Reaction of Tropone with 1,2,3,4-Tetrachlorocyclopentadiene. A Novel Rearrangement Reaction to Fulvenes[1]

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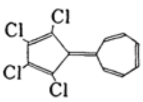
(Received December 20, 1963)

Sesquifulvalene (cycloheptatrienylidenecyclopentadiene),[2] one of the non-alternant hydrocarbons, is an interesting substance, both theoretically and chemically, which has been recently synthesized by Prinzbach and Rosswog;[3] some of its derivatives are also known, such as tetrabenzo-,[4] 1, 2, 3, 4-tetraphenyl-,[5] 1, 2-benzo-3-benzyl-,[6] 1-benzyl-,[3] and 1-(*p*-methoxybenzyl)-sesquifulvalene.[3] Attempts have been also made in this laboratory to synthesize sesquifulvalene, while syntheses of the quinone compounds, sesquifulvalene-1, 4-quinone and 2, 3-benzosesquifulvalene-1, 4-quinone,[7,8] have already been reported.

McBee[9] found that 1, 2, 3, 4-tetrachlorocyclopentadiene[9,10] (I) undergoes condensation with various aromatic aldehydes to form the corresponding fulvene derivatives, while Kitahara and Doi[11] found that tropone (II) undergoes condensation with malononitrile and the cyanoacetic ester to form 8, 8-dicyanoheptafulvene[11,12] and 8-cyano-8-ethoxycarbonylheptafulvene[11,12] respectively.



(III)

Considering these facts, it seemed possible to synthesize 1, 2, 3, 4-tetrachlorosesquifulvalene (III) by the reaction of I and II; examinations were therefore made on this point. A solution of I and II in a large volume of ethanol was allowed to stand at room temperature, and the ultraviolet absorption spectrum[13] of the solution, which gradually turned red, was measured in order to follow the progress of the reaction. The intensity of the absorption maximum of II, near 300 mμ, gradually decreased, and a new maximum appeared at 374 mμ. The ratio of the absorbances at 374 and 300 mμ, taken at definite intervals, gradually increased until the value remained constant at around 1.9 after 40 hr. From this reaction mixture, red prisms (IV), m. p. 116~117°C, were obtained. The analytical values of IV failed to agree with $C_{12}H_6Cl_4$ (III) but unexpectedly agreed with the formula, $C_{14}H_{11}OCl_3$. The infrared spectrum[14] of IV showed absorption bands at 1255 and 1043 cm^{-1} due to aromatic ether bonds, and the NMR spectrum[15] had a triplet at 8.55 τ and a quartet at 5.90 τ corresponding to the protons of an ethoxyl group. Elementary analysis and these spectra suggested that one of the chlorine atoms had been replaced by an ethoxyl group.

When the reaction of I and II in methanol was carried out in a thermostatic bath at 20°C, the absorbancy ratio at 374 and 300 mμ reached a constant value of 3.4 after about 40 hr. From this reaction mixture, two kinds of product were obtained: red prisms (V), m. p. 117~118°C, and reddish orange needles (VI), m. p. 77~78°C. Elementary analyses indicated that both V and VI had the molecular formula $C_{13}H_9OCl_3$. Since the infrared spectrum of V exhibited absorption bands at 1257 and 1026 cm^{-1}, due to aromatic ether bonds, and those of VI exhibited such bands at 1263 and 1025

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[1] Paper read at the Tohoku Local Meeting of the Chemical Society of Japan, Sendai, June 1961.

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[10] A. Roedig and L. Horning, *Chem. Ber.*, **88**, 2003 (1955).

[11] Y. Kitahara and K. Doi, Paper presented at the Tohoku Local Meeting of the Chemical Society of Japan, Akita, October, 1961.

[12] T. Nozoe, T. Mukai, K. Osaka and N. Shishido, This Bulletin, **34**, 1384 (1961).

[13] Ultraviolet spectra were measured with a Hitachi photoelectric spectrometer, model EPU-2.

[14] The infrared spectra were measured with a Perkin-Elmer model 21 spectrophotometer, provided with a NaCl prism.

[15] The NMR spectra were run by the Research Institute of Mitsubishi Chemical Industry Co. on a Varian A-60 instrument in a CS_2 solution. Tetramethylsilane was used as the internal standard.

cm^{-1}, and since the NMR spectrum showed absorptions at $6.13\,\tau$ (singlet) for V and 6.19 τ (singlet) for VI, corresponding to the methoxyl protons, it appeared that a methoxyl group had been introduced by this reaction.

The reaction between II and 1, 2, 3, 4-tetrabromocyclopentadiene[16] (VII) followed an entirely analogous course; red plates (VIII), m. p. 128~129°C, and red prisms (IX), m. p. 90~91°C, were obtaind.

From the foregoing experimental evidence and the presence of an absorption maximum in the comparatively long wavelength region at $374\,m\mu$ in the ultraviolet spectra of the products (V, VI, VIII, IX), V and VI were assumed to be isomers formed by the replacement of one of the four chlorine atoms in III by a methoxyl group.

The examination of the infrared spectrum in the C–H out-of-plane region indicated the presence of an absorption corresponding to an *o*-disubstituted benzene at 749 cm^{-1} in V and that of a *p*-disubstituted benzene at 818 cm^{-1} in VI. The sharp absorption at 852 cm^{-1} in V and at 861 cm^{-1} in VI is considered to be due to the C–H of a tri-substituted double bond.

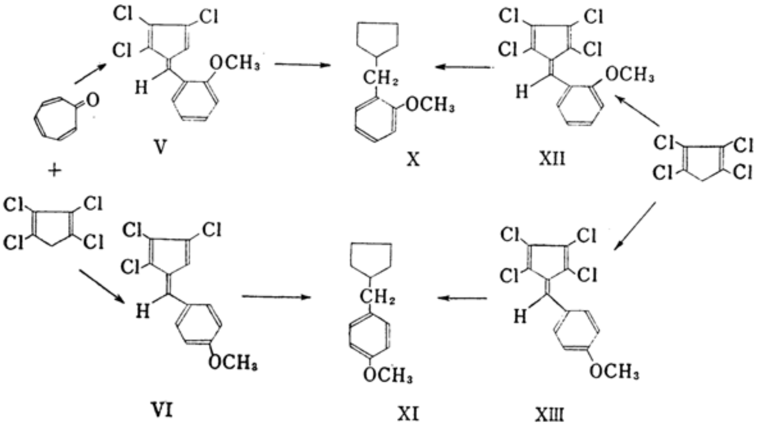
The catalytic reduction of V in methanol, in the presence of sodium acetate and using palladium-carbon as a catalyst, resulted in the absoption of 6 molar equivalents of hydrogen, and a colorless oil (X) was obtained. A similar reduction of VI also afforded a colorless oil (XI).

The infrared spectra of the reduction products, X and XI, indicated the absorption of an aromatic ether bond at 1247 and 1034 cm^{-1} in X and at 1253 and 1039 cm^{-1} in XI, absorptions which are practically unchanged from those of V and VI. If the methoxyl group had been present in the five-membered ring, the absorption of the ether bond in the reduction products (X and XI) would have shifted to about 1150~1060 cm^{-1}.[17] The absorption of the C–H out-of-plane vibration in the *o*-disubstituted benzene still apears at 752 cm^{-1} in X, and that of the *p*-disubstituted benzene, at 833 cm^{-1} in XI.

The ultraviolet absorption spectra of X and XI are very similar to that of anisole.[18]

From these considerations, it may be concluded that the structure of V and VI is not the anticipated sesquifulvalene skeleton, like III, but that the products are probably trichloro-6-(*o*-methoxyphenyl)fulvene and trichloro-6-(*p*-methoxyphenyl)fulvene for V and VI respectively.

In order to prove these structures, the condensation of I with *o*- and *p*-anisaldehyde respectively was carried out in ethanol. When the products thus obtained, 1, 2, 3, 4-tetrachloro-6-(*o*-methoxyphenyl)fulvene (XII), m. p. 166°C, and 1, 2, 3, 4-tetrachloro-6-(*p*-methoxyphenyl)-fulvene[9] (XIII), m. p. 123°C, were submitted to catalytic reduction over palladium-carbon in methanol, in the presence of sodium acetate; 7 molar equivalents of hydrogen were absorbed in each case to give two colorless oils (X′ and XI′). The ultraviolet and infrared spectra of X′ and XI′ were identical in all respects with those of X and XI.



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[16] R. Riemschneider, G. Englemenn and K. Rosswitz, *Z. Naturforsch.*, **116**, 172 (1956).

[17] L. F. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen Co., London (1958), p. 114.

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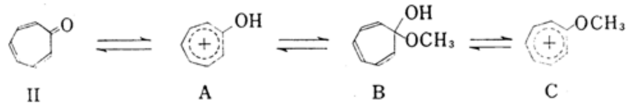
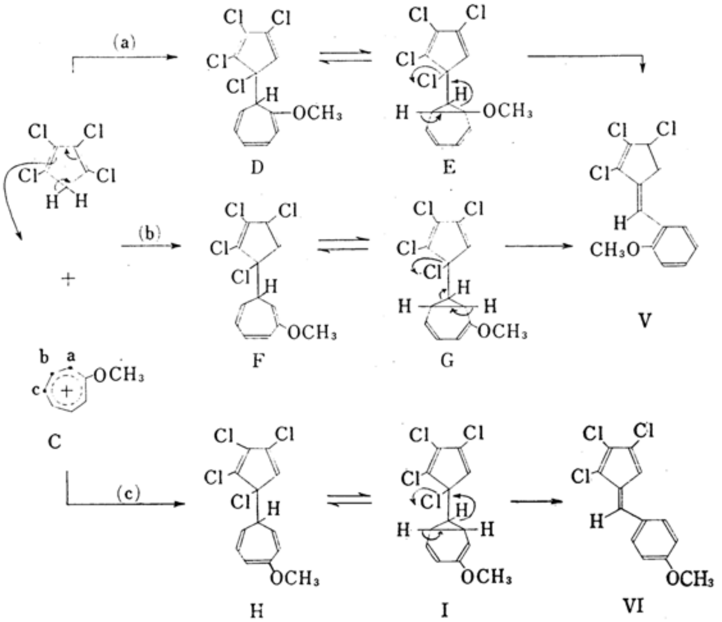
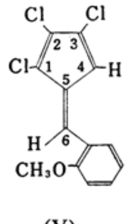




The results have afforded evidence of the structures assigned to V and VI, with the exception of the positions of three chlorine atoms. From the mechanism of this rearrangement reaction, it may be expected that the three chlorine atoms will be located at the 1-, 2- and 3-positions.

An examination of the physicochemical properties of tropone (II) has let us to consider it to have an ionic structure because of the contribution of six π electrons resulting from the polarization of the carbonyl group.[19,20] Consequently, an equilibrium exists, in methanolic solution of tropone, among the hydroxytropylium cation (A), hemiketal (B), and the methoxytropylium cation (C), as is indicated below, and the reaction may be considered to proceed via C. The attack of I on C may be possible at any of the three positions, a, b and c. If the attack occurs at a *o*-methoxy derivatives (V) will form from a norcaradiene type intermediate (E), and then be rearranged. If the reaction takes the b course, the rearrangement of the norcaradiene intermediate (G) will form V by the liberation of the proton adjacent to the methoxyl group. If the reaction follows the c course, the rearrangement of the intermediate (I) may be considered to form the VI by the liberation of the γ-proton of the methoxyl group. From such a rearrangement mechanism, the three chlorine atoms should be in the 1-, 2- and 3-positions in both V and VI.

The structures of V and VI were further confirmed from their NMR spectra. V had signals at 6.13 τ (singlet, OCH_3), 3.52 τ (doublet, $J=1$ c. p. s., 4-H), 2.37τ (partially resolved doublet, 6-H), and 3.3~2.5 τ (multiplet, four protons of the benzene ring). VI had signals



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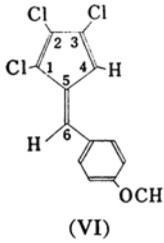

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[20] W. von E. Doering and F. L. Detert, ibid., 73, 876 (1951).

[21] The 4- and 6-protons was assigned by means of a comparison of their spectra with that of 1, 2, 3, 4-tetrachloro-6-(*p*-methoxyphenyl)fulvene (XIII). XIII lacked a signal in the 3.5 τ region, but the peaks due to the methoxyl- (6.18 τ, singlet) and A_2B_2-type absorptions (3.14 τ, doublet, $J=9$ c. p. s., 2.44 τ, doublet, $J=9$ c. p. s.) and the 6-proton (2.52 τ, singlet) were present. Therefore, the more shielded signals in V and VI (3.52 τ, 3.43 τ) can be assigned to a 4-proton, while the more deshielded signals (2.37 τ, 2.78 τ) can be assigned to a 6-proton.

at 6.19 τ (singlet, OCH_3), 3.43 τ (doublet, $J=1$ c. p. s., 4-H), 2.78 τ (partially resolved doublet, 6-H)[21], and at 3.14 τ and 2.55 τ ($J=9$ c. p. s.).

The doublet splitting pattern of the 4- and 6-protons ($J=1$ c. p. s.) can be interpreted only in the case of structures V and VI.[22]

The reaction of 1, 2, 3, 4, 5-pentabromocyclopentadiene (XIV) and tropylium bromide (XV) produced red needles, m. p. 79°C, which were identical with 1, 2, 3, 4-tetrabromo-6-phenylfulvene (XVI), which was obtained by the reaction, under McBee's conditions,[9] of 1, 2, 3, 4-tetrabromocylopentadiene (VII) and benzaldehyde. Since the reaction of XIV and XV, neither of which contains a methoxyl group, results in rearrangement, it seems certain that the liberation of a proton acts as the driving force of this rearrangement reaction.

The foregoing experimental facts have shown that the reaction of I and II in methanol results in an entirely new type of rearrangement reaction in which the methoxyl group enters the seven-membered ring (a six-membered ring after the rearrangement) and in which a chlorine atom in the five-membered ring is liberated.

Experimental

The Reaction of Tropone (II) 1, 2, 3, 4-Tetrachlorocyclopentadiene (I).—*Reaction in Ethanol.*—A solution of tropone (2.12 g.) and 1, 2, 3, 4-tetrachlorocyclopentadiene (4.08 g.) in ethanol (250 ml.) was allowed to stand at room temperature; the ultraviolet absorption spectrum of the reaction mixture was measured at definite intervals. The ratio of absorbances at 374 and 300 mμ became almost constant at 1.9 after about 40 hr.

The reaction mixture was then poured into ice water, and the red oil which separated was washed with water and dried over phosphorus pentoxide. This oil when treated with cyclohexane formed red crystals (0.6 g.), m. p. 110~115°C. Recrystallization from methanol gave IV as red prisms, m. p. 116~117°C.

Found: C, 55.42, 56.00; H, 3.65, 3.80. Calcd. for $C_{14}H_{11}OCl_3$: C, 55.74; H, 3.68%.

UV λ_{max}^{MeOH} mμ (log ε): 248 (3.80), 323 (4.11), 374 (4.27).

Reaction in Methanol.—A solution of tropone (10.0 g.) and 1, 2, 3, 4-tetrachlorocyclopentadiene (19.2 g.) in methanol (1200 ml.) was allowed to stand in a thermostatic bath at 20°C; the ultraviolet spectrum of the reaction mixture was measured at definite intervals. The ratio of absorbances at 374 and 300 mμ became constant at ca. 3.4 after about 45 hr. The methanol solution was evaporated under reduced pressure to one-half the original volume, and then poured into 1000 ml. of ice water and extracted thoroughly with petroleum ether (b. p. 36°C). The petroleum ether layer was washed with water, dried over magnesium sulfate, and evaporated. The oily residue crytasllized on the addition of a small amount of methanol; recrystallization from methanol gave 3.0 g. of crude V, melting at 116~118°C.

The recrystallization mother liquor of V was chromatographed over an alumina column (45×300 mm.). Elution with petroleum ether (600 ml.) gave 2.3 g. of crude V, m. p. 114~116°C, further elution with the same solvent (450 ml.) afforded 2.95 g. of crude VI, m. p. 72~75°C.

The recrystallization of crude V from methanol gave red prisms with a m. p. of 117~118°C.

Found: C, 54.41; H, 2.95. Calcd. for $C_{13}H_9OCl_3$: C, 54.29; H, 3.16%.

UV λ_{max}^{MeOH} mμ (log ε): 248 (3.84), 320 (4.11), 373 (4.27).

The Recrystallization of crude VI from ethanol afforded reddish orange needles, m. p. 77~78°C.

Found: C, 54.33; H, 3.16. Calcd. for $C_{13}H_9OCl_3$: C, 54.29; H, 3.16%.

UV λ_{max}^{MeOH} mμ (log ε): 250 (4.02), 374 (4.55).

The Reduction of 1, 2, 3-Trichloro-6-(*o*-methoxyphenyl)fulvene (V).—A solution of V (2.9 g.) in 100 ml. of methanol, with 5% palladium-carbon (0.1 g.) and anhydrous sodium acetate (2.5 g.), was shaken with hydrogen at an ordinary temperature and pressure; 6 molar equivalents of hydrogen were absorbed in about 1 hr. The solution was then filtered and evaporated. After the addition of water, the residue was extracted with petroleum ether, and the extract was dried over magnesium sulfate and then evaporated. The residual oil was submitted to distillation under reduced pressure gave 1.1 g. of a colorless oil, X.

Found: C, 81.49; H, 9.36. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54%.

UV λ_{max}^{MeOH} mμ (log ε): 220 (3.86), 272 (3.32).

IR: 1609, 1592, 1247, 1034, 752 cm^{-1}.

The Reduction of 1, 2, 3-Trichloro-6-(*p*-methoxyphenyl)fulvene (VI).—The catalytic reduction of VI (2.9 g.) in methanol, under the same conditions as for V, afforded 1.2 g. of a colorless oil, XI.

Found: C, 82.09; H, 9.34. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54%.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.08), 278 (3.16).

IR: 1618, 1590, 1520, 1523, 1039, 833 cm^{-1}.

1, 2, 3, 4-Tetrachloro-6-(*p*-methoxyphenyl)fulvene (XIII).—Synthesis according to the method of McBee yielded XIII as reddish orange needles, m. p. 122~123°C.

UV λ_{max}^{MeOH} mμ (log ε): 255 (3.98), 385 (4.38).

1, 2, 3, 4-Tetrachloro-6-(*o*-methoxyphenyl)fulvene (XII).—A solution of 1, 2, 3, 4-tetrachlorocyclopentadiene (4.1 g.) and *o*-anisaldehyde (2.72 g.) in ethanol (10 ml.) was refluxed on a water bath for 2~3 hr., and then cooled. The crystals which separated were collected by filtration. Recrystallization from ethanol gave red needles m. p. 165~166°C.

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[22] The long range 1, 3-spin-spin coupling of a vinylic proton with an allylic proton is a well-recognized phenomenon. S. Alexander, *J. Chem. Phys.*, **28**, 355 (1958); **32**, 1700 (1960); R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961); E. B. Whipple, J. H. Goldstein and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960); E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961); A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); A. A. Bothner-By, C. Naar-Colin and H. Gunther, ibid., **84**, 2748 (1962).

Found: C, 58.55; H, 4.00. Calcd. for $C_{13}H_8OCl_4$: C, 58.08; H, 3.73%.

UV λ_{max}^{MeOH} mμ (log ε): 255 (3.84), 330 (4.06), 374 (4.19).

The Reduction of XII and XIII.—The catalytic reduction of XII and XIII under the same conditions as in the reduction of V and VI yielded two colorless oils, X′ and XI′. The ultraviolet and the infrared absorption spectra of X′ and XI′ were identical with those of X and XI respectively, indicating the identity of X and X′, and XI and XI′, respectively (*o*- and *p*-methoxybenzylcyclopentanes).

1, 2, 3, 4, 5-Pentabromocyclopentadiene (XIV).—A mixture of 1,2,3,4,5,5-hexabromocyclopentadiene (21.5 g.) in ethanol was hydrogenated. One molar equivalent (900 ml.) of hydrogen was absorbed. Ether was added to the reaction mixture to dissolve the crystal which had separated, and the solution was then filtered and evaporated. The crystalline residue (14.9 g.) after recrystallization from petroleum ether afforded XIV as colorless needles (8.55 g.), m. p. 104°C.

Found: C, 13.17; H, 0.36. Calcd. for C_5HBr_5: C, 13.04; H, 0.22%.

1,2,3,4-Tetrabromo-6-phenylfulvene (XVI). — a) A suspension of tropylium bromide (0.34 g.) and 1, 2, 3, 4, 5-pentabromocyclopentadiene (0.92 g.) in carbon tetrachloride (3 ml.) was refluxed on a water bath for 2 hr.; a vigorous evolution of hydrogen bromide gas was observed during the reaction. The carbon tetrachloride was removed under reduced pressure, and the residual oil was heated for 4 hr. at 80°C to complete the evolution of hydrogen bromide. The oil was dissolved in a small amount of benzene, treated with activated charcoal, and then purified by alumina chromatography, using petroleum ether as an eluant. The crystals so obtained were recrystallized from ethanol to afford reddish-brown, silky needles XVI, m. p. 78∼79°C.

Found: C, 30.73; H, 1.44. Calcd. for $C_{12}H_{16}Br_4$: C, 30.67; H, 1.29%.

UV λ_{max}^{MeOH} mμ (log ε): 280 (3.75), 343 (4.24).

b) A solution of 1,2,3,4-tetrabromocyclopentadiene (0.765 g.) and benzaldehyde (0.215 g.) in ethanol (2 ml.) was refluxed on a water bath for 10 hr. The solvent was then evaporated, and the residue was recrystallized from ethanol to give 0.42 g. of XVI, m. p. 78∼79°C, which showed no depression on admixture with XVI obtained as in a).

Reaction of Tropone (II) and 1, 2, 3, 4-Tetrabromocyclopentadiene (IV).—A solution of tropone (0.65 g.) and 1, 2, 3, 4-tetrabromocyclopentadiene (2.30 g.) in methanol (150 ml.) was allowed to stand at room temperature for 6 hr. The solution was then concentrated under reduced pressure, and the crystals which formed were filtered off. Recrystallization from ethanol afforded VIII as red plates (0.75 g.), m. p. 128∼129°C.

Found: C, 37.57; H, 2.34. Calcd. for $C_{13}H_9OBr_3$: C, 37.09; H, 2.13%.

UV λ_{max}^{MeOH} mμ (log ε): 250 (3.79), 330 (sh.), 375 (4.30).

The evaporation of the mother liquor from VIII, and the chromatography over alumina of the residue in petroleum ether, gave 0.83 g. of crude IX m. p. 85∼87°C. Recrystallization from methanol afforded red prisms, m. p. 90∼91°C.

Found: C, 37.51; H, 2.34. Calcd. for $C_{13}H_9OBr_3$: C, 37.09; H, 2.13%.

UV λ_{max}^{MeOH} mμ (log ε): 250 (3.94), 380 (4.54).

The authors are indebted to the Research Institute of the Mitsubishi Chemical Co., Ltd., for the measurement of NMR spectra, and to Miss Yoko Endo and Miss Yukiko Endo of this Institute for their elementary analyses. The authors are also grateful to the Sankyo Co., Ltd., for its financial support of the present research.

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