The Formation and the Mass Spectra of Adducts from the Reaction of Some α-Substituted Vinylcyclopropanes with Benzyne[1]

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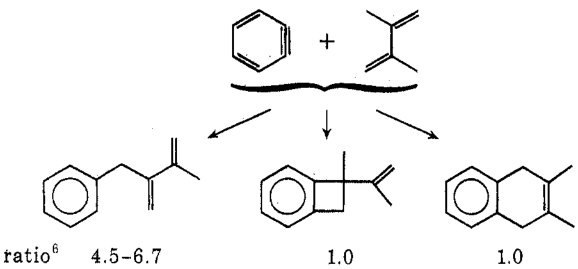
The reactions of benzyne, generated by the thermolysis of benzenediazonium-2-carboxylate, with 1,1-dicyclopropylethylene (**1**), 2-cyclopropylpropene (**6**), and α-cyclopropylstyrene (**11**) are herein described. Benzyne shows no tendency to add across the vinylcyclopropane systems in **1**, **6**, and **11**. With substrates containing proper allylic hydrogens, the "ene" reaction (**6** → **7** → **10**) exceeds that of [2 + 2] cycloaddition (**6** → **9**). When the allylic hydrogens are part of a cyclopropane ring, the [2 + 2] cycloaddition (**1** → **2**) or the Diels–Alder reaction (**11** → **13** → **14**) prevail. In the case of **1**, the **1** → **2** conversion was accompanied by a novel "ene" reaction involving the cyclopropane methine hydrogen (**1** → **3**). The intermediacy of a diradical species of structure **17** was invoked to explain the **1** → **2** and **1** → **3** conversions. Small amounts of 3-cyclopropyl-3-phenylisochroman-1-one (**12**) were isolated from the reaction of **11** with benzyne. Peaks corresponding to ions M − CH_3 and M − C_2H_5, and/or M − C_2H_4, M − C_3H_5, M − C_3H_7, and M − C_4H_3, are prominent in the mass spectra of most of the adducts described herein. The appearance of M − CH_3 and M − C_2H_5 ions implies rearrangement of the cyclopropyl group followed by hydrogen migration prior to fragmentation. Ionized **3** and **10** are featured by the loss of either cyclopropyl or benzyl radical to yield the methylenecyclopropane (**21** and **30**) and phenylvinylcyclopropane (**33**) cations, respectively.

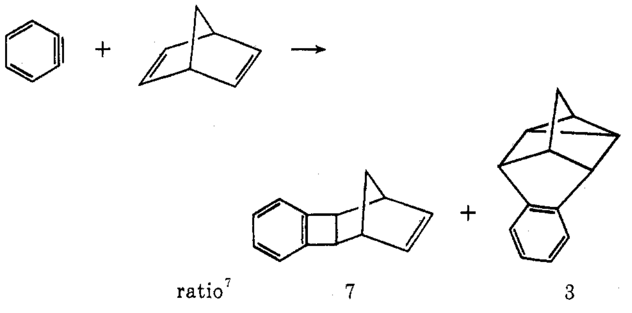
The olefinic character of cyclopropane is manifested by (1) its tendency to undergo addition reactions and (2) its ability to enter into conjugation with adjacent double bonds.[2] Thus, vinylcyclopropanes are analogous to some degree to conjugated dienes. For example, properly activated vinylcyclopropanes lend themselves to thermal [2 + 5] cycloaddition[3] where a cyclopropane bond provides a source of two electrons.[4]

To explore further the scope of the reaction, which can be labeled as a [$_\sigma2 + _\pi2 + _\pi2$] cycloaddition, a study of the reaction of benzyne with some α-substituted cyclopropylethylenes was undertaken. Benzyne is known to react with dienes containing readily accessible allylic hydrogens, preferably by the "ene" synthesis analogous to the Diels–Alder reaction,[5] or, in absence of such hydrogens, by [2 + 2] and/or [2 + 4] cycloaddition (Schemes I, II, and III).[6–8]

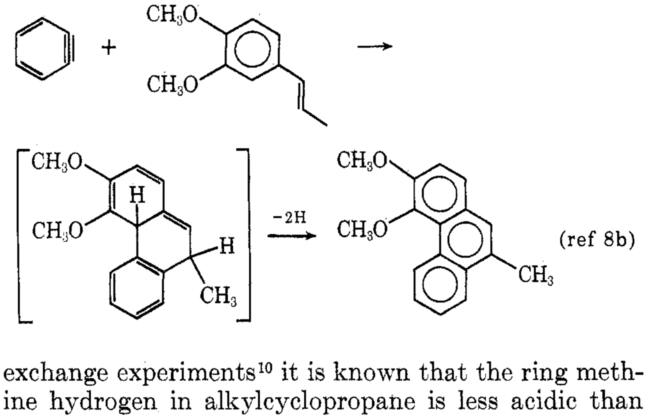
SCHEME I



SCHEME II



SCHEME III



On the McEwen–Streitwieser–Applequist–Dessy pK_a scale[9] the cyclopropane hydrogens are 3.5 pK_a units less acidic than the allylic hydrogen in propylene. Furthermore, from Shatenstein's hydrogen–deuterium exchange experiments[10] it is known that the ring methine hydrogen in alkylcyclopropane is less acidic than the ring methylene hydrogens, which, in turn, are comparable in acidity to aromatic hydrogens in alkylbenzenes. Vinylcyclopropane, therefore, is not ex-

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[1] Presented before the 41st National Meeting of the Israel Chemical Society, Tel Aviv, Oct 1971; V. Usieli, L. Friedman, and S. Sarel, Abstract of Papers, p 201.

[2] (a) M. Smith in Rodd's "Chemistry of Carbon Compounds," Vol. II, 2nd ed, S. Coffey, Ed., Elsevier, Amsterdam, 1967, Part A, pp 19–70; (b) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 233; (c) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964); (d) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968); (e) S. Sarel and R. Ben-Shoshan, *Tetrahedron Lett.*, 1053 (1965); (f) J. A. Landgrebe and J. D. Shoemaker, *J. Amer. Chem. Soc.*, **89**, 4465 (1967); (g) A. Maercker, *Justus Liebigs Ann. Chem.*, **732**, 151 (1970).

[3] For possible [$\sigma2 + _\pi2 + _\pi2$] cycloaddition see (a) S. Sarel and E. Breuer, *J. Amer. Chem. Soc.*, **81**, 6522 (1959); (b) F. W. Fowler, *Angew. Chem., Int. Ed. Engl.*, **10**, 135 (1971); (c) J. E. Baldwin and R. K. Pinschmidt, Jr., *Tetrahedron Lett.*, 935 (1971); (d) R. Noyori, N. Hayashi, and M. Kato, *J. Amer. Chem. Soc.*, **93**, 4948 (1971).

[4] For possible [$_\sigma2_a + \sigma2_a + _\pi2_a$] cycloadditions, see C. D. Smith, *ibid.*, **88**, 4273 (1966).

[5] (a) For a review of "ene" reaction, see H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969); (b) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, London, 1967, p 197.

[6] G. Wittig and H. Dürr, *Justus Liebigs Ann. Chem.*, **672**, 55 (1964).

[7] H. E. Simmons, *J. Amer. Chem. Soc.*, **83**, 1657 (1961); also ref 5b, p 235.

[8] (a) M. Stiles, U. Burkhardt, and A. Haag, *J. Org. Chem.*, **27**, 4715 (1962); (b) S. F. Dyke, A. R. Marshall, and J. P. Watson, *Tetrahedron*, **22**, 2515 (1966).

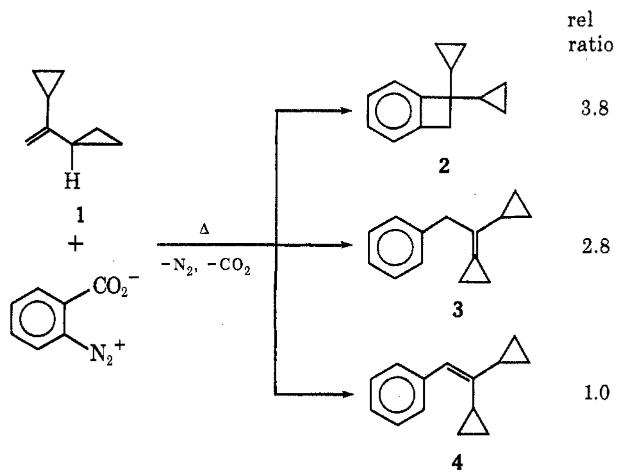
[9] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 19.

[10] A. I. Shatenstein, *Advan. Phys. Org. Chem.*, **1**, 176 (1963); ref 9, pp 22–23.

pected to react with benzyne by the "ene" synthesis but rather to give rise to cycloaddition products.

We found that on exposure of 1,1-dicyclopropylethylene (**1**) to the action of benzyne generated by the thermolysis of benzenediazonium-2-carboxylate in $(CH_2Cl)_2$ a mixture of three isomeric adducts is obtained (30% yield), in the ratio of 3.8:2.8:1 (Scheme IV).

SCHEME IV



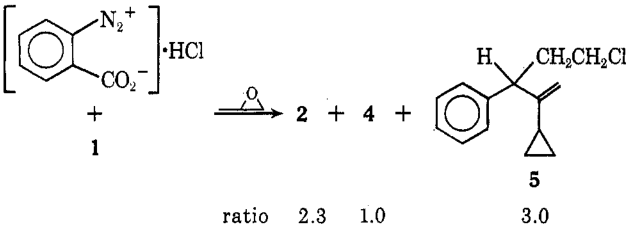
The major component was shown to be a four-membered cycloadduct, identified as 3,3-dicyclopropylbenzocyclobutene (**2**) in the following way. It was analyzed as a $C_{14}H_{16}$ compound. Its nmr and ir spectra indicated the presence of a 1,2-disubstituted benzene ring, and two cyclopropyl groups, with observed resonance up to τ 10.36, and two methylene protons of a cyclobutene ring appearing as a singlet at τ 7.15.

The two other products proved to be isomeric compounds where the more abundant one most likely results from the "ene" synthesis, involving one of the cyclopropane methine hydrogens, and was assigned the α-cyclopropylphenethylidenecyclopropane structure (**3**). Its structure was inferred from the mass spectrum, showing the parent peak at *m/e* 184, and from its nmr spectrum, indicating the presence of one benzyl, one cyclopropyl, and one cyclopropylidene group in the molecule.

The minor product was assigned similarly the 1,1-dicyclopropyl-2-phenylethylene (**4**) structure. Its uv spectrum is characterized by two well-defined peaks of similar intensity at 255 and 205 mμ, attributable to the styrene and the vinylcyclopropane chromophores, respectively. The origin of **4** is not known. It could well be an artifact of **3** as a result of a 1,3-hydrogen shift to yield the thermodynamically more favored conjugated system **4**.

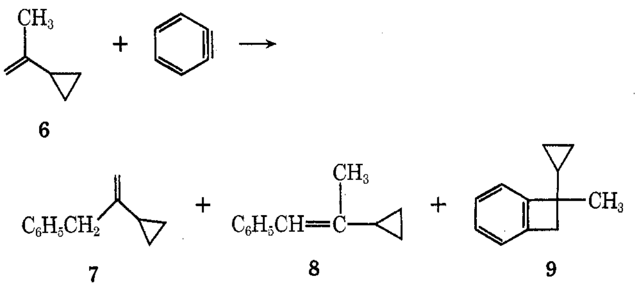
In another experiment, **1** was allowed to react with benzyne which was generated by a slightly different method (method B, Experimental Section), from benzenediazonium-2-carboxylate hydrochloride and propylene oxide. This led to higher yields of reaction products **2** and **4** and a new adduct (major product) which analyzed as a $C_{14}H_{17}Cl$ compound (see Scheme V). Its mass spectrum was characterized by two peaks at *m/e* 220 and 222, corresponding to the molecular ions, in the ratio expected for the presence of the ^{35}Cl and ^{37}Cl isotopes of chlorine. It was assigned the 4-cyclopropyl-3-phenylpent-4-enyl chloride structure (**5**) on the basis of its spectroscopic properties (see Experimental Section).

SCHEME V



The reaction of benzyne with a threefold excess of 2-cyclopropylpropene (**6**) has been shown[11] to give a 38% yield of three adducts, **7**–**9**, in the ratio of 19.5: 4.5:1 (Scheme VI).

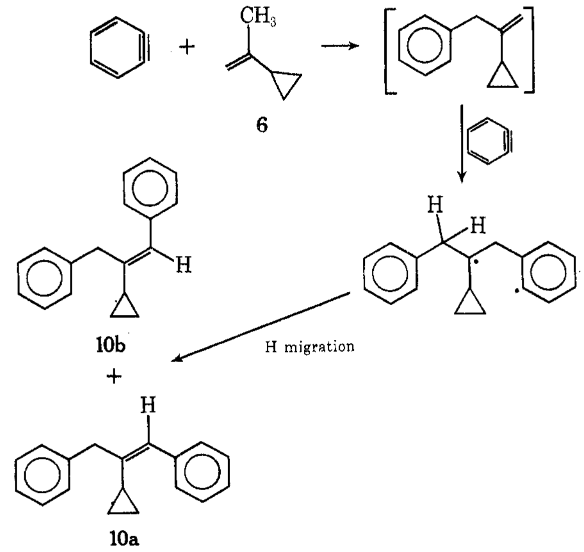
SCHEME VI



When 2 mol of benzyne were allowed to react with 1 mol of **6** (instead of the 1:3 ratio employed by the Japanese authors[11]), a 55% yield of a mixture of two products in the ratio of 5:1 was obtained.

The two products were shown to be geometric isomers of 2-cyclopropyl-1,3-diphenylpropene (**10a** and **10b**, see Scheme VII). The isomeric mixture analyzed as $C_{18}H_{18}$ compounds, exhibiting the parent peak at *m/e* 234 in the mass spectrum. The nmr spectrum shows a ten-proton aromatic multiplet centered at τ 2.9, a singlet at 3.63 for the predominant isomer, and

SCHEME VII



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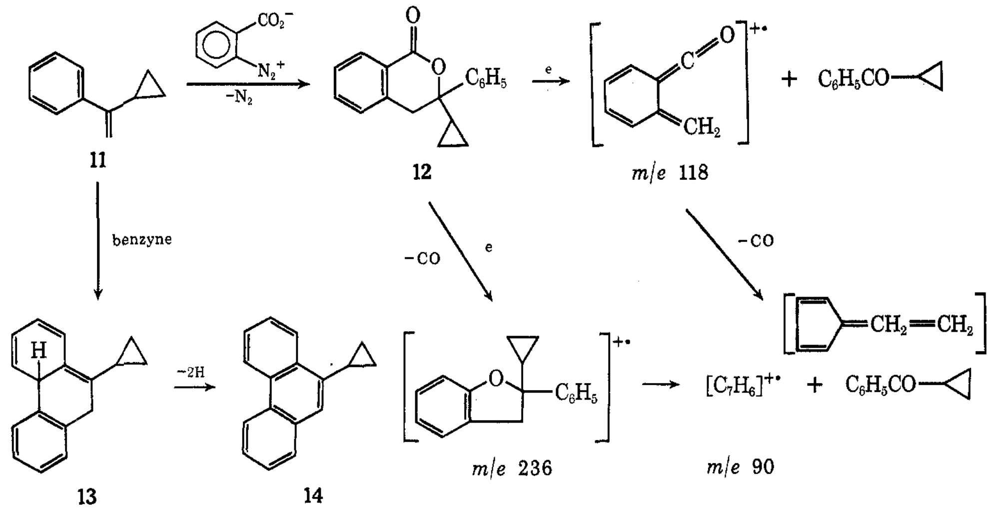
[11] I. Tabushi, K. Okazaki, and R. Oda, *Tetrahedron*, **25**, 4401 (1969).

SCHEME VIII



another singlet at 3.78 for the minor product (the integrated area for the two corresponds to one proton), a singlet at 6.44 for the major product, and another singlet at 6.75 for the minor product (the integrated area of which corresponds to two protons).

It has been shown[2d] that in vinylcyclopropane systems of the a and b types (see Scheme VII) the vinylic proton cis to the cyclopropane resonates at a higher field than the corresponding proton in the trans arrangement. The difference of 0.15 ppm between the vinylic protons permits us to assign the trans geometry (**10a**) to the predominant isomer, and the cis geometry (**10b**) to the minor product.

The uv spectrum of **10a** + **10b** displays two intense bands at 250 and 209 mμ, assignable to the styrene and the vinylcyclopropane chromophores, respectively. The extinction coefficient at the lower wavelength markedly exceeds that at the longer wavelength of the spectrum.

The reaction of α-cyclopropylstryene (**11**) with benzyne (Scheme VIII) resulted in a 10% yield of two compounds in the ratio of 1:8.5. The major product was identified as 9-cyclopropylphenanthrene (**14**) on the basis of its analysis and spectroscopic properties. In its mass spectrum the molecular ion at m/e 218 is the base peak, reflecting the remarkable stability of the aromatic polycyclic nucleus. Other peaks with abundances >25% of the base peak are at m/e 217 (M − 1, 61%), at m/e 203 ($C_{16}H_{11}$, 72%), corresponding to the loss of methyl from the parent ion (as evidenced by the presence of a metastable peak at m/e 189), and at m/e 202 ($C_{16}H_{10}$, 54%) arising from further fragmentation of the ion of m/e 217 by loss of methyl, as substantiated by the presence of a metastable ion (m* 188) in the spectrum. Study has shown that the ion of m/e 217 lends itself to two more reactions: (i) the loss of acetylene to give the ion of m/e 191 ($C_{15}H_{11}$, 40%); (ii) the loss of ethylene to yield the ion of m/e 189 ($C_{15}H_9$, 21%). Its uv spectrum shows the typical phenanthrene absorption bands at 252 and 221 mμ[12] with high extinction coefficients (see Figure 1). The nmr data (see Experimental Section) are in agreement with structure **14**.

The minor product from the reaction of **11** with benzyne was assigned the structure of 3-cyclopropyl-3-phenylisochroman-1-one **12** on the basis of its ir spectrum, exhibiting the lactone carbonyl absorption at 1720 cm^{-1}, and its molecular ion at m/e 264 ($C_{18}H_{16}O_2$) in the mass spectrum. The base peak of the spectrum is at m/e 118 (C_8H_6O) corresponding to the loss of cyclopropyl phenyl ketone.[13] Other peaks with abundances >40% of the base peak are at m/e 236 ($C_{17}H_{16}O$, 50%), corresponding to the loss of carbon monoxide from the parent ion, and m/e 90 (C_7H_6, 40%), arising either from further fragmentation of the ion of m/e 118 by loss of carbon monoxide or from the ion of m/e 236 by loss of cyclopropyl phenyl ketone. The nmr spectrum shows a one-proton aromatic multiplet centered at τ 2.03 and an eight-proton aromatic multiplet between 2.35 and 2.95. In addition, the benzylic protons appear as a singlet at τ 6.43.

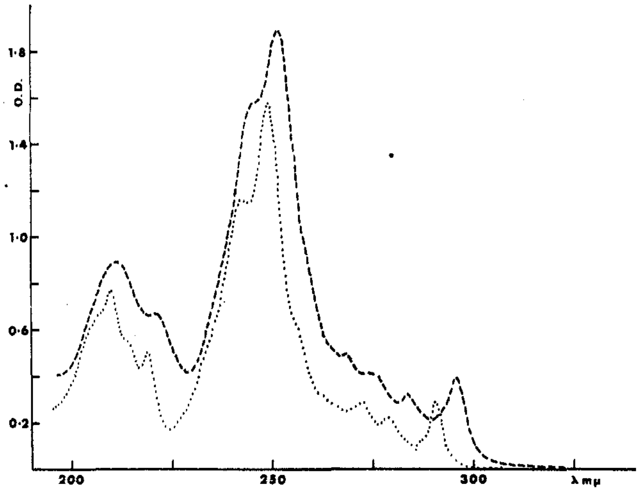


Figure 1—Ultraviolet absorption spectra of 3.10 × 10^{-5} mol/l. 9-cyclopropylphenanthrene (**14**) (----) and of 2.16 × 10^{-5} mol/l. phenanthrene (····) in n-hexane.

The data produced above clearly reflect the tendency of α-cyclopropylstyrene to behave toward

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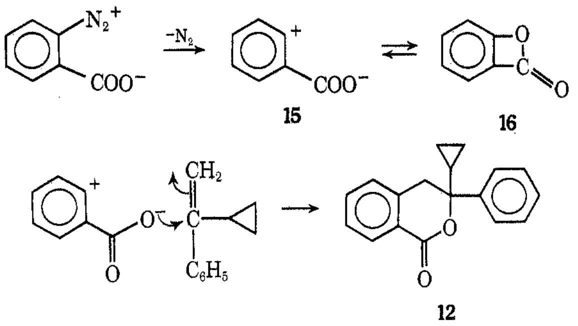
[12] N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, **75**, 2283 (1953).

[13] Compare with similar electron impact induced elimination of acetaldehyde from derivatives of 3-methylisochroman-1-one: (a) M. J. Rix and B. R. Webster, *J. Chem. Soc. B*, 254 (1968); (b) J. F. Grove, *J. Chem. Soc., Perkin Trans. 1*, 2400 (1972); (c) see also D. R. Arnold, E. Hedaya, V. Y. Maritt, L. A. Karnischky, and M. E. Kent, *Tetrahedron Lett.*, 3917 (1972).

benzyne as a true styrene,[14] undergoing a [2 + 4] cycloaddition followed by dehydrogenation (**11** → **13** → **14**). The [2 + 2] cycloaddition and the "ene" reaction, which are displayed by **1**, could not be observed in the case of **11**. Most significantly, benzyne shows no tendency to add across the vinylcyclopropane system, as do the acetylenedicarboxylic acid esters.[3b,c]

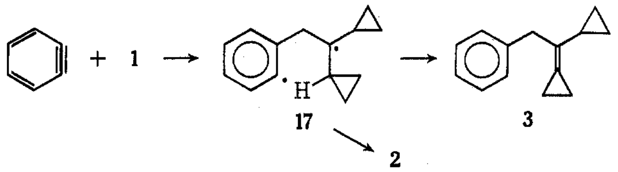
Scheme IX

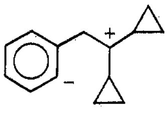


The immediate precursor of **12** is most likely the zwitterion **15**, presumably being formed *via* expulsion of a nitrogen molecule from benzenediazonium-2-carboxylate (Scheme IX). The low yield of **12** suggests that **15** does not appreciably equilibrate with its cyclic form **16**.[5b]

Mechanism.—The formation of **3** from **1** can be best explained in terms of a multistage process involving a diradical intermediate **17**, which *via* intramolecular 1,5-hydrogen shift gives rise to "ene" synthesis (Scheme X).

Scheme X

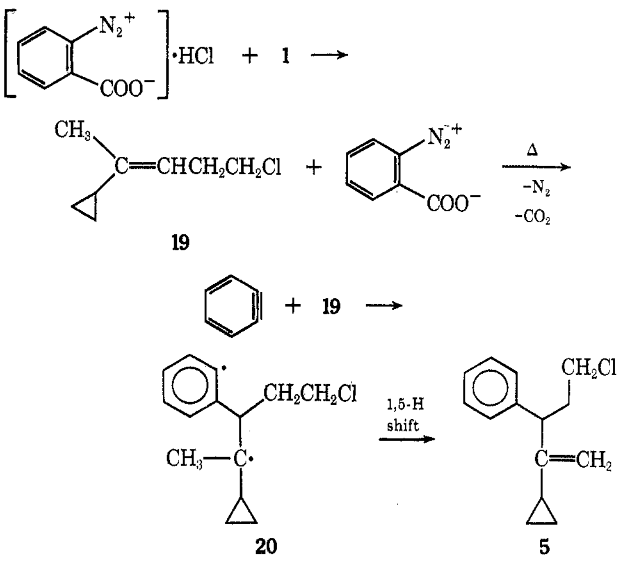




18

The intermediacy of a dipolar adduct **18** appears less likely, since it implies that in the conversion of **18** to **3** the more acidic C–H bond (aromatic) is formed *via* migration of a proton from the less acidic C–H bond (the methine cyclopropane C–H bond). Indeed, formation of **3** in this reaction should be viewed as a substantiation for the radical mechanism.[15] The formation of **5** from **1** (Scheme V) most likely occurs *via* HCl-induced homoallylic rearrangement (**1** → **19**) followed by benzyne addition (**19** → **20** → **5**) as delineated in Scheme XI.

Scheme XI



Mass Spectra.—The mass spectra were measured on a Varian CH5 mass spectrometer using the direct inlet system. The electron energy was maintained at 70 eV and the ionization current at 20 μA. The abundances of the prominent ions in the mass spectra of compounds **2**, **3**, **4**, and **10** are assembled in Table I and given in percentages relative to the base peaks in the spectra.

Table I

Relative Abundances of Prominent Ions in the Mass Spectra of **2**, **3**, **4**, **5**, and **10**

m/e	**2**	**3**	**4**	**5**	**10**
77	11.0	33.0	47.4	21.6	
91	9.0	100	91.7	84.3	60.4
93		35.0	30.0		
115	69.6	28.0	72.4	56.0	35.2
128	63.8	46.1	100		52.1
129	21.7	32.8	49.4	100	14.1
141	100	47.2	99.4		13.8
142	20.6	29.4	39.1		9.4
143	14.2	27.2	80.0	58.2	100
155	37.7	26.7	80.1		
156	46.4	7.8	35.3		
157				56.0	
169	17.7	23.9	70.5		
$M\cdot^+$	3.2	3.9	73.7	46.3	45.0

The principal electron-induced fragmentation of saturated cyclopropanes was shown[16a,b] to involve the rupture of the small ring in two main modes: (a) cleavage of the cyclopropane 1,2 bond to yield ions of a "normal" propane chain which then eject a neutral ethylene derivative, and (b) cleavage of the 2,3 bond to yield a branched ionic biradical propane followed by loss of a neutral C_3 unit with retention of the charge on the substituent (see Scheme XII).

The mass spectra of the [2 + 2] cycloadduct **2** and of the "ene" reaction products, **3** and **4**, from the reaction of **1** with benzyne are characterized by six peaks at *m/e* 169, 155, 143, 141, 128, and 115, corresponding to the ionic fragments $M - CH_3$, $M - C_2H_5$, $M - C_3H_5$, $M - C_3H_7$, $M - C_4H_8$, and $M - C_5H_9$, respectively. The first two ionic species, $M - CH_3$ and $M - C_2H_5$, probably originate from an initial 1,2-bond fission of one of the cyclopropyl groups with concomitant

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[14] (a) W. Davies and J. R. Wilmshurst, *J. Chem. Soc.*, 4079 (1961); (b) T. G. Corbett and Q. N. Porter, *Aust. J. Chem.*, **18**, 1781 (1965).

[15] (a) M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969); (b) P. G. Gassman and H. P. Benecke, *Tetrahedron Lett.*, 1089 (1969).

[16] (a) H. Weitkamp, U. Hasserodt, and F. Korte, *Chem. Ber.*, **95**, 2280 (1962); (b) N. Turro, *et al.*, *J. Amer. Chem. Soc.*, **87**, 4097 (1965).

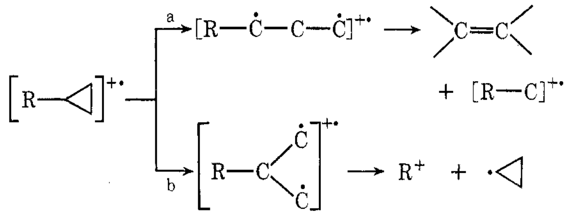
double hydrogen migrations to yield *n*-propyl radical ions which then eject a methyl and/or an ethyl radical.

From Table I it can be seen that the relative intensity of the molecular ion peak in the mass spectra of **2**, **3**, **4**, and **10** decreases in the order **4** > **10** > **3** ≈ **2**, suggesting that the cation radicals produced by loss of an electron from either **4** or **10** are more stable than those derived from **2** or **3**. This is in harmony with the observed unusually low ionization potentials in cyclopropylethylenes[17] probably due to the ability of the small ring to stabilize an adjacent electron-deficient center.[18]

Of particular interest are the two primary mass spectral reactions of geminal benzylcyclopropylmethylenecyclopropane (**3**), featured by the loss of either cyclopropyl radical or benzyl radical to give the respective methylenecyclopropane cations **30** and **21**. The latter subsequently loses two atoms of hydrogen to yield a highly stable ionic fragment (*m/e* 91, base peak) to which we assign the cyclobutenylcylclopropenylium ion structure **22**, constituting an isoelectronic species of the well-known tropylium ion (**23**). A metastable peak observed at *m/e* 46.6 could result from the **3** → **21** route (calculated metastable 47.0) or from the elimination of an acetylene molecule from the tropylium ion (**23**) to form the cyclopentadienylium ion (**24**) of *m/e* 65 (relative abundance 22%; calculated metastable 46.4). Significantly, the abundance of the benzylmethylenecyclopropylium ion (**30**) is considerably less prominent in the spectrum of **3** (see Table I). This suggests that ionized benzylcyclopropylmethylenecyclopropane (**3**) ruptures α to the vinyl bond in two main modes: (i) cleavage of the benzyl–vinyl bond gives the cyclopropylmethylenecyclopropylium ion, which then loses two hydrogen atoms to give the highly stable ion **22**; and (ii) cleavage of the cyclopropyl–vinyl bond with retention of charge on the substituted methylenecyclopropane moiety[19-21] (Scheme XIII).

The importance of the latter mass-spectral pattern is further demonstrated in the case of ionized **10**, in which the dominating primary reaction involves fission of the benzyl–vinyl bond to give a phenylvinylcyclopropane cation (**10** → **33**) and neutral benzyl fragment. The ion **33** then either ejects an ethylene molecule to give the indenylium ion (**29**), or first rearranges into a protonated methylnaphthalene species (**31**) and then loses a methyl radical to give ionized naphthalene (**32**) (Scheme XIV).

SCHEME XII



Experimental Section

Nmr spectra were recorded on JEOL C-60H spectrometer (internal TMS), uv spectra on a Unicam SP 800 A spectrophotometer, ir spectra on a Perkin-Elmer 237 spectrophotometer, and mass spectra on a MAT CH 5 spectrometer.

Cyclopropylethylenes.—Literature procedures were used for the preparation of 1,1-dicyclopropylethylene (**1**), bp 45° (20 mm), $n^{20}\text{D}$ 1.4653,[22a,b] 2-cyclopropylpropene (**6**), bp 70° (690 mm), $n^{20}\text{D}$ 1.4250,[23] and α-cyclopropylstyrene (**11**), bp 102–104° (20 mm), $n^{25}\text{D}$ 1.5467.[22b,24]

General Procedure for the Reaction of Cyclopropylethylenes with Benzyne. Method A.—Benzenediazonium-2-carboxylate (25 mmol), prepared by the method of Logullo, Seitz, and Friedman,[25] was added to a solution of the olefin in ethylene dichloride. The stirred reaction mixture was refluxed for 1 hr or until gas evolution ceased. The dark solution was then concentrated and chromatographed on neutral alumina (40 g) with ethylene dichloride, carbon tetrachloride, or benzene as eluent. The first fractions contained a mixture of the reaction products and unreacted starting olefin. Separation of the reaction products was carried out by preparative vpc or by preparative tlc.

Method B.—The procedure in method A was followed, but instead of benzenediazonium-2-carboxylate the hydrochloride of this reagent was used, and propylene oxide (2 equiv) was added to the reaction mixture.

Reaction of 1,1-Dicyclopropylethylene (1) with Benzyne (1:1). Method A.—The reaction mixture was chromatographed with ethylene dichloride as eluent. A mixture of three isomeric compounds, **2**, **3**, and **4**, was obtained in a yield of 15, 11, and 4%, respectively. The compounds were separated by preparative vpc (6 ft × 0.25 in. 10% SE-30, at 140°, gas flow rate 57 ml/min).

Compound 2 was a liquid: retention time 13.5 min; nmr (CCl_4) τ 2.65–3.40 (m, 4 H), 7.15 (s, 2 H), 8.53–9.08 (m, 2 H), 9.25–10.36 (m, 8 H); ir 3085–2920, 1470, 1430, 1050, 1020, 755, 725 cm^{-1}; mass spectrum M^+ *m/e* 184.

Anal. Calcd for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.50; H, 8.59.

Compound 3 was a liquid: retention time 20 min; nmr (CCl_4) τ 2.6–3.2 (m, 5 H), 6.58 (s, 2 H), 8.80 (m, 1 H), 9.07 (m, 4 H), 9.43 and 9.55 (two apparent s, 4 H); ir 3085–2910, 1605, 1500, 1455, 1045, 1025, 990, 755, 705 cm^{-1}; mass spectrum M^+ *m/e* 184.

Anal. Calcd for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.40; H, 8.45.

Compound 4 was a liquid: retention time 26 min; nmr (CCl_4) τ 2.6–3.1 (m, 5 H), 3.90 (s, 1 H), 8.13 (m, 1 H), 8.85 (m, 1 H), 9.0–9.65 (m, 8 H); ir 3080–3000, 1630, 1600, 1490,

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[17] S. Nishida, I. Moritani, and T. Traji, *J. Chem. Soc., Chem. Commun.*, 1114 (1972).

[18] C. D. Poulton and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2297 (1972).

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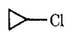
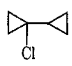
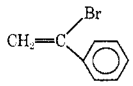


34



35



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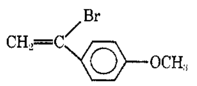

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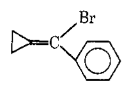
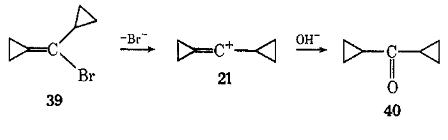


38



39 21 40

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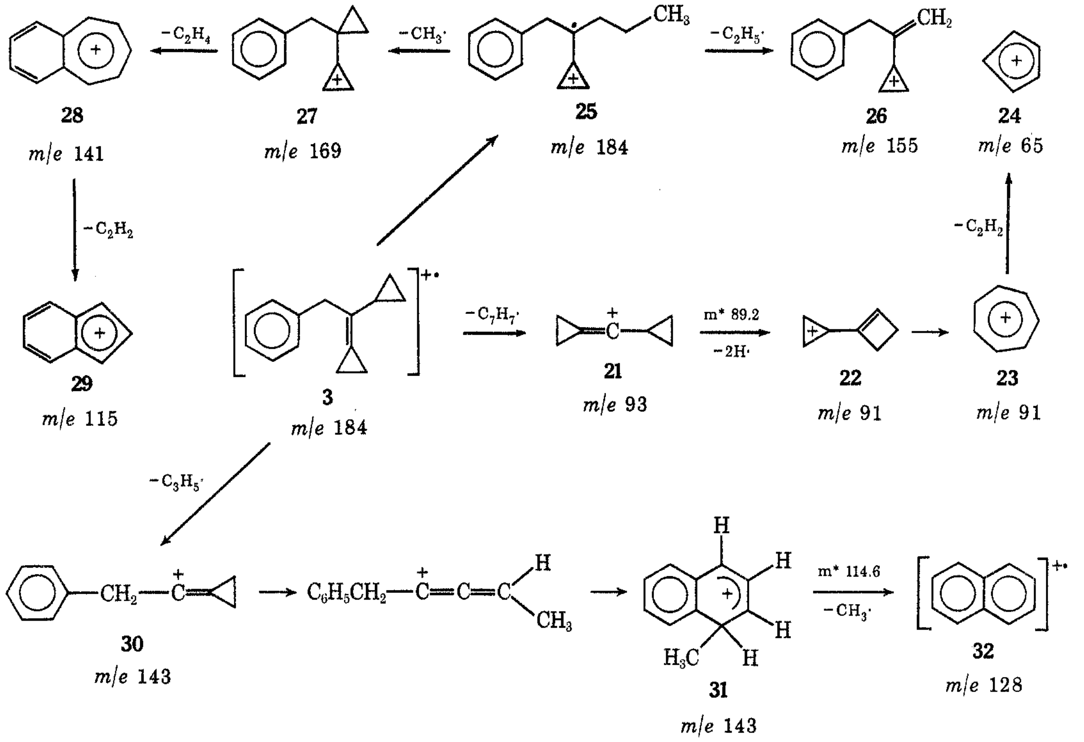
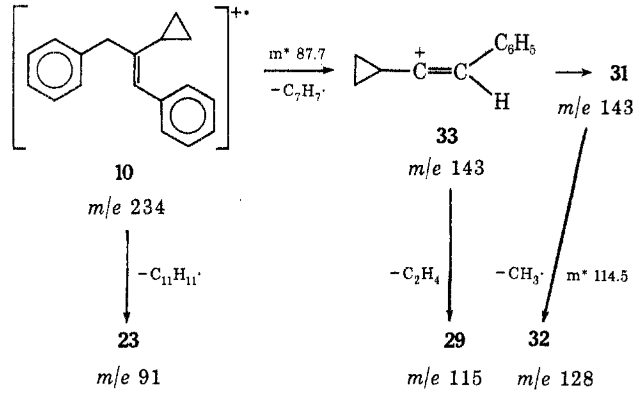
SCHEME XIII



SCHEME XIV



1445, 1020, 930, 915, 755, 700 cm^{-1}; uv (n-hexane) λ_{max} 255 mμ (ϵ 1.3×10^4), 205 (1.4×10^4); mass spectrum M$^+$ m/e 184.

Anal. Calcd for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.10; H, 8.56.

Reaction of 1,1-Dicyclopropylethylene (1) with Benzyne (1:1). Method B.—The reaction mixture was chromatographed with ethylene dichloride as eluent. A mixture of 2, 4, and 5 was obtained in a yield of 17, 7.2, and 21%, respectively. The compounds were separated by preparative vpc, as described above for the reaction of 1 with benzyne, method A.

Compound 5 was a liquid: retention time 40 min; nmr (CCl_4) τ 2.50–2.95 (m, 5 H), 5.25 and 5.33 (2 apparent s, 2 H), 6.31 (t, J = 7.5 cps, 1 H), 6.65 (t, J = 6 cps, 2 H), 7.73 (m, 2 H), 8.60–9.75 (m, 5 H); ir 3095–2880, 1645, 1605, 1500, 1460, 895, 755, 710 cm^{-1}; mass spectrum M$^+$ m/e 220 and 222.

Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.0; H, 7.70; Cl, 16.30. Found: C, 76.08; H, 7.84; Cl, 16.16.

Reaction of 2-Cyclopropylpropene (6) with Benzyne (1:2). Method A.—The reaction mixture was chromatographed with carbon tetrachloride as eluent and one major product, **10**, which consisted of two geometrical isomers, **10a** and **10b** (5:1), was obtained in a yield of 55%. Purification of **10** was effected by preparative vpc without separation of isomers (6 ft × 0.25 in. 10% SE-30, at 205°, gas flow rate 43.5 ml/min).

Isomeric mixture 10 was a liquid: retention time 13.5 min; nmr (CCl_4) τ 2.6–3.1 (m, 10 H), 3.63 (major isomer, **10a**) and 3.78 (minor isomer, **10b**) (two s, 5:1 respectively, 1 H), 6.44 (**10a**) and 6.75 (**10b**) (two s, 5:1 respectively, 2 H), 8.5–9.0 (m, 1 H), 9.3–9.7 (m, 4 H); ir 3080–2900, 1640, 1600, 1495, 1455, 1070, 1045, 1030, 1015, 915, 765, 750, 730, 700 cm^{-1}; uv (n-hexane) λ_{max} 250 mμ (ϵ 1.6×10^4), 209 (2.0×10^4); mass spectrum M$^+$ m/e 234.

Anal. Calcd for $C_{18}H_{18}$: C, 92.31; H, 7.69. Found: C, 92.56; H, 7.70.

Reaction of α-Cyclopropylstyrene (11) with Benzyne (1:1).—The procedure followed was that given in method A with the following variations: (1) chloranil (6.15 g, 25 mmol) was added to the reaction mixture; (2) basic instead of neutral alumina was used for chromatography. The reaction mixture was chromatographed with benzene as eluent. Two products, 14 and 12, were obtained in a yield of 8.5 and 1%, respectively.

Compound 14 was isolated by preparative vpc (retention time 10 min on 3 ft × 0.25 in. 20% SE-30, at 205°, gas flow rate 33 ml/min) and purified by recrystallization from hexane: colorless crystals; mp 78°; nmr ($CDCl_3$), τ 1.2–1.7 (m, 3 H), 2.2–2.8 (m, 6 H), 7.4–8.0 (m, 1 H), 8.65–9.3 (m, 4 H); ir 3060–2820, 1615, 1590, 1480, 1440, 1010, 875, 750, 735, 715 cm^{-1}; uv (n-hexane) λ_{max} 252 mμ (ϵ 6×10^4), 221 (3×10^4); mass spectrum M$^+$ m/e 218.

Anal. Calcd for $C_{17}H_{14}$: C, 93.58; H, 6.42. Found: C, 93.77; H, 6.48.

Compound 12 was isolated by preparative tlc on silica gel: R_f 0.18 (benzene as eluent); mp 70–72°; nmr ($CDCl_3$) τ 2.03 (m, 1 H), 2.35–2.95 (m, 8 H), 6.43 (s, 2 H), 8.63 (apparent q, 1 H), 9.41 and 9.51 (two apparent s, 4 H); ir 3080–2850, 1720, 1605, 1490, 1460, 1445, 1285, 1235, 1120, 1080, 1025, 1010, 990, 925, 910, 750, 715, 695 cm^{-1}; mass spectrum M$^+$ m/e 264, base peak 118.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.81; H, 6.06. Found: C, 81.0; H, 6.05.

Registry No.—**1,** 822-93-5; **2,** 38662-40-7; **3,** 38662-41-8; **4,** 23772-96-5; **5,** 38662-43-0; **6,** 4663-22-3; **10a,** 38662-44-1; **10b,** 38662-45-2; **11,** 825-76-3; **12,** 38661-79-9; **14,** 38661-80-2; benzyne, 462-80-6.

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