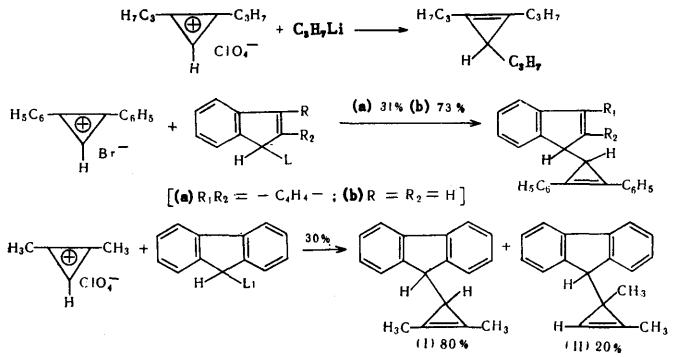


Interaction of the dimethylcyclopropenyl cation with indenylmagnesium bromide gives a mixture of two isomeric indenyldimethylcyclopropenes [28]:



The appearance of two isomers in the reaction product indicates that the positive charge in the cyclopropenylium cation is distributed among its three ring carbon atoms, and is not fixed on one of them. Since two of the three positions of the charge in the ring are equivalent, two—not three—isomers are formed.

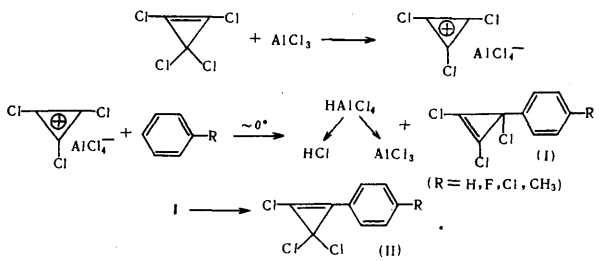
In all the reactions of organolithium compounds with cyclopropenyl cations, the electrophilic cation displaces the metal in the form of a cation from the organolithium compound [17,29,30]:



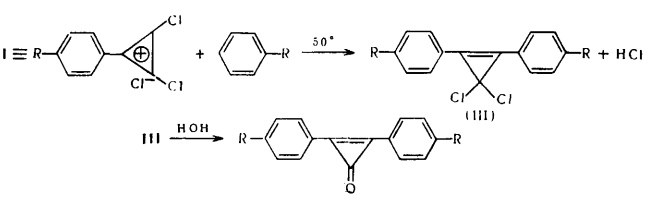
In conformity with the result observed for the reaction of dimethylcyclopropenyl with indenylmagnesium bromide, two isomeric cyclopropene hydrocarbons might have been expected to result also from the interaction of diphenyl- and dimethyl-cyclopropenyl cations with organolithium compounds. This has been confirmed, however, only for the reaction of the dimethylcyclopropenyl cation with fluorenyl-lithium. In other cases the expected isomers could not be isolated. The fourfold yield of the isomer (I) relative to that of (II) is probably to be explained not only by the not entirely uniform distribution of the cationic charge inside the cyclopropenyl ring but also by the unexpected magnitude of the steric hindrance accompanying the attack of the nucleophilic reagent on the electrophilic centres of the cation—ring carbon atoms 1 (or 2) and 3.

4. AROMATIC SUBSTITUTIONS INVOLVING THE CATIONS

The cyclopropenyl cation can take part in the electrophilic substitution of an aromatic nucleus, just like other carbonium ions. An example is the interaction of the trichlorocyclopropenylium cation with benzene, toluene, chlorobenzene, and fluorobenzene, studied by Tobey and West [31,32]. The reaction proceeds under the conditions of the Friedel–Crafts reaction. The aluminium chloride employed as catalyst is necessary to convert the tetrachlorocyclopropene into a trichlorocyclopropenyl salt. If the reaction is conducted at 0°C, it can be represented by the equations



The trichloro-derivative (I), which is the normal product of reaction between the cation and an aromatic hydrocarbon or its halogeno-derivative, cannot be isolated, since under the conditions of the reaction it undergoes allylic rearrangement into the isomer (II), which is more stable as a consequence of conjugation of the endocyclic double bond with the aromatic ring. This isomer is the final product of the Friedel–Crafts reaction. However, the conversion of the cyclopropene (I) into (II) is not a simple allylic isomerisation. It must probably be interpreted as reaction of the aryldichlorocyclopropenyl cation, already present in (I), with its own chloride anion, which attacks the sterically least hindered site in this cation. This is consistent with the fact that, when the reaction with the trichlorocyclopropenyl cation is conducted at a higher temperature (50°C), the reaction products are found to contain diphenyl-*gem*-dichlorocyclopropenes (III), formed by secondary interaction of (I) with the initial aromatic derivative. The compounds (III) are readily converted by water into the corresponding cyclopropenones [31]:

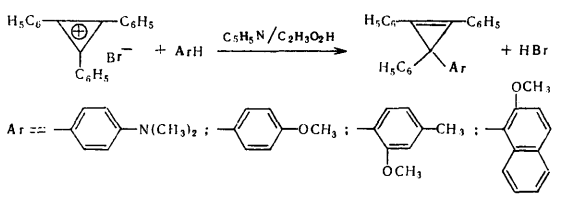


where R = H, F, Cl, CH_3.

This reaction can thus be regarded as a kind of "capture", by the aromatic hydrocarbon or its halogeno-derivative, of the saltlike compound (I), which exists only at a relatively low temperature. Attempts to obtain in this way triarylcyclopropenyl cations or tetra-arylcyclopropenes by the more prolonged and severe heating of trichlorocyclopropenyl tetrachloroaluminate with the same benzene derivatives proved unsuccessful [32].

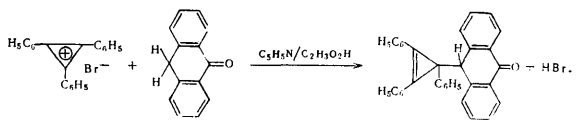
In contrast to tetrachlorocyclopropene, a cyclopropenyl cation is already present in triphenylcyclopropenyl bromide. In this case, therefore, cyclopropenylation of the aromatic ring can be carried out even in the absence of aluminium chloride [33]. No other cycloalkenyl or alkyl

halide alkylates an aromatic ring in the absence of a catalyst. This can be regarded as some indication of a cationic mechanism for the Friedel–Crafts reaction.

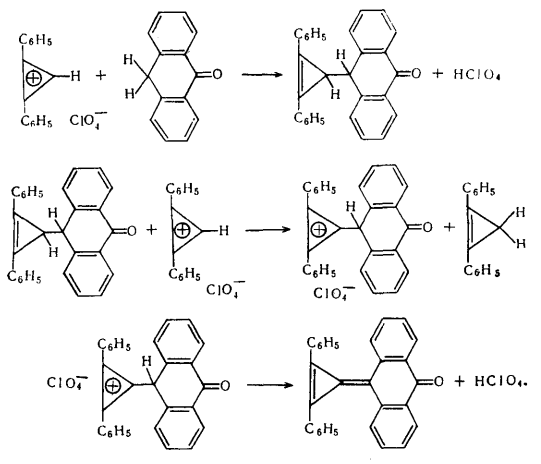


5. REACTIONS OF CYCLOPROPENYL CATIONS WITH COMPOUNDS CONTAINING AN ACTIVE METHYLENE GROUP

The literature contains a large number of examples of the reactions of tropylium cations with compounds containing a reactive methylene group. Little work has been done on such reactions with cyclopropenyl cations. It is known, however, that heating triphenylcyclopropenyl bromide with anthrone in the presence of pyridine and acetic acid yields 10-(1,2,3-triphenylcycloprop-2-enyl)anthrone[33]:

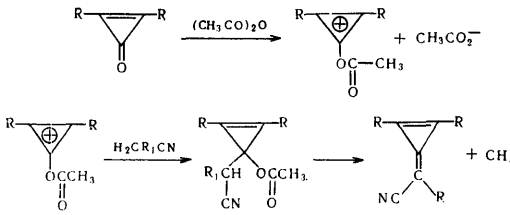


Another example is the reaction between anthrone and diphenylcyclopropenyl perchlorate. This gave a new compound of the triafulvene (methylenecyclopropene) series[33], 10-(2,3-diphenylcycloprop-2-enylidene)anthrone. The formation of this ketone can be represented by the following sequence of reactions



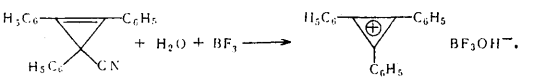
The first stage in the process is electrophilic substitution of a methylene proton in anthrone by the diphenylcyclopropenyl cation with formation of 10-(2,3-diphenylcycloprop-2-enyl)anthrone. In the second stage the cyclopropenyl cation reacts with the reaction product of the first stage, the latter losing a hydride ion and anthronyldiphenylcyclopropenyl perchlorate being formed. In the third (and last) stage of the reaction, perchloric acid is eliminated, and the final product—10-diphenylcyclopropenylideneanthrone—is obtained.

Compounds of the triafulvene series are formed also when dipropyl- and diphenyl-cyclopropenones are heated with malononitrile or cyanoacetic ester in the presence of acetic anhydride[20,34–38]. Available data on the mechanism of this reaction indicate that the primary product is the acetoxydipropyl(or diphenyl)cyclopropenyl cation, formed by the action of acetic anhydride on the dipropyl(or diphenyl)cyclopropenone[37]. The resulting cation then undergoes a substitution reaction with the labile hydrogen atoms of the methylene group in the malononitrile (or cyanoacetic ester). Subsequent elimination of acetic acid from the cyclopropenyl acetate formed as an intermediate stage leads to the triafulvene:

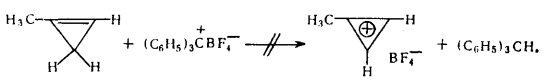


6. METHODS OF PREPARING CYCLOPROPENYL CATIONS

The first experimental confirmation of the existence of the two-π-electron aromatic cyclopropenyl system was obtained by Breslow, who treated cyano-1,2,3-triphenylcyclopropene with a moist ethereal solution of boron trifluoride and isolated triphenylcyclopropenyl hydroxotrifluoroborate[27]:

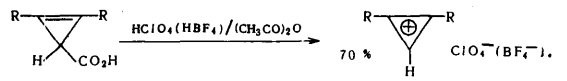


The unsubstituted cyclopropenyl cation has not yet been obtained[6]. Several investigators consider, however, that the ion $C_3H_3^+$ (M = 39), which is frequently met in the mass spectra of various organic compounds, has the cyclopropenyl cation structure rather than that of a prop-2-ynyl or allenyl cation[6,39–41]. Nor has it proved possible to obtain the methylcyclopropenyl cation[42] by abstracting a hydride ion from the hydrocarbon by means of the triphenylmethyl cation:

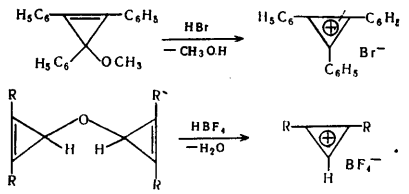


Formation of certain mono- and di-substituted cyclopropenyl cations has been observed mass-spectrometrically in the fragmentation of monocyclic 2-pyrones[43].

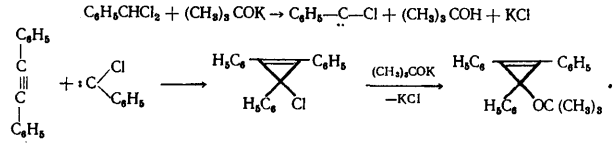
The simplest stable cation known at the present time is the dimethylcyclopropenyl ion[28]. To obtain this ion, and also several of its disubstituted homologues, wide use is made of a method proposed for preparing the tropylium cation from cycloheptatrienecarboxylic acid[44]. This method consists essentially in converting the cyclopropene(or cycloheptatriene)carboxylic acid, by means of a solution of perchloric or fluoroboric acid in acetic anhydride, into the cyclopropenyl (or tropylium) perchlorate or fluoroborate[17,26,28,45]:



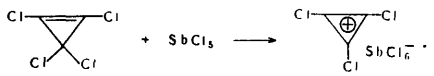
Good yields of cyclopropenyl cations are obtained also by the cleavage of cyclopropenyl ethers [7,16,17,19,25,46] with mineral acids:



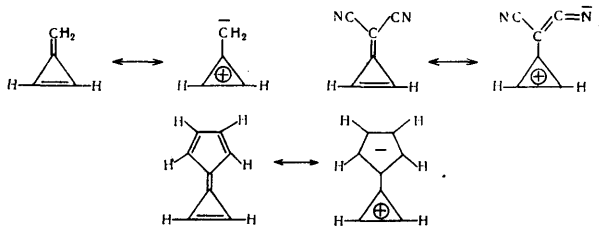
Ethers of cyclopropenols can be obtained by the interaction of arylchlorocarbenes with mono- or di-arylacetylenes in the presence of excess of an alkali-metal alkoxide: e.g.



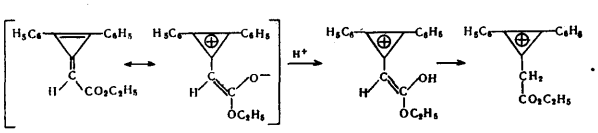
As already mentioned above, tetrachloro- and tetrabromo-cyclopropenes react with Lewis acids ($AlCl_3$, $SbCl_5$) to give stable trihalogenocyclopropenyl cations [21]:



Vigorous attempts have recently been made to synthesise methylenecyclopropene (triafulvene) and its derivatives [47-49]. Success has been achieved with derivatives containing electronegative substituents (CN, $COOC_2H_5$) in the methylene group of triafulvene [34-36,38,50,51] and with compounds having this group in a pentadiene ring (calicenes) [20,28-30,37,52,53]. Calculations made by the simple Hückel method indicate that triafulvene should be relatively stable (DE = 0.96β [3,13]). This result and also the calculated dipole moment of triafulvene (μ = 5.26 [2], 5.00 [54], 1.21 [55] D) are consistent with the view [34] that a considerable contribution to its ground state is made by a dipolar structure.



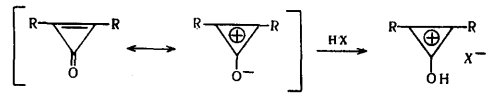
This contribution can be strengthened by introducing electronegative substituents into the methylene group of the triafulvene. The presence of a dipolar structure in the ground state of the molecule is indicated by the tendency of certain triafulvene derivatives to form salts of the corresponding cyclopropenyl derivatives by the action of strong mineral acids: e.g. [51]



This reaction has quite often been used to confirm the structure of triafulvenes [20,28,46,50].

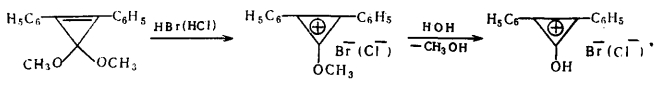
Quantum-mechanical calculation by the LCAO-MO method indicates [3] that cyclopropenylidenecyclopentadiene (calicene) should possess a delocalisation energy of 2.94β (almost 50% greater than that of benzene) and exhibit a dipole moment, as a consequence of its tendency to form a dipolar structure [53] in which the three-carbon ring is positively charged, while the five-carbon ring is negatively charged.

The oxygen analogue of methylenecyclopropene—cyclopropenone—is unknown, like methylenecyclopropene itself. However, several disubstituted cyclopropenones are now known [18,19,56-60]. In agreement with theoretical predictions, the physical and chemical properties of these compounds indicate a considerable contribution by a dipolar structure to the ground state. As a result, cyclopropenones are able to yield salts with strong mineral acids:

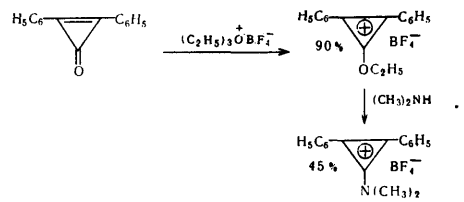


where R = C_3H_7, C_6H_5 and X = Cl, Br.

This reaction involves the formation of hydroxycyclopropenyl cations. The hydroxydiphenylcyclopropenyl cation can be obtained also by dealkylating 3,4-dimethoxydiphenylcyclopropene with a hydrohalic acid [56], and then hydrolysing [19,57,58] the methoxydiphenylcyclopropenyl cation formed as intermediate:

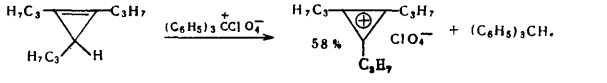


Several new derivatives of the cyclopropenyl cation have recently been prepared from diphenylcyclopropenone [19]:



On treatment with triethyloxonium fluoroborate, diphenylcyclopropenone is converted into ethoxydiphenylcyclopropenyl fluoroborate, which with dimethylamine yields *NN*-dimethylaminodiphenylcyclopropenylium fluoroborate. This last compound is so difficult to hydrolyse with water that it can be recrystallised from it.

At the present time the most widely used method for obtaining cyclopropenyl cations is abstraction of a hydride ion from derivatives of cyclopropene [17,28-30,61,62]: e.g.



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Department of Organic Chemistry,
Leningrad State University

U. D. C. 541.6

"LADDER" AND "PARQUET" POLYMERS

Yu. E. Doroshenko

CONTENTS

I. Ladder polymers 564
A. Carbocyclic ladder polymers 564
1. Alicyclic ladder polymers 564
2. Aromatic ladder polymers 566