benzene. A few milligrams of benzene, which served as an internal standard for the gas chromatographic analyses, was also added to the mixture. During any storage periods, the tubes were immersed in a −80° bath to prevent reaction or evaporation of the components. After warming to room temperature, a 5-μl. sample was withdrawn by a Fisher pipet; the sample was analyzed on a gas chromatographic column packed with Oronite 20 on Chromosorb W. The components were eluted on this column in the order ethanethiol, benzene, norbornene, methylenenorbornane, and bromobenzene. The tubes were again cooled to −80°, sealed with tight-fitting serum caps, and placed in a water bath thermostated at the appropriate temperature. The reaction mixtures were illuminated for 10 to 12 min. with a 275-w. General Electric sun lamp placed 6 to 8 in. from the bath. The tubes were withdrawn from the bath and the reaction immediately quenched by cooling to −80°. After warming to room temperature, another 5-μl. sample was withdrawn and subjected to gas chromatographic analysis. The amounts of the two alkenes remaining after reaction were determined by comparing their peak areas with those obtained before illumination using the peak area of benzene to correct for any differences in the sizes of the samples injected on the gas chromatographic column. Duplicate chromatograms were made in all cases. Knowing the amounts of the two alkenes before and after reaction, the relative reactivity ratios of the two alkenes toward addition of ethanethiol were calculated using eq. 1. The results of these competition reactions are given in Table I.

**Competition Reactions of I and IV with Bromotrichloromethane.**—Solutions consisting of accurately weighed amounts of norbornene, methylenenorbornane, bromotrichloromethane, bromobenzene, and benzene were prepared and placed in Pyrex tubes. Samples of the mixtures were subjected to gas chromatographic analysis on a column packed with S.E.-30 on Chromosorb W. The mixtures were placed in a water bath thermostated at 35° and illuminated with a 275-w. General Electric sun lamp for about 1 hr. Samples were again chromatographed, and the amounts of the two alkenes remaining were determined from their peak areas using the area of the benzene to correct for any differences in sample size. The relative reactivity ratios were calculated using eq. 1, and the results are shown in Table II.

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# The Isomerization of Cyclooctadienes to *cis*-Bicyclo[3.3.0]oct-2-ene

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Treatment of either 1,5- or 1,3-cyclooctadiene with phenylpotassium or other strong bases has been shown to give *cis*-bicyclo[3.3.0]oct-2-ene as the major product in 50–65% yield. The use of elemental potassium as a catalyst for the rearrangement of 1,3-cyclooctadiene provides a very useful synthesis of this hitherto difficultly obtainable olefin. Investigation of dimeric by-products in the isomerization of 1,3-cyclooctadiene has shown that a cyclooctenyl-*cis*-bicyclo[3.3.0]octene, a cyclooctenylcyclooctadiene, and an octadienyl-*cis*-bicyclo[3.3.0]octene were produced.

*cis*-Bicyclo[3.3.0]oct-2-ene has been reported as a minor product formed by a transannular hydride shift in the solvolysis of *cis*- and *trans*-1,2-cyclooctanediol ditosylate,[1] and in the solvolysis of 4-cycloocten-1-yl brosylate.[2] Blanchard and Germain[3] have shown that *cis*-bicyclo[3.3.0]oct-2-ene is also obtained as one of the products of the isomerization of various eight-carbon cyclic olefins and diolefins over a silicophosphoric acid catalyst at 250°. The compounds that were isomerized include 4-vinylcyclohexene, 2-methylenenorbornane, 5-methyl-2-norbornene, and bicyclo[2.2.2]oct-2-ene. Previously described synthetic routes to this olefin have been based on the difficultly accessible *cis*-bicyclo[3.3.0]octan-2-one.[4] It has now been found that either 1,5- or 1,3-cyclooctadiene undergoes a facile rearrangement when heated with catalytic quantities of strong base to give *cis*-bicyclo[3.3.0]oct-2-ene in good yield.

1,5-Cyclooctadiene was heated with 15 wt. % of phenylpotassium (from anisole and potassium[5]) in heptane in a stirred autoclave at 175°. Gas chromatographic analysis of the $C_8$ fraction, obtained in 72% yield, showed it to contain at least six components with the predominant isomer accounting for 70% of the total. This major product was purified by fractionation and was shown to be *cis*-bicyclo[3.3.0]oct-2-ene by its mass spectrum (mol. wt. 108), boiling point, and refractive index, and by comparison of its infrared spectrum with a published spectrum.[3c] Further confirmation was provided by oxidation with potassium permanganate and sodium metaperiodate[6] to the known *cis*-2-carboxycyclopentaneacetic acid.[7]

Four of the remaining five components were identified (see Experimental) as 1,5-cyclooctadiene, cyclooctene, 1,3-cyclooctadiene, and 4-vinylcyclohexene by a combination of gas chromatographic retention times and hydrogenation of different fractions. Two large-scale runs were combined and carefully fractionated to give a forecut enriched in the lower boiling $C_8$ by-products for characterization. After hydrogenation, analysis with a gas chromatograph–mass spectrometer combination showed that ethylbenzene, *n*-propylcyclopentane (corresponding to the unidentified olefin in the initial run), and *n*-octane were also present in addition to the previously identified compound. Attempts to detect bicyclo[4.2.0]octane in the saturated hydrocarbon mixture were unsuccessful.

A plausible mechanism, consistent with the formation of *cis*-bicyclo[3.3.0]oct-2-ene, involves the well-known base-catalyzed isomerization of 1,5-cyclooctadiene to the 1,3 isomer.[8] Allylic proton abstraction, followed by a transannular addition of the resulting carbanion to the end of the conjugated system, would lead to the observed product. A previous proposal of a transannular attack of a carbanion upon an

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[1] A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1650 (1959).

[2] A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

[3] (a) J. E. Germain and M. Blanchard, *Compt. rend.*, **248**, 3301 (1959); (b) J. E. Germain and M. Blanchard, *ibid.*, **250**, 3476 (1960); (c) J. E. Germain and M. Blanchard, *Bull. soc. chim. France*, 473 (1960); (d) M. Blanchard, *ibid.*, 1264 (1961).

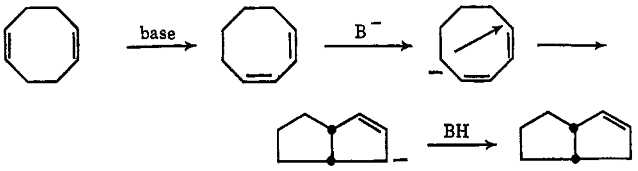
[4] (a) A. C. Cope and W. R. Schmitz, *J. Am. Chem. Soc.*, **72**, 3056 (1950); (b) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 946 (1934).

[5] A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958).

[6] W. G. Dauben and R. L. Cargill, *ibid.*, **27**, 1910 (1962).

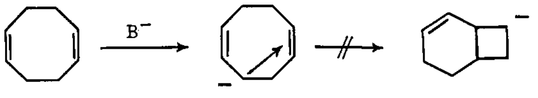
[7] R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).

[8] T. M. O'Grady, R. M. Alm, and M. C. Hoff, Preprint of Division of Petroleum Chemistry, American Chemical Society, Vol. 4, No. 4, Sept. 1959, p. B-65.



epoxide ring in the reaction of *cis*- and *trans*-cyclooctene oxides with bases,[9] and dimerization of olefins by addition of a carbanion (or ion pair) to a double bond,[10] as well as the identification of 1,3-cyclooctadiene in the reaction mixture, all lend support to the proposed mechanism. In order to verify this hypothesis, 1,3-cyclooctadiene[11] underwent reaction under the same conditions used for the large-scale runs above. A 96% conversion of the starting material was obtained giving a 63% yield of *cis*-bicyclo[3.3.0]oct-2-ene. Gas chromatographic analysis of the bicyclic olefin showed it to contain only *ca.* 2% of a single contaminant; this was identified as *cis*-bicyclo[3.3.0]octane by its retention time and mass spectrum.

The freedom from $C_8$ side reactions in the latter isomerization is particularly noteworthy. This indicates that the by-products obtained in rearrangement of 1,5-cyclooctadiene are derived from intermediate carbanions involved in the course of isomerization to the 1,3 isomer. Transannular addition of the carbanion obtained by simple allylic proton abstraction from 1,5-cyclooctadiene is apparently not a major factor in view of the absence of detectable amounts of bicyclo[4.2.0]octane in the hydrogenated product.



Although mechanisms can be written to account for the $C_8$ by-products, it would be premature to speculate on their mode of formation without additional supporting data. The formation of ethylbenzene can undoubtedly be ascribed to isomerization and dehydrogenation of the vinylcyclohexene; control experiments demonstrated that under these conditions 4-vinylcyclohexene is slowly aromatized to ethylbenzene.

Several additional transannular rearrangements of 1,3-cyclooctadiene were conducted at atmospheric pressure in glass equipment using various basic catalysts in order to define more fully the scope of the reaction. Phenylpotassium, phenylsodium, and potassium metal were effective catalysts, but neither sodium metal nor the lithium salt of ethylenediamine caused rearrangement. A particularly convenient laboratory preparation of *cis*-bicyclo[3.3.0]oct-2-ene consists of refluxing 1,3-cyclooctadiene, under nitrogen, with small quantities of potassium until rearrangement is complete as judged by gas chromatographic analysis.

In each of the isomerization reactions considerable high-boiling residue remained after distillation of the $C_8$ products. The yield of residue was *ca.* 10% when 1,5-cyclooctadiene was isomerized and ranged from 16 to 27% when 1,3-cyclooctadiene was treated with potassium catalysts. When phenylsodium was used to rearrange 1,3-cyclooctadiene, a 67% yield of high-boiling materials was obtained. Vacuum distillation showed these residues to contain from 55 to 75% of dimeric products boiling in the $C_{16}$ range depending on the run. The dimers from 1,3-cyclooctadiene in each case were found to be mixtures of three compounds. Quantitative hydrogenation of samples containing various proportions of the three compounds indicated that the major product was a diene and the other two were trienes. In order to simplify the mass spectral cracking patterns, one sample of these dimers, containing 73% of the diene I, 6% of one triene II, and 21% of the remaining triene III, was hydrogenated, and the resulting mixture of saturated hydrocarbons (IV, V, and VI, respectively) was examined on the gas chromatograph–mass spectrometer combination. The cracking pattern of IV gave a base peak at an *m/e* ratio of 111 and other prominent peaks at 109, 69, 67, 55, and 41, in agreement with a cyclooctyl-*cis*-bicyclo[3.3.0]octane.[12] Compound V gave a cracking pattern consistent with the structure of a *n*-octyl-*cis*-bicyclo[3.3.0]octane. The base peak had an *m/e* value of 67 with other prominent peaks at 109, 81, 55, and 41, as well as several minor peaks separated by 14 mass numbers, indicating the loss of $CH_2$ fragments as occur in a normal alkane. Compound VI had a major peak at *m/e* 69 and prominent peaks at 111, 55, and 41, and lacked a strong 67 peak, which is consistent with VI being cyclooctylcyclooctane. The mass spectrum and gas chromatographic retention time on a high-resolution capillary column of authentic cyclooctylcyclooctane and VI were identical.

The identification of VI indicates that the dimers were produced by 1,2 and/or 1,4 addition of the cyclooctadienyl carbanion to 1,3-cyclooctadiene, yielding 5-(2- and/or -3-cyclooctenyl)-1,3-cyclooctadiene (III). Similarly, the bicyclooctenyl carbanion on addition to 1,3-cyclooctadiene would give 4- (2- and/or -3-cyclooctenyl-) *cis*-bicyclo[3.3.0]oct-2-ene (I). Because of the strongly basic reaction media, the olefins are undoubtedly mixtures of double-bond positional isomers which are not readily separable by gas chromatography.

## Experimental[13]

**Isomerization of 1,5-Cyclooctadiene.**—A 1-l. stirred autoclave was charged with 10.8 g. (0.1 mole) of anisole, 7.8 g. (0.2 g.-atom) of potassium, and 200 ml. of dry *n*-heptane. The autoclave was sealed, pressure tested with dry nitrogen, vented, and then heated at 70° with stirring for 1 hr. After it was cooled, a solution of 65 g. (0.6 mole) of 1,5-cyclooctadiene in 100 ml. of heptane was added and the mixture was stirred and heated at 175° for 22 hr. The autoclave was cooled to room temperature, the catalyst was decomposed with methanol, and the resulting dark solution was washed several times with water and dried over anhydrous magnesium sulfate.

After filtration, the reaction mixture was analyzed by gas chromatography on a 25-ft. silicone column operated at 150° and 20-p.s.i.g. helium pressure. It was found to contain six

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[9] A. C. Cope, H. H. Lee, and H. E. Petree, *J. Am. Chem. Soc.*, **80**, 2849 (1958).

[10] H. Pines and L. A. Schaap, "Advances in Catalysis," Vol. XII, Academic Press Inc., New York, N. Y., 1960, p. 143.

[11] J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

[12] The predominant peaks in the cracking pattern of cyclooctane appear at *m/e* values of 111, 69, 55, and 41, while those of *cis*-bicyclo[3.3.0]-octane appear at 109, 67, 55, and 41. The minor peaks are also in agreement with the assigned structures.

[13] All melting and boiling points are uncorrected. Individual components were separated and identified by a combination of an F and M Model 202 gas chromatograph and a Consolidated Electrodynamics Corp. Model 21-130 mass spectrometer. The mass spectrometer is connected through a heated capillary line to sample continuously the effluent from the chromatograph.

$C_8$ components, two of which were identified as 1,5-cyclooctadiene and 1,3-cyclooctadiene by comparison of their retention times with authentic samples. The mixture was then carefully fractionated through a 1 in. × 18 in. column packed with 0.25-in. Penn State protruded S.S. packing to remove the heptane, after which the following fractions were collected: (1) b.p. 103–128°, 2.7 g.; (2) b.p. 128–131, 8.3 g.; (3) b.p. 131–132, 14.5 g.; (4) b.p. 132–133, 10.0 g.; (5) b.p. 133–140, 2.7 g.; and (6) b.p. 140–146, 4.7 g.

Fractions 3–5, each containing *ca.* 80% of one major component, were combined and carefully fractionated at a 100:1 reflux ratio through a Podbielniak Minical column. A center cut containing only the major compound had a mass spectral parent peak at 108 and its infrared spectrum was identical with a published spectrum[3c] of *cis*-bicyclo[3.3.0]oct-2-ene. The pure material had b.p. 132–133°, $n^{20}\text{D}$ 1.4750; lit.[3c] b.p. 131–132°, $n^{20}\text{D}$ 1.4760.

A portion of fraction 6, containing 1,5- and 1,3-cyclooctadiene and another component having the same retention time as cyclooctene, was hydrogenated at atmospheric pressure over platinum in acetic acid. The catalyst was removed by filtration, and the hydrocarbon was extracted into pentane after dilution with water. Gas chromatographic analysis of the pentane solution showed only one peak having an identical retention time with cyclooctane.

A sample of fraction 3, containing 76% of *cis*-bicyclo[3.3.0]-oct-2-ene, 18% of a component having the same retention time as 4-vinylcyclohexene, and 6% of another compound (A), was hydrogenated. Gas chromatographic analysis of the hydrocarbons, after extraction into pentane, showed three peaks in the same ratios indicating that the 6% component had a different ring system. Thus, the original reaction mixture had the following product distribution (in order of increasing g.l.c. retention time): compound A (1.9%), vinylcyclohexene (6.7%), *cis*-bicyclo[3.3.0]oct-2-ene (68.6%), 1,3-cyclooctadiene (2.7%), cyclooctene (4.2%), and 1,5-cyclooctadiene (15.9%).

In order to obtain larger amounts of the unidentified component for further characterization, two large-scale runs were made in which 265 g. (2.46 moles) of 1,5-cyclooctadiene was heated with potassium and anisole in the 1-l. stirred autoclave. In the first, 15.6 g. (0.4 g.-atom) of potassium and 21.6 g. (0.2 mole) of anisole were heated for 16 hr. at 200°. The second run used 23.4 g. (0.6 g.-atom) of potassium and 32.4 g. (0.3 mole) of anisole as catalyst for 6 hr. After catalyst decomposition and washing with water, the products were distilled at atmospheric pressure. From run 1 was obtained 210 g. (80%) of liquid, b.p. 126–152°, and 36 g. (11%) of residue. Run 2 gave 216 g. (82%) of liquid, b.p. 130–156°, and 26 g. (10%) of residue. The distillates were analyzed by gas chromatography with the results shown in Table I. These products were combined and fractionated at a 100:1 reflux ratio through a 0.5-in.-diameter Todd column packed with 0.25-in. Penn State protruded S.S. packing. There was obtained 78.0 g. of material, b.p. 123–131°, which contained chiefly *cis*-bicyclo[3.3.0]oct-2-ene along with the lower boiling impurities, 126.7 g. of pure bicyclic olefin, b.p. 131–132°, and 185.3 g. of the cyclooctadiene–cyclooctene mixture, b.p. 143–151°. A sample of the lower boiling material was hydrogenated over platinum, extracted into pentane in the usual fashion, and analyzed with the gas chromatograph–mass spectrometer combination by comparison of the individual cracking patterns with published data.[14]

TABLE I

| Compound | Run 1, % | Run 2, % |
|---|---|---|
| Compound B | 1.7 | 2.6 |
| Compound A | 1.3 | 1.8 |
| Vinylcyclohexene | 3.8 | 6.3 |
| *cis*-Bicyclo[3.3.0]oct-2-ene | 53.6 | 47.4 |
| 1,3-Cyclooctadiene | 16.8 | 5.9 |
| Cyclooctene | 3.2 | 4.6 |
| 1,5-Cyclooctadiene | 19.3 | 31.5 |

Compounds definitely identified were *cis*-bicyclo[3.3.0]octane, ethylbenzene (not previously detected), ethylcyclohexane, *n*-propylcyclopentane (from compound A), and *n*-octane (from compound B). Several unidentified trace components were also detected which had not been found previously. Bicyclo[4.2.0]octane was not found.

**Oxidation of Bicyclo[3.3.0]oct-2-ene.**—To a solution of 12.84 g. (60 mmoles) of sodium metaperiodate, 0.26 g. (1.6 mmoles) of potassium permanganate, and 0.51 g. (3.7 mmoles) of potassium carbonate in 400 ml. of water was added 1.11 g. (10.3 mmoles) of *cis*-bicyclo[3.3.0]oct-2-ene. The mixture was magnetically stirred at room temperature for 19 hr. and then acidified with 15% sulfuric acid and continuously extracted with ether for 20 hr. The ether extracts were dried over magnesium sulfate and evaporated leaving a viscous oil which could not be induced to crystallize. The oil was dissolved in saturated sodium bicarbonate solution, extracted with ether to remove neutral materials, and again acidified and continuously extracted with ether. After this was dried, the ether was evaporated to leave 500 mg. of gummy material which solidified. This was dissolved in a little water, filtered, and saturated with hydrogen chloride. After 2 days at 0–10°, the resulting crystals were collected, washed with cold pentane, and air dried; the yield was 150 mg., m.p. 90–91°. The melting point was not depressed on admixture with an authentic sample[7] of m.p. 89°, and the infrared spectra (potassium bromide) were superimposable.

*Anal.* Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.02. Found: C, 55.8; H, 7.1.

**Isomerization of 1,3-Cyclooctadiene.**—The 1-l. stirred autoclave was charged with 15.6 g. (0.4 g.-atom) of potassium, 21.6 g. (0.2 mole) of anisole, and 265 g. (2.46 moles) of 1,3-cyclooctadiene and heated at 200° for 18 hr. After this was cooled, the catalyst was decomposed with methanol, and the product was washed with water, dried, and distilled at atmospheric pressure. There was obtained 171 g. of colorless oil, b.p. 122–134°, and 45 g. of higher boiling residue. Gas chromatographic analysis of the distillate showed that it contained 5% of unchanged 1,3-cyclooctadiene, 93% of *cis*-bicyclo[3.3.0]oct-2-ene, 2% of *cis*-bicyclo[3.3.0]octane, and a trace of cyclooctene. This represents a 96% conversion of the starting cyclooctadiene and a 63% ultimate yield of the bicyclic olefin. Vacuum distillation of the pot residue gave 28.2 g. of dimeric material as a bright yellow oil, b.p. 91–96° (0.3 mm.), which was analyzed on a 10-ft. silicone column at 225° and 20 p.s.i.g. and found to contain three components: I (73%), II (6%), and III (21%).

**Atmospheric Pressure Isomerization of 1,3-Cyclooctadiene.**—Only the most convenient laboratory procedure is given. A 500-ml., three-necked, creased flask fitted with a sealed stirrer and a reflux condenser was flamed dry under nitrogen. A mixture of 108 g. (1.0 mole) of 1,3-cyclooctadiene and 3.9 g. (0.1 g.-atom) of potassium was introduced, and the contents were refluxed, under nitrogen, with vigorous stirring for 7 hr. After this was cooled, the catalyst was destroyed and the product worked up to give 72 g. of $C_8$ materials which were composed of 67.0 g. of *cis*-bicyclo[3.3.0]octene and 5.0 g. of unchanged 1,3-cyclooctadiene. There was also obtained 20.5 g. of dimers containing 79.4% I, 0.6% II, and 20% III, and 7 g. of undistillable tar.

**Hydrogenation of 1,3-Cyclooctadiene Dimers.**—Several samples of cyclooctadiene dimers from different runs were subjected to quantitative hydrogenation at atmospheric pressure over platinum in a methylcyclohexane–acetic acid solution. One sample, which contained 87.2% I and 12.8% II, exhibited an average of 2.20 double bonds/molecule for four analyses. Another, composed of 46.4% I, 2.2% II, and 51.4% III indicated 2.48 double bonds/molecule. These data indicate that I is a diene and II and III are trienes. A hydrogenated sample containing 73% IV, 6% V, and 21% VI was analyzed using the gas chromatograph–mass spectrometer combination. The individual cracking patterns were consistent with the following structures: IV, a cyclooctyl-*cis*-bicyclo[3.3.0]octane; V, *n*-octyl-*cis*-bicyclo[3.3.0]octane; and VI, cyclooctylcyclooctane. An authentic sample of cyclooctylcyclooctane was prepared by coupling cyclooctyl bromide with magnesium in ether: b.p. 118–120° (0.5 mm.), m.p. 9–10°, $n^{20}\text{D}$ 1.5020; lit.[15] m.p. 10–11°, $n^{20}\text{D}$ 1.5015. The mass spectra of VI and of the synthetic cyclooctylcyclo-

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(14) The mass spectra of individual components were compared with authentic spectra of A.P.I. Project 44, "Catalog of Mass Spectra," with the exception of bicyclo[4.2.0]octane which was prepared by the catalytic hydrogenation of bicyclo[4.2.0]oct-7-ene.[6]

(15) (a) A. C. Cope and D. J. Marshall, *J. Am. Chem. Soc.*, **75**, 3208 (1953); (b) A. C. Cope and F. A. Hochstein, *ibid.*, **72**, 2517 (1950).

octane were identical. Their gas chromatographic retention times were superimposable using a Perkin-Elmer 226 instrument with a 200-ft. silicone rubber capillary column operated isothermally at 200° and 12-p.s.i.g. helium pressure.

**Acknowledgment.**—We wish to thank Dr. John A. Favre for the determination and interpretation of the mass spectral data.

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# The Hydrolysis and Oxidation of α,ω-Bis(methylthio)polyfluoroalkanes

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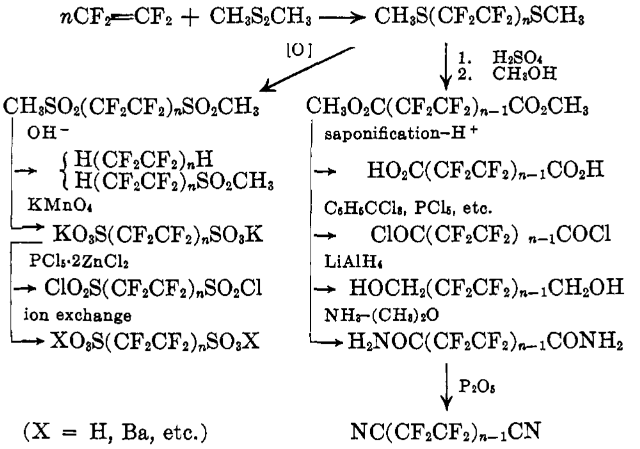
*Received April 13, 1965*

The α,ω-bis(methylthio)polyfluoroalkanes are shown to be sources of perfluoroalkanedioic acids, bis(methylsulfonyl)polyfluoroalkanes, αH,ωH-polyfluoroalkanes, and the new perfluoroalkanedisulfonic acids.

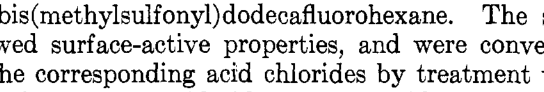
The telomerization of tetrafluoroethylene with methyl disulfide in the presence of *t*-butyl peroxide as a catalyst produces a series of telomers containing a straight perfluoroalkane chain having terminal methylthio groups.[1] These functional groups are utilized to prepare several difunctional fluorocarbons.[2]

Treatment of 1,6-bis(methylthio)dodecafluorohexane with concentrated sulfuric acid at temperatures of 150–180° in Hastelloy B pressure equipment causes hydrolysis of the terminal difluoromethylene groups, removal of the sulfur function, and formation of octafluorohexanedioic acid, isolated as the dimethyl ester. Similarly, the dimethyl esters of tetrafluorosuccinic, dodecafluorooctanedioic, and hexadecafluorodecanedioic acids were prepared, in yields as high as 80%. The free acids were obtained by saponification and the amides, nitriles,[3] and glycols[4] were prepared by standard techniques as shown below.



A convenient technique for isolating the dimethyl esters was used in which the acidic reaction product was suspended in water and methanol, and the ester was continuously extracted with 1,2-dichloroethane at 60°. The extract was dried and fractionally distilled.

Oxidation of 1,6-bis(methylthio)dodecafluorohexane with a variety of oxidizing agents, and especially with hydrogen peroxide in glacial acetic acid, gave high yields of the corresponding sulfone, 1,6-bis(methylsulfonyl)dodecafluorohexane. Treatment of the disulfone with aqueous alkali yielded sodium methanesulfonate and 1H,6H-dodecafluorohexane in high yield. An intermediate hydrolysis product, 1H-6-(methylsulfonyl)dodecafluorohexane, was isolable. The direction of this alkaline hydrolysis was indicated by the preparation of sodium 3,3,4,4-tetrafluoro-1-butanesulfonate from 2,2,3,3-tetrafluorothiolane 1,1-dioxide, and by the formation of 1,1,2,2-tetrafluoroethane from 2H-tetrafluoroethyl phenyl sulfone.



$$C_6H_5SO_2CF_2CF_2H \xrightarrow{OH^-} C_6H_5SO_2O^- + CHF_2CHF_2$$

Treatment of the disulfones with aqueous potassium permanganate gave the perfluoroalkanedisulfonic acids, isolated as the potassium salts. Thus, dipotassium dodecafluoro-1,6-hexanedisulfonate was obtained from 1,6-bis(methylsulfonyl)dodecafluorohexane. The salts showed surface-active properties, and were converted to the corresponding acid chlorides by treatment with phosphorus pentachloride–zinc chloride.[5] Attempts to prepare sulfonamide derivatives from the sulfonyl chlorides were unsuccessful; however, perfluoroalkane monosulfonyl chlorides have been converted to the amides.[6] In the case of tetrafluoro-1,2-ethanedisulfonyl chloride,[7] attempts to effect alkaline hydrolyses or reaction with amines in aqueous media resulted in the liberation of tetrafluoroethylene, while chloride, sulfate, and sulfite ions were formed. The reaction ran so smoothly that this particular sulfonyl chloride could be used as a laboratory source of pure tetrafluoroethylene (yield by weight 33%). A wash with aqueous alkali followed by drying gave material >99% pure by vapor phase chromatography.

When 1,4-bis(methylsulfonyl)octafluorobutane was oxidized with aqueous sodium dichromate, the main products were 1H,4H-octafluorobutane and 1H-4-(methylsulfonyl)octafluorobutane. When chromium trioxide and concentrated sulfuric acid were used, sodium 4-(methylsulfonyl)octafluoro-1-butanesulfonate was isolated.

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[1] W. E. Hanford, U. S. Patent 2,443,003 (June 8, 1948).

[2] I. L. Knunyants, L. Chih-yüan, and V. V. Shokina, *Russ. Chem. Rev.* (Eng. Transl.), **32**, 462 (1963): a review on difunctional fluorocarbons.

[3] E. T. McBee, P. A. Wiseman, and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

[4] M. P. Krasuskaya and I. L. Knunyants, Russian Patent 132,212 (Oct. 5, 1960).

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