tionation of $HBBr_2$ would allow conversion of 75% of the boron bromide. Conversion of more than 50% of cycloheptatriene to tropenium ion has been observed, but not to an extent that would rule out path 1. Experiments designed to isolate the boronic acid derived from a possible cycloheptadienylboron dibromide intermediate or $HBBr_2$ as an etherate by the methods used for $HBCl_2$ by Brown and Tierney[39] are being investigated in an attempt to resolve this issue.

Kursanov and Vol'pin[40] have obtained low yields of tropenium ion by treatment of cycloheptatriene with boron fluoride or aluminum chloride, and suggest a hydride transfer mechanism such as 2 for these reactions. However, they report that extensive polymerization lowered yields and made workup difficult. This is in contrast to the clean, rapid reaction of boron bromide with cycloheptatriene and suggests that boron fluoride and aluminum chloride may react primarily by addition 1 accompanied by polymerization while boron bromide reacts to an appreciable extent by hydride abstraction 2. In the reaction of boron bromide with triphenylmethane no additive mechanism such as 1 is reasonable, and the fact that the triphenylmethylcarbonium ion is produced is indicative of the ability of boron bromide to abstract hydride from an organic molecule.

When *t*-butyl bromide is present, two other paths are possible: abstraction of bromide from *t*-butyl bromide by boron bromide to give *t*-butylcarbonium ion, followed by hydride transfer from cycloheptatriene to *t*-butylcarbonium ion (eq. 3), or

$$t\text{-BuBr} + BBr_3 \longrightarrow t\text{-Bu}^+ + BBr_4^- \qquad (3)$$
$$t\text{-Bu}^+ + TrH \longrightarrow t\text{-BuH} + Tr^+$$

addition of *t*-butylcarbonium ion (formed as in 3) to cycloheptatriene, followed by hydride transfer to the cycloheptadienyl carbonium ion so formed. Yield data indicate that either or both of these may occur to some extent in neat boron bromide, but are not important in methylene chloride solution.

The preparation and properties of other carbonium ion haloborates are presently under investigation.

Acknowledgment.—We wish to thank Dr. Hyp J. Dauben, Jr., for many helpful discussions of this work, and Mr. Ronald Schwartz for technical assistance.

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[40] D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk. S. S. S. R.*, **113**, 339 (1957); *C. A.*, **51**, 14572f (1957).

[CONTRIBUTION NO. 2611 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

Small-Ring Compounds. XXXI. Cyclobutane Derivatives from Adducts of Cyclohexenylacetylene and Fluorochloroethylenes[1]

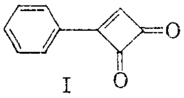
BY CLAY M. SHARTS[2] AND JOHN D. ROBERTS

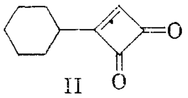
RECEIVED AUGUST 30, 1960

Cycloadditions of 1-ethynylcyclohex-1-ene with trifluorochloroethylene and difluorodichloroethylene gave 1,1,2 trifluoro-2-chloro- (IV) and 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI), respectively. Both IV and XI were hydrolyzed by sulfuric acid to the corresponding monoketones, 2-fluoro-2-chloro- and 2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutenones. With iodide and ethoxide ions IV or XI appeared to give S_N2′ displacement products. Diels–Alder adducts were obtained from IV and maleic anhydride or dicarbethoxyacetylene. The triethylamine-catalyzed rearrangement of XI at 150° gave 1,1 difluoro-2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXXI), but at 180° an unexpected elimination rearrangement led to 2-fluoro-1,3-dichloro-5,6,7,8-tetrahydronaphthalene (XXXIII).

The synthesis of substituted fluorinated cyclobutanes and cyclobutenes by cycloaddition reactions between fluorinated alkenes and appropriately substituted alkenes and alkynes provides a method of synthesis of useful intermediates that can often be converted to novel non-fluorinated four-membered carbon-ring compounds.[3] Thus several phenylcyclobutenones have been prepared from cycloadducts of phenylacetylene and various fluoroethylenes.[4,5]

Of particular interest is the product from hydrolysis of the cycloadduct from trifluorochloroethylene and phenylacetylene: phenylcyclobutadienoquinone (I), a bright, yellow compound rather more stable than would be expected for a substance with its considerably strained ring system.[6,7]


I


II

In an effort to evaluate the influence of the phenyl group on the properties of the cyclobutadienoquinone ring in I, we have assayed the preparation of cyclohexylcyclobutadienoquinone (II) by way of the cycloadducts from 1-ethynylcyclohex-1-ene with trifluorochloroethylene and difluorodichloroethylene. The plan was to utilize the cyclohexenyl group to facilitate the addition reaction[3] and the formation of the cyclobutadienoquinone, and sub-

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[1] Supported in part by the National Science Foundation.

[2] General Electric Co. Fellow, 1957–1958.

[3] J. D. Roberts and C. M. Sharts in A. C. Cope, "Organic Reactions," in press.

[4] J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *J. Am. Chem. Soc.*, **75**, 4765 (1953).

[5] (a) E. F. Jenny and J. D. Roberts, *ibid.*, **78**, 2005 (1956); (b) E. F. Silversmith and J. D. Roberts, *ibid.*, **78**, 4023 (1956), and **80**, 4083 (1958); (c) E. F. Silversmith, Y. Kitahara and J. D. Roberts, *ibid.*, **80**, 4088 (1958); (d) E. F. Silversmith, Y. Kitahara, M. C. Caserio and J. D. Roberts, *ibid.*, **80**, 5840 (1958); (e) S. L. Manatt, Ph.D. Thesis, California Institute of Technology, 1959.

[6] E. J. Smutny and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 3420 (1955).

[7] E. J. Smutny, M. C. Caserio and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

sequently to saturate the vinyl group. Although attainment of the goal was thwarted by formation of an apparently more stable isomer of II, the properties of many of the intermediate and related substances are of considerable interest.

Results and Discussion

1-Ethynylcyclohex-1-ene (III)[8] reacts with trifluorochloroethylene at 95° to give the cycloadduct, 1,1,2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (IV). The alternate structure for the adduct 1,2,2-trifluoro-1-chloro-3-(cyclohex-1-enyl)-cyclobutene (V) was eliminated by aromatization of the cyclohexene ring of IV to the known cycloadduct VI from trifluorochloroethylene and phenylacetylene.[6,7] The aromatization of IV was accomplished by bromination with N-bromosuccinimide to give a distillable dibromide assigned the structure 1,1,2-trifluoro-2-chloro-3-(3,6-dibromocyclohex-1-enyl)-cyclobutene (VII) and by dehydrobromination, which gave a product identical with authentic VI. Some further interrelation of the cycloadducts previously reported[4] was achieved by conversion of VIII from trifluorochloroethylene and styrene[5b,d] to VI from trifluorochloroethylene and phenylacetylene[6,9] by way of 1,1,2-trifluoro-2-chloro-3-bromo-3-phenylcyclobutane (IX).[5e]

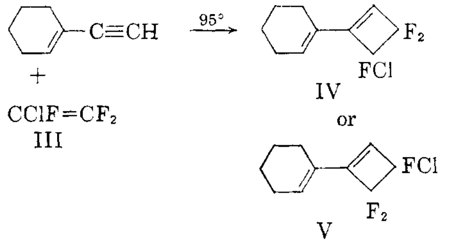
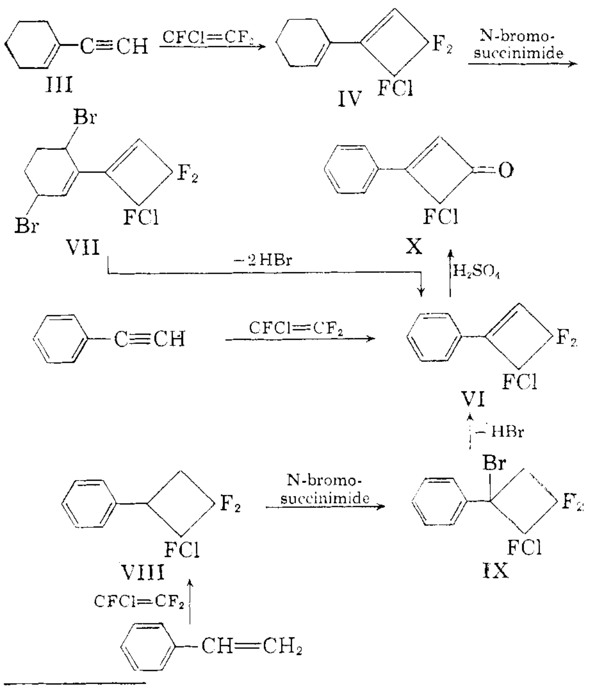


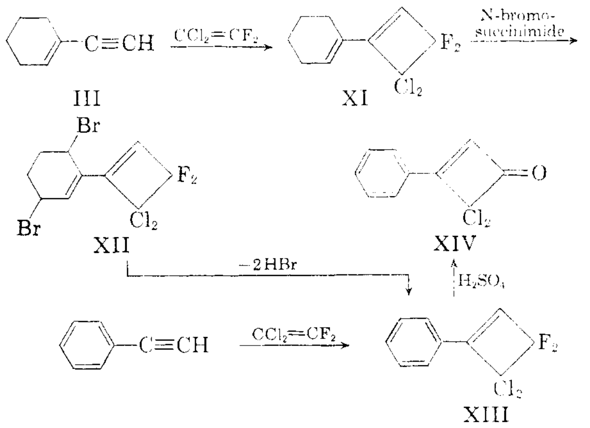
Chart 1



The VI prepared from VIII showed some infrared absorptions, which indicated impurities (one of which was the starting material VIII). Identification of VI was fortified by hydrolysis to the known solid monoketone 2-fluoro-2-chloro-3-phenylcyclobutenone (X), also obtainable from authentic VI.[6,7] The above reactions are summarized in Chart 1.

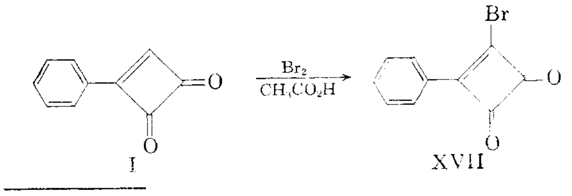
The cycloadduct XI formed from 1-ethynylcyclohex-1-ene and difluorodichloroethylene at 95° (m.p. 44–45°) was established as 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI) by similar reactions. Thus, two moles of N-bromosuccinimide reacted with XI to give 1,1-difluoro-2,2-dichloro-3-(3,6-dibromocyclohex-1-enyl)-cyclobutene (XII), which was dehydrobrominated to 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (XIII)[4] and then hydrolyzed to 2,2-dichloro-3-phenylcyclobutenone (XIV)[4] as shown in Chart 2.

Chart 2



The cycloaddition reactions shown in Charts 1 and 2 appear in each case to give only a single product. Similar selectivity has been found in a number of related cycloadditions and is discussed in detail elsewhere.[3]

The hydrolysis reactions of the cycloadduct IV were similar to those of its phenyl analog VI. At room temperature with concentrated sulfuric acid, IV gave the white crystalline monoketone 2-fluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutenone (XV) and at 55–60° yellow, crystalline cyclohex-1-enylcyclobutadienoquinone (XVI). Since phenylcyclobutadienoquinone (I) is readily substituted in the four-membered ring by bromine to give 4-bromo-3-phenylcyclobutene-1,2-dione (XVII),[6,7] it was hoped that XVI would react similarly. However, with bromine in acetic acid,



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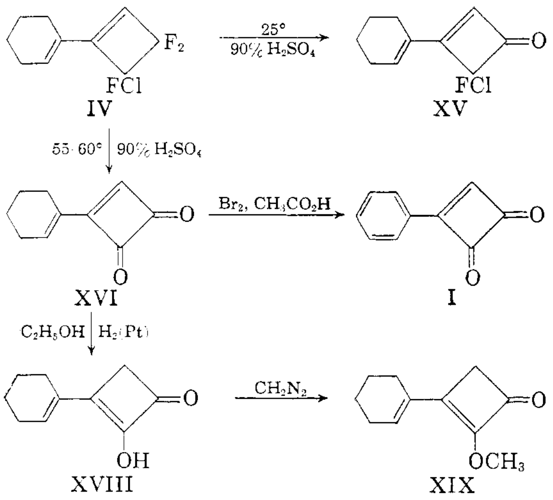
[8] J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 2652 (1951).

[9] Authentic VI was prepared from phenylacetylene purified through the mercury derivative to remove styrene, which was found to be present in commercial phenylacetylene. Thus VI was obtained free of VIII, which was apparently present in earlier preparations of VI; see ref. 6.

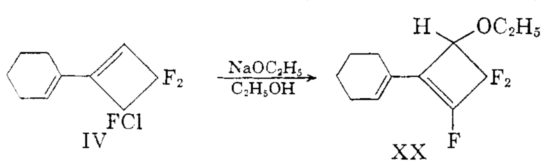
the cyclohexene ring of XVI was aromatized and a small yield of I was formed. This reaction provides confirmation for the structure assigned to XVI.

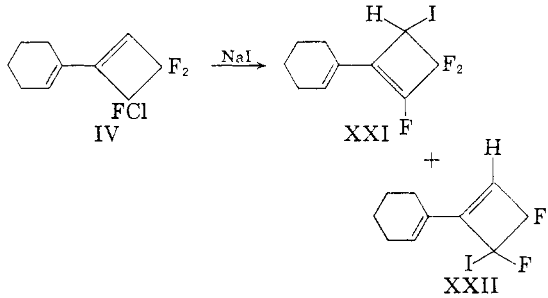
Attempts were made to prepare cyclohexylcyclobutadienoquinone (II) by reduction of the cyclohexenyl double bond of XVI. In ethanol, XVI readily absorbed one mole of hydrogen over a platinum catalyst at room temperature, but when the filtered reaction mixture was poured into water XVIII was obtained instead of II. Compound XVIII was unstable in air and was assigned the structure 2-hydroxy-3-(cyclohex-1-enyl)-cyclobut-2-en-1-one on the basis of a positive enol test with ferric ion; through formation of a 2,4-dinitrophenylhydrazone; and by infrared, ultraviolet and nuclear magnetic resonance (n.m.r.) spectra. With diazomethane, XVIII gave a monomethyl derivative (XIX). It is not known how XVIII is formed in the reduction of XVI. Several possible routes can be formulated, including one which involves reduction of XVI to cyclohexenyldihydroxycyclobutadiene and subsequent ketonization, but no evidence is available on this score. It appears that the conjugated system of XVIII is more stable than that of II. Chart 3 summarizes the above reactions.

CHART 3

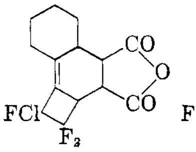


With either sodium ethoxide in ethanol or sodium iodide in acetone, IV underwent displacement reactions similar to those reported previously for the phenyl analog.[10,11] Sodium ethoxide gave an S_N2' displacement product, 1,1,2-trifluoro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XX), while sodium iodide gave two inseparable products identified by their proton magnetic resonance spectra as the S_N2' displacement product 1,1,2-trifluoro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXI) and the S_N2 displacement product 1,1,2-trifluoro-2-iodo-3-(cyclohex-1-enyl)-cyclobut-3-ene (XXII).

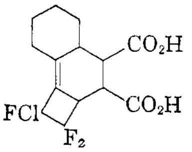




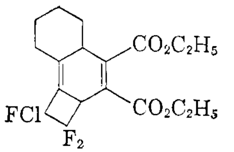
When IV was heated under reflux in toluene with either maleic anhydride or dicarbethoxyacetylene, Diels–Alder adducts appeared to be formed that were considered to be 1,2-dicarboxyanhydro-3,4-(1,1,2-trifluoro-2-chloroethano)-1,2,3,5,6,7,8,9-octahydronaphthalene (XXIII) and 1,2-dicarbethoxy-3,4-(1,1,2-trifluoro-2-chloroethano)-3,5,6,7,8,9-hexahydronaphthalene (XXV), respectively. The maleic anhydride adduct XXIII was purified and characterized as the corresponding diacid XXIV. Addition of one mole of bromine to XXV, dehydrobromination with potassium *t*-butoxide, and saponification of the resultant product with 6 *N* sodium hydroxide resulted in the formation of a compound believed to be 1,2-dicarboxy-3,4-(1,1,2-trifluoro-2-chloroethano)-5,6,7,8-tetrahydronaphthalene (XXVI). Sulfuric acid hydrolysis of XXVI to the corresponding diketone XXVII was not successful.



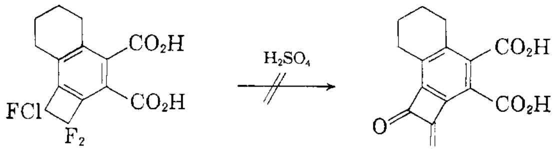
XXIII



XXIV



XXV



1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI) undergoes reactions similar to those reported for its phenyl analog 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (XIII).[4,5] Compound XI, like XIII, could be hydrolyzed to a monoketone, 2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXVIII). Compound XI reacted with iodide and ethoxide ions, presumably by the S_N2' mechanism, to give 1,1-difluoro-2-chloro-4-iodo- (XXIX) and 1,1-difluoro-2-chloro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXX), respectively. When XI was heated with triethylamine in a sealed tube at 140° for 24 hours, it rearranged to 1,1-difluoro-2,4-dichloro-3-(cyclohex-1-

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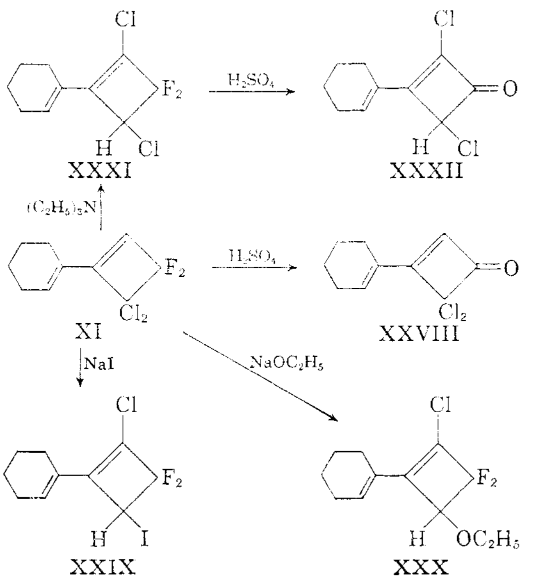
(10) M. C. Caserio, H. E. Simmons, Jr., A. E. Johnson and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3102 (1960).

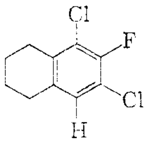
(11) Y. Kitahara, M. C. Caserio, F. Scardiglia and J. D. Roberts, *ibid.*, **82**, 3106 (1960).

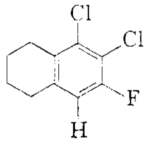
enyl)-cyclobutene (XXXI); XXXI hydrolyzed to a monoketone, 2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXXII). Unlike XI, XXXI did not react significantly with sodium iodide in acetone even when heated for extended periods. Sodium ethoxide in ethanol gave poorly defined products. The reactions discussed above are summarized in Chart 4.

CHART 4



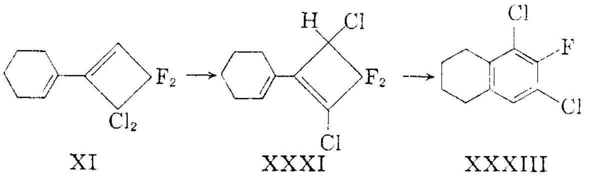
As mentioned earlier, XXXI was obtained by heating XI in a sealed tube with a catalytic amount of triethylamine at 140–150°. On some occasions, incomplete rearrangement occurred. In an attempt to ensure complete reaction, a trial run was carried out with XI at 180° for 36 hours with triethylamine. Hydrogen halide was formed and no XXXI could be isolated; instead, there was obtained a white solid of composition $C_{10}H_9Cl_2F$, which accounted for 41% of the starting XI. Infrared, ultraviolet and n.m.r. spectra as well as lack of reactivity toward bromine and permanganate provided evidence in favor of the tetrahydronaphthalene structures XXXIII or XXXIV.


XXXIII

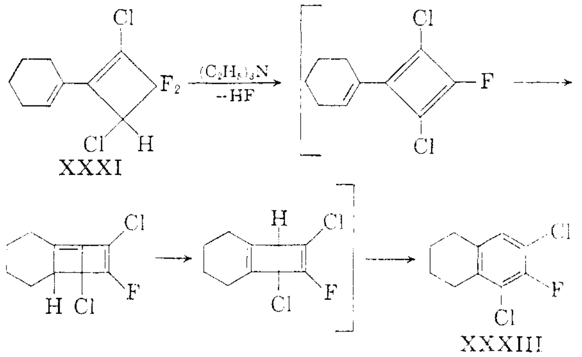

XXXIV

The proton n.m.r. spectrum at 40 m.c. consisted of four peaks at 16, 26, 196, and 236 c.p.s. relative to benzene in the ratio 0.5:0.5:4.1:4.1, respectively. These resonances were assigned to vinyl hydrogen split by fluorine (16, 26; J_{HF} = 10 c.p.s.) and the eight cyclohexyl ring hydrogens (196 and 236 c.p.s.). The fluorine spectrum was a single clean doublet with J_{HF} = 10 c.p.s. Gutowsky, Holm, Saika and Williams[12] have shown that hydrogen–fluorine interactions in benzene derivatives show J_{HF} = 6.2–10.1, 6.2–8.3, 0.0–2.2 c.p.s. for *ortho, meta* and *para* couplings, respectively. The *para* arrangement of hydrogen and fluorine is therefore reasonably excluded.

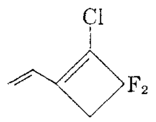
The rearranged dichloride XXXI appears to be the precursor of tetrahydronaphthalene rather than the *gem*-dichloride XI since the conditions of the reaction are those which convert XI to XXXI, and XXXI affords the tetrahydronaphthalene when heated with triethylamine.

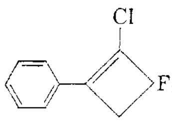


On this basis, the tentative structure XXXIII was assigned to the product since it has an arrangement of halogens like XXXI. Assuming the structure is XXXIII, the following mechanism is attractive for its formation from XXXI and is in accord with triethylamine being the active agent



Although this mechanism is reasonable in terms of the character of the reaction and the reaction products, it is not so satisfactory in accounting for the apparent failure of the phenyl analog of XI to undergo anything but nucleophilic displacement with nucleophilic reagents.[10,11] The contrast is further heightened by the fact that 1,1-difluoro-2-chloro-3-vinylcyclobut-2-ene(XXXV) is very easily converted by basic reagents to polymeric materials,[13] while its phenyl analog XXXVI is quite stable to base (even to ethoxide, with which it eventually undergoes nucleophilic substitution at the vinyl halogen position[5b]). The difference could


XXXV


XXXVI

conceivably be due to the somewhat greater electronic stabilization predicted[14] for a vinylcyclobutadiene than a phenylcyclobutadiene such as would arise from the phenyl analog of XI. Some support for this notion comes from the fact that when the phenyl analog of XI is treated with excess phenyllithium, nucleophilic substitution is followed

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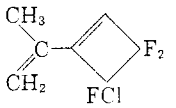
(12) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

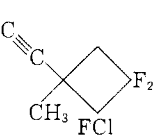
(13) W. H. Graham, unpublished research.

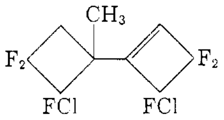
(14) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

by elimination of hydrogen fluoride and a product such as might be expected from a cyclobutadiene intermediate is formed.[11]

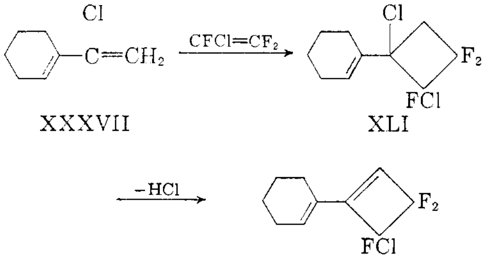
In addition to the other cycloadditions reported in this paper, the additions of trifluorochloroethylene to isopropenylacetylene and 1-(1-chloroethenyl)-cyclohex-1-ene (XXXVII) were studied. With isopropenylacetylene three products were isolated. These were assigned the structures XXXVIII–XL on the basis of their infrared, ultraviolet and proton and fluorine magnetic resonance spectra, as well as by physical properties, analysis and analogy with the course of other cycloadditions that yield four-membered rings.[3]


XXXVIII


XXXIX


XL

The addition of 1-(1-chloroethenyl)-cyclohex-1-ene (XXXVII) to trifluorochloroethylene clearly gave the same type of orientation as for 1-ethynylcyclohex-1-ene because dehydrochlorination of the adduct 1,1,2-trifluoro-2,3-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XLI) afforded the adduct IV.


XXXVII XLI IV

A rather complete tabulation and comparison of the infrared, ultraviolet and n.m.r. absorptions of the compounds described in this and earlier[4,5] papers is given elsewhere.[15]

Experimental

1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (IV).—To each of four, heavy-walled Pyrex tubes (19 × 25 × 615 mm.) was added 25.0 ml. (22.0 g., 0.208 mole) of 1-ethynylcyclohex-1-ene[8] [b.p. 54–59° (29–31 mm.), $n^{25}D$ 1.4938] prepared from 1-ethynylcyclohexan-1-ol.[16] The tubes were cooled in Dry Ice and 25 ml. (~37 g., 0.32 mole) of trifluorochlorethylene condensed into each tube. The tubes were sealed, allowed to warm to room temperature, and then heated over a 4-hr. period to 95°. After 20 hr. at 95°, the tubes were cooled to room temperature, then in Dry Ice, vented, and the contents allowed to degas. The combined products were distilled and gave 149 g. (79%) of IV, b.p. 71–73° (1 mm.), $n^{25}D$ 1.4808. When cooled in ice, the product crystallized to sharp white needles, m.p. 11–13°.

The analytical sample had b.p. 68.5–70.0° (1 mm.), $n^{25}D$ 1.4800, $d^{25}4$ 1.268; ultraviolet spectrum: λ_{max} 2415 A. (ϵ 18,500); infrared spectrum: bands at 1594, 1643, 3040 and 3095 cm.$^{-1}$.[17] The n.m.r. spectra showed cross-ring coupling between fluorine and hydrogen[18] and confirmed the assigned structure. Compound IV did not react readily with ethanolic silver nitrate or sodium iodide in acetone at room temperature.

Anal. Calcd. for $C_{10}H_{10}F_3Cl$: C, 53.94; H, 4.53; Cl, 15.93. Found: C, 53.89; H, 4.57; Cl, 15.82.

Conversion of 1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (IV) to 1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene (VI).—A mixture of 24.0 g. (0.135 mole) of N-bromosuccinimide, 15.0 g. (0.0673 mole) of IV, 0.3 g. of benzoyl peroxide and 100 ml. of carbon tetrachloride (previously dried over phosphorus pentoxide) was heated under reflux for 22 hr. The succinimide was removed by filtration and the solvent distilled from the filtrate. Distillation of the residual liquid gave 12.5 g. (49%) of crude product, b.p. 123–127° (2 mm.), which was believed to be principally 1,1,2-trifluoro-2-chloro-3-(3,6-dibromocyclohex-1-enyl)-cyclobutene (VII). A center cut, $n^{25}D$ 1.5534, of the crude product gave a poor carbon analysis.

Anal. Calcd. for $C_{10}H_8F_3ClBr_2$: C, 31.57; H, 2.12. Found: C, 33.57; H, 2.12.

A 4.9-g. (0.013 mole) sample of the dibromide VII was dehydrobrominated with a solution of potassium hydroxide in *t*-butyl alcohol over 1.5 hr. at room temperature. The solvent was distilled and the residue extracted with chloroform. Distillation of the extract gave 3.0 g. of VI, b.p. about 66° (0.7 mm.), in two fractions of $n^{25}D$ 1.5140 and 1.5134. The infrared spectrum of each fraction was identical with the spectrum of VI, b.p. 74° (1.5 mm.), $n^{25}D$ 1.5128, prepared from purified phenylacetylene.[9]

1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI).—The preparation of XI was identical to that of IV with the exception that difluorodichloroethylene replaced trifluorochloroethylene. From 88 g. (0.830 mole) of acid-washed, redistilled 1-ethynylcyclohex-1-ene was obtained 180 g. (0.754 mole, 91%) of XI, b.p. 87–90° (2 mm.); XI crystallized from ethanol as white needles, m.p. 44–45°. In other runs, yields from 69–91% were obtained; temperatures greater than 100° adversely affected the yields. Addition of 0.5 g. of hydroquinone had no detectable effect. An oil was sometimes obtained, $n^{25}D$ 1.5090–1.5100, which eventually crystallized.

The analytical sample after six recrystallizations from ethanol had m.p. 44.9–45.4°; ultraviolet spectrum: λ_{max} 2450 Å. (ϵ 18,400); infrared spectrum: bands at 1590 and 1645 cm.$^{-1}$. Solutions of bromine and potassium permanganate were decolorized by XI. A white precipitate formed when XI was treated with ethanolic silver nitrate; no precipitate formed with sodium iodide in acetone.

Anal. Calcd. for $C_{10}H_{10}F_2Cl_2$: C, 50.23; H, 4.22; Cl, 29.66. Found: C, 50.23; H, 4.39; Cl, 29.56.

Conversion of 1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI) to 1,1-Difluoro-2-2-dichloro-3-phenylcyclobutene (XIII) and 2,2-Dichloro-3-phenylcyclobutenone (XIV).—A mixture of 25.0 g. (0.105 mole) of XI, 38.6 g. (0.210 mole) of N-bromosuccinimide, 0.7 g. of benzoyl peroxide and 100 ml. of phosphorus pentoxide-dried carbon tetrachloride was heated under reflux for 14 hr. The succinimide was removed by filtration, the solvent was distilled, and the residue separated by distillation through a 30-cm. Vigreux column into two fractions of b.p. 124.5–134.0° (2.2–3.3 mm.), $n^{25}D$ 1.5670, and 132° (2.2 mm.), $n^{25}D$ 1.5722. These fractions showed infrared absorption for double bonds at 1590 and 1640 cm.$^{-1}$ and were believed to consist primarily of 1,1-difluoro-2,2-dichloro-3-(3,6-dibromocyclohex-1-enyl)-cyclobutene (XII). The distilled dibromide XII was dehydrobrominated with a solution of potassium hydroxide in t-butyl alcohol. The product had b.p. 90.5–94° (1.6 mm.) and $n^{25}D$ 1.5505–1.5542 and an infrared spectrum containing all the bands for XIII, but it also showed the presence of some impurities. The n.m.r. spectrum confirmed that the liquid was primarily XIII. Hydrolysis of the product with sulfuric acid gave a yellow solid, which was purified by chromatography and after crystallization from hexane gave white needles, m.p. 80.2–80.5°, identical (mixed m.p. and infrared spectra) with authentic XIV prepared earlier.[4]

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(15) Clay M. Sharts, Ph.D. Thesis, California Institute of Technology, 1959.

(16) A generous sample of 1-ethynylcyclohexan-1-ol was kindly furnished by the Air Reduction Co.

(17) The ultraviolet spectra were observed in spectral-grade cyclohexane solution. Infrared bands reported for liquids are for pure liquids in fixed cells. Infrared bands for solids were observed in carbon tetrachloride solution or pressed potassium bromide disks.

(18) C. M. Sharts and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1008 (1957). Proton and fluorine (where appropriate) n.m.r. spectra were taken for most of the compounds prepared. These are discussed in detail elsewhere.[15]

2-Fluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutenone (XV).—A mixture of 24.8 g. (0.123 mole) of 1,1,2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene and 130 ml. of 96% sulfuric acid was stirred vigorously for 20 min. An exothermic reaction occurred with evolution of hydrogen fluoride. The dark-red solution was poured into 1500 ml. of an ice-water slurry. A cream-colored precipitate amounting to 22.4 g. (0.123 mole, 100%) was obtained, which was collected, washed with water, and dried. Crystallization from cyclohexane followed by chromatography over alumina and another crystallization gave 6.0 g. of white crystals, m.p. 46.7–47.5°; ultraviolet spectrum: λ_{max} 2730 Å. (ϵ 28,000); infrared spectrum: bands at 1548, 1616, 1776 and 3067 cm.$^{-1}$. The observed dipole moment was 5.46 D.[19]

Anal. Calcd. for $C_{10}H_{10}OFCl$: C, 59.48; H, 5.03; Cl, 17.68. Found: C, 59.72; H, 5.11; Cl, 17.58.

Ketone XV decolorized solutions of potassium permanganate in acetone and bromine in carbon tetrachloride but did not give precipitates with either silver nitrate in ethanol or sodium iodide in acetone at room temperature. Microhydrogenation of XV over a platinum catalyst in ethanol at room temperature resulted in uptake of one mole-equivalent of hydrogen. Hydrogenolysis of chlorine appeared to occur since one mole-equivalent of silver chloride precipitated on addition of excess silver nitrate to an aqueous extract of the reaction mixture.

The 2,4-dinitrophenylhydrazone derivative of XV was obtained as red needles from ethyl acetate–acetonitrile, m.p. 198.5–198.6°.

Anal. Calcd. for $C_{16}H_{14}O_4FCl$: C, 50.47; H, 3.71; N, 14.71. Found: C, 50.43; H, 3.77; N, 14.62.

Cyclohex-1-enylcyclobutadienoquinone (XVI).—The yield of XVI from the hydrolysis of IV was found to be very sensitive to changes in the reaction conditions; the following procedure gave the best results: A mixture of 24–28 g. of 1,1,2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene and 75 ml. of 97% sulfuric acid was stirred vigorously for 10–15 min. The reaction was exothermic and the temperature rose to 40–45°. After the rise in temperature was over, the mixture was heated with an oil-bath at 60–65° for 20–30 min. Hydrogen halide was evolved vigorously. The dark-red solution was then slowly poured into 1500 ml. of an ice-water slurry and the resulting yellow-brown precipitate collected by filtration. The solid was repeatedly washed with copious amounts of water, dried, and then dissolved in hot hexane; a black insoluble oil remained. From the cooled hexane extracts, 3–5 g. (23–41%) of dull yellow XVI crystallized. Alternate recrystallizations from 95% ethanol (1 g. XVI/5 ml. ethanol) and hot hexane gave bright yellow XVI, m.p. 77–78°. The recrystallized product was stable, in contrast to unpurified XVI, which decomposed in a few days at room temperature. The analytical sample was purified by sublimation at 50° (1 mm.) and had m.p. 77.8–78.4°; ultraviolet spectrum: λ_{max} 2720 Å. (ϵ 20,200); infrared spectrum: bands at 1538, 1620, 1780, 3030 and 3090 cm.$^{-1}$; dipole moment 5.62 D.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 73.89; H, 6.24.

The mono-2,4-dinitrophenylhydrazone derivative of XVI was obtained as red needles, m.p. 260° dec.

Anal. Calcd. for $C_{16}H_{14}O_5N_4$: C, 56.14; H, 4.12; N, 23.37. Found: C, 56.72; H, 4.30; N, 22.96.

When 1 g. (0.0062 mole) of XVI was heated in acetic acid at 50° and 1.05 g. (0.0062 mole) of bromine added dropwise, hydrogen bromide was evolved; and the subsequent work-up afforded the recovery of some XVI along with phenylcyclobutadienoquinone (10 mg.) and other unidentified products.

2-Hydroxy-3-(cyclohex-1-enyl)-cyclobut-2-en-1-one (XVIII).—A solution of 3.0 g. (0.0185 mole) of cyclohex-1-enylcyclobutadienoquinone (XVI) in 60 ml. of 95% ethanol was shaken overnight with hydrogen at 60 p.s.i. over a platinum catalyst at room temperature. Isolation and purification of the product was carried out in a cold room at 2°. The catalyst was removed by filtration and 200 ml. of water added to the filtrate. The resulting white solid (3 g., 100%) was separated by centrifugation and recrystallized six times from 50% ethanol; XVIII was obtained as long, sharp, white needles, m.p. 151–152° (dec., capillary) and 154° (dec., block); ultraviolet spectrum: λ_{max} 3000 Å. (ϵ 9,750); infrared spectrum: bands at 1613, 1638, 1745 and 3200 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.06; H, 7.30.

The purified XVIII was dried at 1 mm. over phosphorus pentoxide and stored under nitrogen. When exposed to air at room temperature, XVIII rapidly decomposed to a yellow-orange solid with different spectral characteristics; XVIII decolorized solutions of potassium permanganate and bromine and gave an intense green-black solution with ferric chloride. A 2,4-dinitrophenylhydrazone derivative was formed, m.p. 250–251° dec.

With diazomethane,[20] 0.2 g. of XVIII gave the crude methyl ether XIX which, when recrystallized from ethanol–water, amounted to 50 mg., m.p. 125–130°; ultraviolet spectrum: λ_{max} 2975 Å. (ϵ 16,800); infrared spectrum: bands at 1610, 1628 and 1780 cm.$^{-1}$. The disappearance of the enolic hydrogen band in the infrared spectrum of XIX compared to the starting material XVIII (3200 cm.$^{-1}$ absorption) suggested that ether formation had occurred. This was confirmed by comparison of the n.m.r. spectra of XVIII and XIX in which the low field absorption of a single proton was replaced by three protons of the methyl group. Compound XIX decolorized solutions of bromine and potassium permanganate. Addition of XIX to a 2,4-dinitrophenylhydrazine solution gave a precipitate. A satisfactory elemental analysis was not obtained.

1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (IV) with Sodium Iodide in Acetone and Sodium Ethoxide in Ethanol.—A saturated solution (50 ml.) of sodium iodide in acetone was heated under reflux for 8 days with 12.5 g. (0.0564 mole) of IV. The acetone was distilled and the residue extracted with hexane. The hexane extracts were dried over calcium chloride and the hexane distilled. The residue was fractionated and 7.9 g. of IV recovered, b.p. 77–85° (2.5–3.0 mm.). The monoiodide fraction had b.p. 94–98° (3.0 mm.) and amounted to 3.1 g.; ultraviolet spectrum: λ_{max} 2395 Å. (ϵ 14,000); infrared spectrum: bands at 1590, 1635, 1647 and 1695 cm.$^{-1}$. The infrared and n.m.r. spectra suggested the product was a mixture of 1,1,2-trifluoro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXI) and 1,1,2-trifluoro-2-iodo-3-(cyclohex-1-enyl)-cyclobutene (XXII). On standing the product lost iodine.

To a solution of sodium (1.86 g., 0.0890 mole) in 50 ml. of absolute ethanol was added 18.0 g. (0.0810 mole) of IV. The mixture was heated under reflux for 16 hr. and then poured into water. The organic material was separated with methylene chloride and distilled. The product, 1,1,2-trifluoro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XX), and the starting IV appeared to codistil. Chromatography in hexane solution of the distillate on silicic acid gave a fair separation of IV and XX. The best sample of XX obtained had $n^{25}D$ 1.4579; ultraviolet spectrum: λ_{max} 2475 Å. (ϵ 13,900); infrared spectrum: bands at 1635 and 1695 cm.$^{-1}$. This sample was still contaminated by some IV as shown by infrared analysis, and a satisfactory elemental analysis was not obtained.

1,2-Dicarboxyanhydro-(XXIII) and 1,2-Dicarboxy-3,4-(1,1,2-trifluoro-2-chloroethano)-1,2,3,5,6,7,8,9-octahydronaphthalene (XXIV).—Maleic anhydride (19.7 g., 0.201 mole), 1,1,2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (44.7 g., 0.201 mole) and 125 ml. of toluene were heated under reflux for 40 hr. Distillation of toluene gave a yellow oil that would not crystallize. The oil was taken up in 100 ml. of toluene and heated 3 days on a steam-bath. Slow evaporation of the toluene gave a solid product that was taken up in hot dioxane. The solution was diluted with hexane to the cloud point and then set aside to cool. Three crops of crystals were obtained in this manner that amounted to 7.45 g. (m.p. 233–234° dec.), 8.0 g. (m.p. 230–234° dec.), and 12.7 g. (m.p. 225–232° dec.); total, 28.2 g. (42%). After several months, 15–20 g. of additional adduct XXIII crystallized from the mother liquors.

Anal. Calcd. for $C_{14}H_{12}F_3ClO_3$: C, 52.43; H, 3.77; Cl, 11.05; neut. equiv., 160. Found: C, 52.20; H, 3.92; Cl, 11.15; neut. equiv., 169.

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(19) Dipole moments were kindly measured by Professor R. M. Badger and associates.[7,15]

(20) M. C. Caserio, J. D. Roberts, M. Neeman and W. S. Johnson, *J. Am. Chem. Soc.*, **80**, 2584 (1958).

Bromine was decolorized by XXIII in an autocatalytic reaction with evolution of hydrogen bromide.

Neutralization of 3.0 g. of XXIII with sodium hydroxide and acidification of the resulting solution with sulfuric acid gave the diacid XXIV, which was recrystallized from 50% ethanol–water; m.p. 246–248°.

The analytical sample of XXIII was dried at 78° (1 mm.) for 48 hr. and had a somewhat lower m.p. of 237–238°, but it had the correct elemental analysis.

Anal. Calcd. for $C_{14}H_{14}O_4F_3Cl$: C, 49.64; H, 4.16; Cl, 10.46. Found: C, 49.71; H, 4.43; Cl, 10.86.

1,2-Dicarbethoxy-3,4-(1,1,2-trifluoro-2-chloroethano)-3,5,6,7,8,9-hexahydronaphthalene (XXV).—Dicarbethoxyacetylene (10.0 g., 0.0585 mole, n^{25}D 1.4405), 1,1,2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (13.0 g., 0.0585 mole, n^{25}D 1.4807) and 15 ml. of toluene were heated 44 hr. under reflux. Distillation gave 8.8 g. of XXV, b.p. 180–190° (2–3 mm.), n^{25}D 1.5080–1.5120. The highest boiling fraction, b.p. 186–190° (2–3 mm.), n^{25}D 1.5120, was submitted for analysis.

Anal. Calcd. for $C_{18}H_{20}O_4F_3Cl$: C, 55.04; H, 5.13; Cl, 9.03. Found: C, 54.84; H, 5.13; Cl, 9.10.

Compound XXV did not react at room temperature with sodium iodide in acetone or ethanolic silver nitrate but did react exothermically with potassium *t*-butoxide solution. The infrared spectrum showed absorption at 1596 and 1600 cm.$^{-1}$ in the double bond region; the ultraviolet spectrum had maxima at 2150, 2840 and 2925 Å.

1,2-Dicarboxy-3,4-(1,1,2-trifluoro-2-chloroethano)-5,6,7,8-tetrahydronaphthalene (XXVI).—To a solution of 6.55 g. (0.0167 mole) of XXV in carbon tetrachloride was added dropwise a solution of 2.94 g. (0.0184 mole) of bromine in 50 ml. of carbon tetrachloride. After the bromine was decolorized, 60 ml. of a 0.604 *M* potassium *t*-butoxide solution was added dropwise; an exothermic reaction occurred and a precipitate formed. Water (200 ml.) was added and the organic phase separated with methylene chloride. The solvent was evaporated from the organic phase and the residue was heated overnight under reflux with 15 ml. of 6 *N* sodium hydroxide solution. Acidification of the homogeneous aqueous phase, extraction with ether, and removal of the ether gave 1.4 g. of crude material, m.p. 65–72°. Recrystallization of 0.3 g. from carbon tetrachloride gave material of m.p. 167–169°.

Anal. Calcd. for $C_{14}H_{10}O_4F_3Cl$: C, 50.24; H, 3.01; Cl, 10.59. Found: C. 50.33; H, 3.21; Cl, 10.51.

2,2-Dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXVIII).—A mixture of 25.0 g. (0.105 mole) of 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene and 200 ml. of 96% sulfuric acid was stirred vigorously and heated at 65° for 40 min.; then it was poured into an ice–water slurry. The resulting yellow precipitate (15 g., 66%) was collected, washed repeatedly with water, and dried at room temperature (1 mm.). Several recrystallizations from hexane gave white rhombohedra, m.p. 86.0–86.5°; ultraviolet spectrum: $\lambda_{\max}$ 2730 Å. (ϵ 22,400); infrared spectrum: bands at 1548, 1625, 1787, 3030 and 3080 cm.$^{-1}$; dipole moment 5.46 D.

Anal. Calcd. for $C_{10}H_{10}OCl_2$: C, 55.30; H, 4.65; Cl, 32.68. Found: C, 55.26; H, 4.74; Cl, 32.75.

Solutions of bromine and potassium permanganate were decolorized by XXVIII; no precipitate was formed at room temperature with either ethanolic silver nitrate or with sodium iodide in acetone. It gave a red precipitate with 2,4-dinitrophenylhydrazine reagent.

1,1-Difluoro-2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXXI).—A mixture of 1 ml. of triethylamine and 60 g. of 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene was heated in a sealed Pyrex tube at 150–160° for 16 hr. The resulting dark-brown liquid was washed with water and distilled through a 30-cm. Vigreux column. Purified XXXI amounted to 55 g. (93%), n^{25}D 1.5188, d^{25}_{4} 1.300; ultraviolet spectrum: $\lambda_{\max}$ 2180 and 2550 Å. (ϵ 11,900 and 16,500, resp.); infrared spectrum: bands at 1608, 1640 and 3030 cm.$^{-1}$; XXXI decolorized solutions of bromine and potassium permanganate.

Anal. Calcd. for $C_{10}H_{10}F_2Cl_2$: C, 50.32; H, 4.22; Cl, 29.66. Found: C, 50.24; H, 4.19; Cl, 29.70.

2,4-Dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXXII)—Attempts to prepare XXXII from 2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutenone (triethylamine or chloride ion catalysts) were unsuccessful. Compound XXXII was obtained by hydrolysis of 4.2 g. of 1,1-difluoro-2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXXI) with 10 ml. of 97.1% sulfuric acid at 95° for 5 min. The mixture was poured onto ice, and the oil that separated was extracted with methylene chloride. The methylene chloride solution was washed with bicarbonate solution and with water and then dried over calcium chloride. Evaporation of the solvent in a stream of air left a pale-yellow oil, which was dissolved in a minimum of benzene and poured onto a 2 × 10-cm. column packed with silicic acid–Celite. Elution with hexane followed by 50% hexane–benzene resulted in separation of unreacted XXXI and XXXII. Compound XXXII had b.p. 95–100° (3–4 mm.), n^{25}D 1.6053; ultraviolet spectrum: $\lambda_{\max}$ 2840 Å. (ϵ 21,700), shoulder 2900 Å. (ϵ 21,100); infrared spectrum: bands at 1560 , 1610, 1785 and 3030 cm.$^{-1}$. Compound XXXII decolorized solutions of bromine and potassium permanganate but gave no precipitate with either ethanolic silver nitrate or sodium iodide in acetone. For analysis, the ketone was converted to the **2,4-dinitrophenylhydrazone** which was obtained as red needles after three recrystallizations from ethyl acetate; m.p. 204–206°.

Anal. Calcd. for $C_{16}H_{14}O_4N_2Cl_2$: C, 48.38; H, 3.55; N, 14.11; Cl, 17.85. Found: C, 48.54; H, 3.79; N, 14.70; Cl, 18.10.

1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI) with Sodium Iodide in Acetone.—A mixture of 12.4 g. (0.052 mole) of XI, 22.7 g. (0.152 mole) of sodium iodide and 100 ml. of reagent grade acetone was heated under reflux for 8 days. The precipitated sodium chloride (3.0 g., 100%) was removed by filtration and the filtrate poured into water. The organic phase was extracted with methylene chloride and the extract washed with water, potassium iodide solution, and more water. Distillation through a 30-cm. Vigreux column gave 10.8 g. (63%) of pale-yellow monoiodo compound, b.p. 109–112° (1.0–1.4 mm.); ultraviolet spectrum: $\lambda_{\max}$ 2515 A. (ϵ 16,700); infrared spectrum: bands at 1600, 1634 and 3020 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{10}F_2ClI$: C, 36.01; H, 3.02; total silver halide from 11.31 mg., 12.95 mg. Found: C, 36.20; H, 3.20; total silver halide from 11.310 mg., 12.13 mg.

The product decolorized solutions of bromine and potassium permanganate and gave a precipitate of silver halide with ethanolic silver nitrate. It remained pale yellow under nitrogen, but slowly turned violet in air. The structure 1,1-difluoro-2-chloro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene was assigned on the basis of the above information and the proton and fluorine n.m.r. spectra.[15]

1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI) with Ethanolic Potassium Hydroxide Solution.—To a solution of 4.3 g. (0.066 mole) of 87% potassium hydroxide in 50 ml. of absolute ethanol was added 11.9 g. (0.050 mole) of XI, and the resulting mixture was heated 3 hr. under reflux. Potassium chloride (3.1 g., 83%) was separated by filtration and the filtrate poured into water. The mixture was acidified and the organic phase separated with the aid of methylene chloride. The combined methylene chloride extracts were washed with bicarbonate and water, then dried over magnesium sulfate, and distilled. The monoethyl ether amounted to 4.9 g. (41%) of b.p. 87–88.5° (1 mm.). A redistilled sample had b.p. 87.5° (1 mm.), n^{25}D 1.4920; ultraviolet spectrum: $\lambda_{\max}$ 2475 Å.; infrared spectrum: bands at 1608, 1638 and 3030 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{15}OF_2Cl$: C, 57.95; H, 6.08; Cl, 14.25. Found: C, 57.78; H, 6.23; Cl, 14.33.

The product decolorized solutions of bromine and potassium permanganate but gave no precipitates with silver nitrate in ethanol or sodium iodide in acetone. The structure 1,1-difluoro-2-chloro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXX) was assigned on the basis of the above data and the fluorine and proton n.m.r. spectra.[15]

2-Fluoro-1,3-dichloro-5,6,7,8-tetrahydronaphthalene (XXXIII).—A mixture of 30 g. of 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI) and 1 ml. of triethylamine was heated in a heavy-walled Pyrex tube for 24 hr. at 105° and then for 36 hr. at 180°. When the cooled tube was vented, a large volume of hydrogen halide escaped. The black tarry product was dissolved in benzene and washed with water until the washes were neutral. The benzene solution was concentrated to 50 ml. and 250 ml, of hexane added. The resulting precipitate was separated and extracted with three 250-ml. portions of hot hexane. Evaporation of hexane gave 4.0 g. of solid, which, after five recrystallizations from ethanol, afforded white crystals of XXXIII having m.p. 68.1–68.4°; ultraviolet spectrum: λ_{max} 2740, 2800 and 2835 Å. (ϵ 1350, 1270 and 1520, resp.); infrared spectrum: bands at 1565, 1577 and 1600 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_9FCl_2$: C, 54.82; H, 4.14; Cl, 32.27; mol. wt., 203. Found: C, 54.88; H, 4.78; Cl, 33.54; mol. wt. (Rast), 227.

Further repeated extractions of crude reaction product eventually gave in all 10 g. (41%) of product; XXXIII did not decolorize bromine or potassium permanganate solutions and did not react with sodium iodide in acetone or ethanolic silver nitrate.

Similar results were obtained when 1,1-difluoro-2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutene was substituted for XI.

Isopropenylacetylene and Trifluorochloroethylene.—To four heavy-walled Pyrex tubes (19 × 25 × 615 mm.), cooled in Dry Ice, were added 53.2 g. (75 ml., 0.81 mole) of isopropenylacetylene and 110 g. (75 ml., 0.9 mole) of trifluorochloroethylene. The tubes were sealed, heated at 95° for 20 hr., cooled in Dry Ice, vented, and the contents distilled. The low-boiling material was removed at water aspirator pressure, and the residue was separated by distillation through a 30-cm. Vigreux column into seven fractions.

Fraction 1 amounted to 30 g., b.p. 44–49° (35.3–36 mm.), $n^{25}D$ 1.4039. The infrared spectrum had strong acetylenic carbon–hydrogen absorption at 3290 cm.$^{-1}$ and weak carbon–carbon triple-bond absorption at 2100 cm.$^{-1}$. The material was assigned the structure 1,1,2-trifluoro - 2 - chloro - 3 - methyl - 3 - ethynylcyclobutane (XXXIX).

Anal. Calcd. for $C_7H_6F_3Cl$: C, 46.05; H, 3.31; Cl, 19.42. Found: C, 45.91; H, 3.42; Cl, 19.38.

Fractions 4 and 5 amounted to 27.2 g., b.p. 60–65° (32–37 mm.), $n^{25}D$ 1.4288–1.4295, and were assigned the structure 1,1,2-trifluoro-2-chloro-3-isopropenylcyclobutene (XXXVIII) on the basis of proton and fluorine magnetic resonance spectra and infrared absorptions at 1588 and 1635 cm.$^{-1}$.

Anal. Calcd. for $C_7H_6F_3Cl$: C, 46.05; H, 3.31; Cl, 19.42. Found: C, 45.93; H, 3.24; Cl, 19.37.

Fraction 7 amounted to 9.4 g., b.p. 51–53° (1 mm.), $n^{25}D$ 1.4206, and was believed to be 1,1,2-trifluoro-2-chloro-3-methyl-3-(3,3,4-trifluoro-4-chlorocyclobutenyl)-cyclobutane (XL), by analogy with the course of the reaction of vinylacetylene and tetrafluoroethylene.[21]

1,1,2-Trifluoro-2,3-dichloro-3-(cyclohex-1-enyl)-cyclobutane (XLI).—The procedure was similar to that used for the preparation of IV. Trifluorochloroethylene (30 g., 0.258 mole) and 1-(1-chloroethenyl)-cyclohex-1-ene[22] (20.0 g., 0.14 mole) were heated at 125° for 18 hr. Distillation gave starting material (10 g.), b.p. 51–53° (2 mm.), and 10 g. of the pale-yellow adduct XLI, b.p. 91–94° (2 mm.), $n^{25}D$ 1.4737.

Anal. Calcd. for $C_{10}H_{11}F_3Cl_2$: C, 46.35; H, 4.28; Cl, 27.37. Found: C, 46.47; H, 4.35; Cl, 27.17.

The infrared spectrum of XLI showed a single double-bond absorption at 1666 cm.$^{-1}$. There was no maximum in the ultraviolet spectrum above 2200 Å. With ethanolic silver nitrate, XLI formed a precipitate rapidly; however, XLI gave no reaction with sodium iodide in acetone. Microhydrogenation resulted in absorption of one mole-equivalent of hydrogen with apparent hydrogenolysis of the allylic chlorine. The structure XLI was indicated by the fact that dehydrochlorination with potassium hydroxide in *t*-butyl alcohol gave IV, identical in all respects with material prepared from trifluorochloroethylene and 1-ethynylcyclohex-1-ene.

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(21) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

(22) Obtained as a side-reaction product from the preparation of 1-ethynylcyclohex-1-ene by phosphorus oxychloride dehydration of 1-ethynylcyclohexan-1-ol.

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Small-Ring Compounds. XXXII. The Reaction of Allylcarbinylamine-α-^{14}C (3-Butenyl-1-^{14}C-amine) with Nitrous Acid[1,2]

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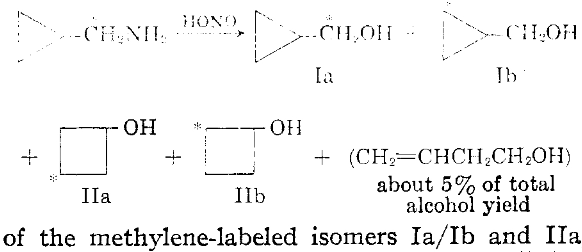
The isotopic analysis of the cyclopropylcarbinol and cyclobutanol formed in the reaction of allylcarbinylamine-α-^{14}C with nitrous acid has indicated that all of the possible methylene-labeled, isotope-position isomers are formed but not quite to the extent expected for statistical equilibrium. The compositions of the alcohols resulting from treatment of cyclopropylcarbinyl-, cyclobutyl- and allylcarbinylamines with nitrous acid have been measured accurately and correlated with the degree of isotope-position rearrangement obtained with ^{14}C-labeled amines. The results are in agreement with the previously postulated interpretation of these reactions as involving rapid but not instantaneous equilibration of unsymmetrical non-classical cations.

Cyclopropylcarbinylamine-α-^{14}C with nitrous acid has been reported to give a mixture of alcohols, with the isomers Ia and Ib being formed to the relative extents of 52 and 48%, respectively, and the isomers IIa and IIb being formed to the relative extents of 28 and 72%, respectively.[3]



The degree of isotope-position rearrangement in this reaction is extraordinarily high, and the ratios of the methylene-labeled isomers Ia/Ib and IIa/IIb approach but do not reach the equilibrium values of $^1/_2$. These results, in conjunction with many other findings regarding carbonium ion-type interconversion reactions of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives,[4] have led

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(2) Presented at the Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June, 1959.

(3) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959). The rearrangement figures used in the present paper are rounded values normalized to 100%.

(4) (a) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951);