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A New Synthesis of Tropolone

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Tropolone has been prepared in three steps from cyclopentadiene and tetrafluoroethylene in an over-all yield of 20%. Vapor phase addition of tetrafluoroethylene to cyclopentadiene at 475° gave a mixture of a cyclobutane, 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene (I) and a Diels–Alder adduct, 5,5,6,6-tetrafluorobicyclo[2.2.1]hept-2-ene (II). Pyrolysis at 700–750° converted this mixture to 5,5,6,6-tetrafluoro-1,3-cycloheptadiene (III) and 6,6,7,7-tetrafluoro-1,4-cycloheptadiene (IV). Tropolone was formed by hydrolysis of the tetrafluorocycloheptadienes with potassium acetate in aqueous acetic acid.

A number of ingenious routes to tropolone have been reported,[1] all of which involve multistep syntheses in low over-all yields. The purpose of this paper is to describe a new three-step synthesis which has given yields of tropolone as high as 20%. As shown in Fig. 1, the key to this synthesis was the discovery that 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene (I) and 5,5,6,6-tetrafluorobicyclo[2.2.1]hept-2-ene (II) are rearranged at high temperatures to (III) 5,5,6,6-tetrafluoro-1,3-cycloheptadiene and 6,6,7,7-tetrafluoro-1,4-cycloheptadiene (IV). Both cycloheptadienes, upon hydrolysis, give tropolone.

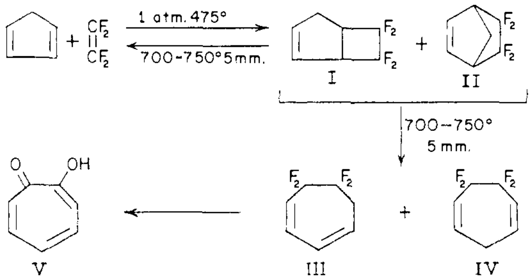

Fig. 1.

The cycloalkylation of cyclopentadiene with tetrafluoroethylene under pressure to form 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene (I) has been reported earlier.[2] Reëxamination of the reaction has revealed that a Diels–Alder adduct, 5,5,6,6-tetrafluorobicyclo[2.2.1]hept-2-ene (II), is also formed in an amount approximately half that of the cyclobutane I and that combined conversion to I and II is about 30%. It has now also been found that the reaction proceeds rapidly at atmospheric pressure when high temperatures are used.[3] Passage of vapors of cyclopentadiene and tetrafluoroethylene at atmospheric pressure through a tube heated to 475° has given combined yields of I and II as high as 70%. The conversion in a single pass calculated by compensating for unused cyclopentadiene amounted to about 10 to 15%.

Thermal rearrangement of the cyclopentadiene–tetrafluoroethylene adducts to tetrafluorocycloheptadienes was accomplished by pyrolysis of the *mixture* of I and II at 700–750° under reduced pressure (less than 5 mm.). A brief study of the temperature dependence of this reaction was made and the results are shown in Table I. Yields and conversions reported for pyrolysis of the mixture of I and II are based arbitrarily on the cyclobutane I in the starting mixture.

TABLE I

PYROLYSIS OF BICYCLOHEPTENES I AND II[d]

Reactor was $^3/_8''$ nominal nickel pipe bent to form a U-tube and immersed in a salt-bath at the indicated temperature. The charge at each temperature was 42 g. of fluorocarbon mixture vaporized in 52–54 min. at 1–2 mm. Gases passing from the reactor were condensed in liquid nitrogen traps. The traps were allowed to warm to room temperature and the remaining liquid was analyzed by gas chromatography.

	I	II	III	IV	Unidentified liquids	Solids, gases and mechanical losses
Compn. of feed,[a] g.	28	13	0	0	1	..
Compn. of prod.,[a] g., at indicated temp.						
645°	22	13	1	1	3	2
700°	11	16	3	4	6	2
750°	4	13	7	6	7	5
830°	1	3	6	2	14	14
% I converted to indicated isomer at indicated temp.						
645°	−21[c]	0	4	4	..	..
700°	−61	11	11	14	..	..
750°	−86	0	25	21	..	..
830°	−96	..	21	7	..	..
Yield of indicated isomer[b] at indicated temp., %						
645°	..	0	17	17	..	..
700°	..	18	18	24	..	..
750°	..	0	29	25	..	..
830°	..	..	22	7	..	..

[a] Based on gas chromatographic analysis. [b] Based on 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene (I). [c] % I destroyed. [d] For formulas see Fig. 1.

The tetrafluorocycloheptadienes III and IV are formed mainly from the cyclobutane I. This was shown by pyrolysis of I at 700° to give a mixture of fluorocarbons composed of about half III and IV. The remainder was unchanged cyclobutane containing some Diels–Alder adduct. Tetrafluoroethylene also was formed, probably by dissociation of the cyclobutane. At the same temperature (700°) the Diels–Alder adduct II passed through the reactor unchanged. At 745° it underwent rearrangement to the tetrafluorocycloheptadienes in 25% yield and 10% conversion.

Best evidence for the structures of the isomeric bicycloheptenes I and II and cycloheptadienes III and IV has been obtained through nuclear magnetic resonance studies. Non-equivalent fluorine atoms

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(1) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955); E. E. van Tamelen and C. T. Hildahl, THIS JOURNAL, **78**, 4405 (1956).

(2) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *ibid.*, **71**, 490 (1949).

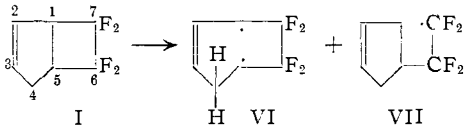
(3) We are indebted to Dr. D. C. England of This Laboratory who first demonstrated the feasibility of these conditions.

bonded to a common ring carbon atom give rise to two spin–spin doublets.[4] As shown in Fig. 2, the fluorine magnetic resonance spectrum of the cyclobutane I exhibits six lines. The lines at +1212, +1031, +606 and +392 c.p.s. arise from the mutual spin–spin interaction of the two non-equivalent fluorine atoms of one CF_2 group. The lines at +914 and +878 c.p.s. are the strong components of the two spin–spin doublets belonging to the other CF_2 group. The failure to detect the weak components of these spin–spin doublets is not unexpected, since Phillips[4] has shown that the weak components may be too small to be detected if the chemical shift between non-equivalent fluorine atoms is less than 50 c.p.s. For the Diels–Alder adduct II, although the C_5- and C_6-positions are equivalent, the *exo* and *endo* fluorines are non-equivalent and give rise to spin–spin interactions. As shown in Fig. 2, only the strong components of the spin–spin doublets are observed.

The fluorine spectrum of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene (III) consists of two major peaks separated by a chemical shift. The singlet at +1363 c.p.s. arises from the two equivalent fluorine atoms at C_5, and the triplet at +1033 c.p.s. from the two equivalent fluorine atoms at C_6 which are split by spin–spin interaction with the adjacent CH_2 group. The four fluorine atoms of 6,6,7,7-tetrafluoro-1,4-cycloheptadiene (IV) are essentially equivalent and its fluorine magnetic resonance spectrum consists of a single resonance at +1425 c.p.s. The proton resonance pattern for IV shows vinyl CH at +41 c.p.s. and saturated CH at −75 c.p.s. in the ratio 4:2. The proton spectrum of III is similar to that of IV except that the resonance of the saturated CH is split into a triplet by the two fluorine atoms at C_6.

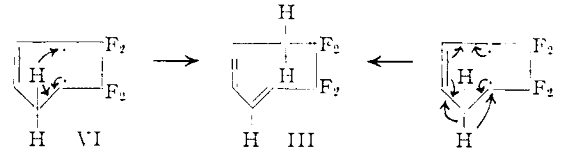
The structures of the tetrafluorocycloheptadienes III and IV, then, are based on nuclear magnetic resonance spectra and on hydrolysis to tropolone as described subsequently. In addition, the isomer III was found to have a conjugated diene absorption in the ultraviolet [λ_{max} 240 mμ (ϵ 9460)], and isomer IV underwent quantitative hydrogenation with absorption of two moles of hydrogen per mole of sample. Further, the infrared absorption spectra of the compounds are in complete agreement with these assignments.

It appears reasonable to assume that the first step in the rearrangement of the cyclobutane I is cleavage of the allyl bonds joining the 1,5- and 1,7-carbon atoms.



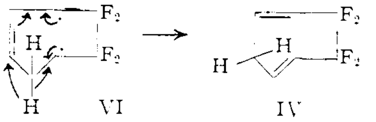
I VI VII

The intermediate VII could cleave to cyclopentadiene and tetrafluoroethylene, which would account for the formation of these products in the pyrolysis mixture, and it also could rearrange to the Diels–Alder adduct. It appears probable that VI undergoes a hydrogen shift to give the tetrafluorocycloheptadienes III and IV. The conjugated cycloheptadiene III could be formed either by a transannular hydrogen shift or by a 1,2-hydrogen shift.



VI III

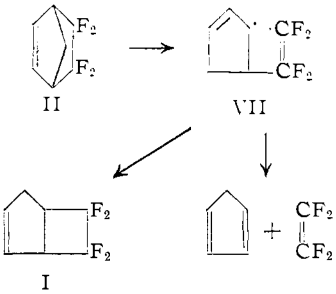
Formation of the non-conjugated tetrafluorocycloheptadiene (IV) could occur by a 1,2-hydrogen shift in a direction opposite to that pictured above.



VI IV

It is conceivable that rearrangement is a concerted reaction in which a hydrogen shift and carbon–carbon bond cleavage occur simultaneously.

Scission of an allylic bond is also proposed for rearrangement of the Diels–Alder adduct II to give VII which is capable of condensing to the cyclobutane I or dissociating to cyclopentadiene and tetrafluoroethylene. It is assumed that at high temperatures the Diels–Alder adduct is converted to the cyclobutane which then rearranges to a seven-membered ring.



II VII I

Tropolone was obtained in 70% yield by hydrolysis of the tetrafluorocycloheptadienes III and IV with potassium acetate dissolved in acetic acid containing a small amount of water. Aqueous

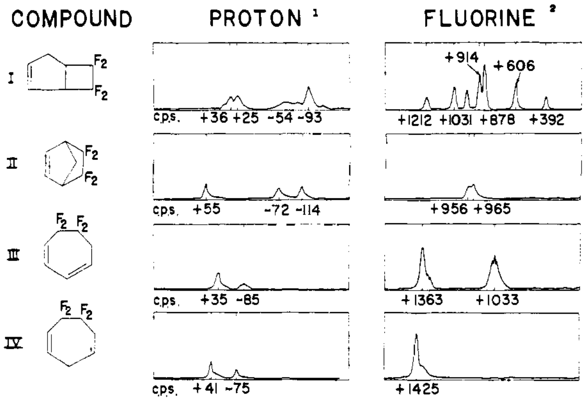


Fig. 2.—Nuclear magnetic resonance spectra of $C_7H_6F_4$ isomers; frequency: 40 Mc. [1] Water used as reference compound for I and II; toluene as reference compound for III and IV. [2] Reference compound: octafluorocyclobutane. The extraneous peak at +960 c.p.s. in the fluorine spectrum of I is due to the Diels–Alder adduct II.

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[4] W. D. Phillips, *J. Chem. Phys.*, **25**, 949–955 (1956).

alkali also converted III and IV to tropolone, but in slightly lower yields. In general the pyrolysis product from the second step of the synthesis was used directly without separation of the isomeric tetrafluorocycloheptadienes. The mechanism of this hydrolysis is under investigation.

Experimental

Preparation of 6,6,7,7-Tetrafluorobicyclo[3.2.0]hept-2-ene (I) and 5,5,6,6-Tetrafluorobicyclo[2.2.1]hept-2-ene (II).[5]—The reactor was a 40-mm. Pyrex glass tube 75 cm. long that contained 25 ml. of sodium fluoride pellets and 25 ml. of phenothiazine powder as a loose layer[6] at the bottom or exit end. Indentations near the middle of the tube supported the packing of 6 by 6 mm. Pyrex glass rings (400 ml.) which was 35 cm. in depth. Five thermocouple junctions were placed in a well in this packing to indicate the temperature profile during reaction. The top of a reflux condenser was attached to the top of the reactor. The bottom of the reflux condenser was attached to a 3-neck, 5-l. flask, which served as a vaporizer. This flask was fitted with a thermometer and a coarse sintered glass bubbler. The exit end of the reactor was attached to a series of traps cooled with a solid carbon dioxide–acetone mixture. The reactor was heated by a copper-lined electric furnace 18 in. long. Appropriate connections were made to allow the system to be flushed with nitrogen and to allow both nitrogen and tetrafluoroethylene to be passed through the bubbler.

To the vaporizer was added 3.5 l. of dicyclopentadiene and then the entire system was flushed with nitrogen and the reactor was heated to 450°. The dicyclopentadiene in the vaporizer flask was then heated to 150° and nitrogen and tetrafluoroethylene were passed through the bubbler, each at a rate of about 3 moles/hr. Under these conditions the vapor leaving the vaporizer was approximately a 1:1:1 molar mixture of nitrogen–cyclopentadiene–tetrafluoroethylene. Entrained dicyclopentadiene was removed by the reflux condenser. Initially the temperature inside the reactor increased, but after the first few minutes it was necessary to increase the furnace temperature to maintain the reactor at 470–480°. Products were condensed in the cold traps and uncondensed gases were vented.

In a typical experiment in which the maximum temperature was 470°, 1657 g. of liquid products was formed in 7 hours. Distillation gave 1061 g. of cyclopentadiene, 21 g. of an intermediate fraction, b.p. 25–75° (100 mm.), 391 g. of isomers I and II (12.7% conversion, 70% yield based on cyclopentadiene), b.p. 65–75° (100 mm.), and 61 g. of high-boiling compounds and residue.

Separation of 6,6,7,7-Tetrafluorobicyclo[3.2.0]hept-2-ene (I) and 5,5,6,6-Tetrafluorobicyclo[2.2.1]hept-2-ene (II).—A 2-kg. sample of a mixture of I and II, obtained by the reaction of cyclopentadiene with tetrafluoroethylene under pressure,[2] was distilled through a Podbielniak column (48 in. by 25 mm., Hyper-cal). The main fractions were 800 g. of 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene (I), b.p. 122–123.5°, and 400 g. of 5,5,6,6-tetrafluorobicyclo-[2.2.1]hept-2-ene (II), b.p. 128–130°.

Gas chromatography indicated that a center cut of the fraction boiling at 123°, n^{25}D 1.3845, was at least 90% of the cyclobutane I. A small amount of the Diels–Alder adduct II also was present. The infrared spectrum of I showed vinyl hydrogen absorption at 3120 cm.$^{-1}$, saturated CH absorption at 2900 and 2980 cm.$^{-1}$, C=C absorption at 1628 cm.$^{-1}$ and strong bands in the range of 1000 to 1250 cm.$^{-1}$ for CF absorption.

Gas chromatography of a center cut of the fraction boiling at 128–130°, m.p. 70–80°, indicated this cut to contain 99% of the Diels–Alder adduct II. The infrared spectrum of II, measured in carbon tetrachloride, showed weak bands for C=C at 1670 cm.$^{-1}$, for vinyl hydrogen at 3080 cm.$^{-1}$, saturated CH absorption at 2900, 2970 and 3000 cm.$^{-1}$, and strong bands for CF absorption in the range of 1000 to 1250 cm.$^{-1}$.

Anal. Calcd. for $C_7H_6F_4$: C, 50.61; H, 3.64. Found: C, 49.98, 49.88; H, 4.07, 3.95.

The mixture of I and II obtained by vapor phase reaction of cyclopentadiene and tetrafluoroethylene was analyzed by gas chromatography as described above. For a typical gas chromatographic analysis the retention times of isomers I through IV were, respectively, 7.55, 8.4, 16.05 and 25.85 min. Throughout this work gas chromatographic analyses were determined in a 78.7 in. (2 m.) by 0.25 in. i.d. column with di-*n*-decyl phthalate on 30–60 mesh Fisher Columpak maintained at 100°. Helium at 100 ml./min. was used as the carrier gas. This procedure indicated a composition of 58% I, 38% II, 0.2% III, 0.2% IV, with the remainder being cyclopentadiene, dicyclopentadiene and eight unidentified components. This product was employed without further purification as the starting material for the preparation of the tetrafluorocycloheptadienes.

Pyrolysis of 6,6,7,7-Tetrafluorobicyclo[3.2.0]hept-2-ene (I).[7]—The cyclobutane I fraction that was at least 90% pure was pyrolyzed in a Vycor glass tube packed with quartz rings and heated to 700°. During the pyrolysis the pressure was maintained at 2–5 mm. The product was condensed in a liquid nitrogen trap containing 10 g. of potassium carbonate. From 658 g. of I there was obtained 382 g. of fluorocarbons, b.p. 40–50° (20–23 mm.), and approximately 13 liters of a gas. The gas was shown by mass spectroscopy to be mainly tetrafluoroethylene (68%) and trifluoromethane (19%). N.m.r. spectra indicated that about half of the pyrolysis product was tetrafluorocycloheptadienes III and IV and half unchanged cyclobutane containing a small amount of the Diels–Alder adduct II.

Pyrolysis of the Mixture of Tetrafluorobicycloheptenes I and II.—A brief study was made of the effect of temperature upon the pyrolysis of I and II to tetrafluorocycloheptadienes. Pyrolyses were carried out in a $^3/_8$-inch nominal nickel pipe which was bent to form a U and immersed in a salt-bath. A mixture of I and II obtained by vapor phase reaction of tetrafluoroethylene and cyclopentadiene was pyrolyzed in the nickel tube as shown in Table I. The highest yield (54% at 46% conversion) of the tetrafluorocycloheptadienes was obtained at 750°.

Preparation of tetrafluorocycloheptadienes for the hydrolysis study involved pyrolysis of the mixture of I and II using a 1-in. nominal unpacked nickel pipe 73 cm. long heated in a furnace 18 in. long. Addition of I and II to the reactor was made by vaporization from a 1-l. round-bottom flask heated to 30° and attached to the top of the reactor. During the pyrolysis the pressure at the top of the reactor was less than 4 mm. Vapors leaving the bottom of the reactor were condensed in liquid nitrogen traps. From a mixture of 591 g. of I, 473 g. of II and 33 g. of unidentified compounds pyrolyzed at 740° over a period of 8 hours there was obtained a product composed of 175 g. of the conjugated tetrafluorocycloheptadiene III, 115 g. of the unconjugated tetrafluorocycloheptadiene IV, 129 g. of the cyclobutane I, 345 g. of the Diels–Alder adduct II and 187 g. of unidentified liquids. Gases, carbonaceous solids and mechanical losses amounted to 146 g. The yield of tetrafluorocycloheptadienes, based on the cyclobutane I, was 63% (49% conversion). This crude pyrolysis product could be hydrolyzed without further purification, or preferably it could be purified by steam distillation or distillation at reduced pressure.

5,5,6,6-Tetrafluoro-1,3-cycloheptadiene (III).—An attempt was made to separate the pyrolysis product into its components by precision distillation. Fractions of gradually increasing boiling points were collected at 60.5–67° (50 mm.) containing the conjugated cycloheptadiene III and at 75–78° (50 mm.) containing the unconjugated cycloheptadiene IV.

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(5) This reaction should be carried out in a well ventilated area. The use of a barricade is recommended, although there has been no indication of an explosion hazard in many hours of operation.

(6) This mixture of an acid acceptor for hydrogen fluoride and a polymerization inhibitor appeared to have some desirable effect in diminishing the formation of a troublesome white hydrocarbon polymer containing approximately 7% fluorine. This polymer formed throughout the product recovery system, particularly in any constriction in cold traps or exit lines. Polymer as formed had some solubility in carbon tetrachloride. Complete removal of the polymer from Pyrex glass apparatus could be effected by air oxidation at 540° or by oxidation of small quantities with refluxing nitric acid (CAUTION—vigorous reaction). Formation of this polymer also was retarded by keeping the maximum temperature in the vapor phase reactor below 480° and by the use of dicyclopentadiene low in peroxide content.

(7) J. J. Drysdale, U. S. Patent 2,819,320, January 7, 1958.

A middle cut of the fraction assigned the structure III was purified by gas chromatography to obtain about 0.5 g. of material that contained no more than 1–2% impurities. This sample, b.p. 63° (50 mm.), $n^{25}\text{D}$ 1.4141, was analyzed.

Anal. Calcd. for $C_7H_6F_4$: C, 50.61; H, 3.64. Found: C, 51.06; H, 4.29.

The infrared spectrum of III showed vinyl hydrogen absorption at 3080 cm.$^{-1}$, weak saturated CH absorption at 3010 cm.$^{-1}$, C=C absorption at 1635 cm.$^{-1}$, and strong CF absorption in the region at 1000–1250 cm.$^{-1}$. The ultraviolet spectrum of III contained a single band, $\lambda_{\max}$ 240 mμ (ϵ 9460). The value for 1,3-cycloheptadiene[8] is $\lambda_{\max}$ 248 mμ (ϵ 5700).

6,6,7,7-Tetrafluoro-1,4-cycloheptadiene (IV).—A middle cut of the fraction, b.p. 75–78° (50 mm.), which contained the unconjugated cycloheptadiene IV was purified by gas chromatography. There was obtained 6,6,7,7-tetrafluoro-1,4-cycloheptadiene (IV), b.p. 78° (50 mm.), $n^{25}\text{D}$ 1.4014, containing no more than 2% of impurities. Absorption in the infrared region took place at 3030, 3080 and 3120 cm.$^{-1}$ (vinyl hydrogen), at 2900 and 2940 cm.$^{-1}$ (weak saturated CH absorption), at 1695 cm.$^{-1}$ (C=C), and at 1000–1250 cm.$^{-1}$ (strong CF absorption).

Anal. Calcd. for $C_7H_6F_4$: C, 50.61; H, 3.64; F, 45.75; hydrogenation, 0.0245 g. H_2/g. sample. Found: C, 50.95; H, 3.92; F, 45.99; hydrogenation, 0.0231, 0.0230 g. H_2/g. sample.

Pyrolysis of 5,5,6,6-Tetrafluorobicyclo[2.2.1]hept-2-ene (II).—The Diels–Alder adduct II was recovered unchanged from pyrolysis at 700° (1 mm.) over quartz packing. At 740–745° (1 mm.) in the nickel tube a mixture containing 38 g. of the cyclobutane I, 765 g. of the Diels–Alder adduct II, and 59 g. of unidentified liquids was pyrolyzed in 4 hours to give 32 g. of cyclobutane I, 455 g. of recovered Diels–Alder adduct II, 47 g. of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene (III), 32 g. of 6,6,7,7-tetrafluoro-1,4-cycloheptadiene (IV), 187 g. of unidentified liquids and 110 g. of solids, gases and mechanical losses. At 850° (2 mm.) 98% of the Diels–Alder adduct was converted to products that were not precursors of tropolone.

Hydrolysis of Tetrafluorocycloheptadienes to Tropolone.—To a stirred solution of 60 ml. of water in 2 l. of acetic acid was added 1.35 kg. (14 moles) of potassium acetate. Fluorocarbon pyrolysis product (1400 g.) containing approximately 33% (460 g., 2.77 moles) of the tetrafluorocycloheptadienes was added all at one time. The reaction mixture was heated to 120–130° and stirred for 24 hours. Approximately 1 l. of water was added and the unreacted fluorocarbons (598 g.) were steam distilled from the reaction flask (more water was added as necessary). The fluorocarbon layer was recovered from the distillate and stirred with 500 ml. of 5% potassium hydroxide solution for 2 hours. The aqueous layer was separated, combined with the aqueous layer from the steam distillation, and added to the original reaction mixture. The fluorocarbon layer after the aqueous potassium hydroxide treatment weighed 567 g.

The material from the reaction flask was filtered through Celite and the filtrate was diluted to twice its volume with water. Ammonium chloride (1.35 kg.) was dissolved in the diluted solution, which was then divided into portions of about 3 l. each. Each portion was extracted with methylene chloride and extracts were combined and concentrated by distillation. When the temperature of the distillation flask reached 90°, the pressure was reduced to 50 mm. and distillation resumed until the temperature of the distillation flask again reached 90°. The contents of the distillation flask were dissolved in carbon tetrachloride, cooled in an ice-bath, and hydrogen chloride gas was passed over the solution with stirring for 3 hours. Tropolone hydrochloride separated as a tan solid and was collected on a filter. The solid was washed with carbon tetrachloride and added to 1 l. of water. This mixture was stirred 0.5 hour and extracted with methylene chloride, and the combined extracts were distilled through a Vigreux column. Tropolone (248 g., 73% yield), b.p. 67–73° (0.2–0.3 mm.), was collected in a receiver cooled in ice. The tropolone was further purified by recrystallization from cyclohexane, to give white needles, m.p. 50–51°. The tropolone was positively identified by determination of its mixed m.p. (50–51°) and by comparison of its infrared spectrum with authentic material[9] and by conversion to the green copper chelate.

The reaction products after six hours of hydrolysis with potassium acetate in acetic acid contained an appreciable amount of unconverted 5,5,6,6-tetrafluoro-1,3-cycloheptadiene (III) long after all of the 6,6,7,7-tetrafluoro-1,4-cycloheptadiene (IV) had disappeared. A mixture of 14.7 g. of cyclobutane I, 38 g. of Diels–Alder adduct II, 14 g. of conjugated cycloheptadiene III, 14 g. of non-conjugated cycloheptadiene IV and 11 g. of unidentified liquids was hydrolyzed for 6 hours to obtain 10.5 g. (57% yield) of tropolone and 3 g. of the conjugated cycloheptadiene. No unconjugated cycloheptadiene was detected.

The unconverted 5,5,6,6-tetrafluoro-1,3-cycloheptadiene could be effectively hydrolyzed by stirring the recovered fluorocarbons for 1 hour with 5% aqueous potassium hydroxide as described in the preferred procedure above. However, hydrolysis of the original pyrolysis product with 10–30% aqueous potassium hydroxide for 12–24 hours at 5–50° gave slightly lower yields of tropolone. Hydrolysis in concentrated sulfuric acid gave only traces of tropolone.

Acknowledgments.—Valuable contributions by Drs. O. W. Webster and W. R. Brasen of this Laboratory are gratefully acknowledged.

Wilmington 98, Del.

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(8) E. Pesch and S. C. Friess, This Journal, **72**, 5556 (1950).

(9) Prepared by Dr. E. G. Howard of this Laboratory by bromination of 1,2-cycloheptanedione.