Anal. Calcd for $C_{36}H_{26}O_2$: C, 88.13; H, 5.34; mol wt, 490.57. Found: C, 87.92; H, 5.47; mol wt (in dioxane), 495.

Registry No.—**1**, 6093-03-4; **2**, 19550-96-0; **3**, 19550-98-2; **3** (diacetate), 19550-99-3; **4**, 19550-97-1.

Acknowledgment.—The author is very much indebted to Drs. A. S. Hay and J. R. Ladd for providing the 2,4-diphenylphenol.

Decabromopentacyclo-
$[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$decan-5-one

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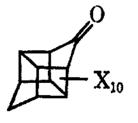
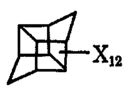
Despite many investigations of the chemistry of decachloropentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$decan-5-one (**1a**) and its derivatives,[2,3] the synthesis of the analogous bromine compound has not been reported in the literature, although the synthesis of the parent bromocarbon, dodecabromopentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$decane (**2b**), has been described.[4,5] Recent interest in the synthesis and reactions of hexabromocyclopentadiene[6] (**3b**) prompts us to report our results on the reaction of **3b** with fluoro- and chlorosulfonic acids. This investigation has led to the successful syntheses of the first derivatives of **2b**.



1



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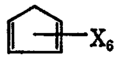
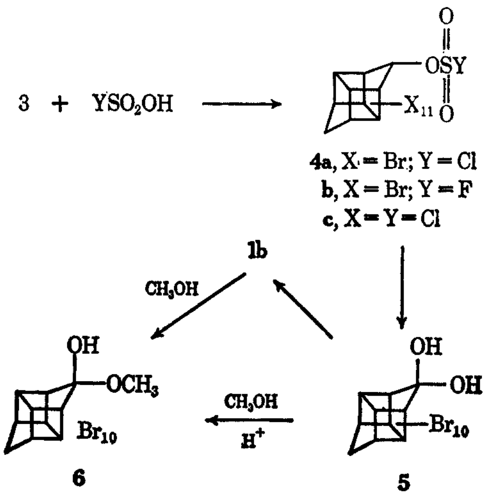


3

a, X = Cl
b, X = Br

Hexabromocyclopentadiene (**3b**) and excess fluorosulfonic acid were stirred and heated at 60–80° for about 2 hr. The reaction mixture was cooled to room temperature or less, filtered, and product washed with water, dried, and recrystallized from ether–methanol to give a white solid, mp >310° dec. The elucidation of the structure of the product as the fluorosulfate ester of undecabromopentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$decan-5-ol (**4b**) follows unmistakably from the elemental analyses and spectral data. The mass spectrum had a parent peak at *m/e* 1088 (^{79}Br) and the ^{19}F nmr spectrum showed a singlet at −51.2 ppm from $CFCl_3$ in good agreement with the proposed structure. The infrared spectrum did not show carbon–hydrogen or double bond absorption but the $-SO_2-$ symmetric and antisymmetric stretching modes were present at 1259 and 1438 cm^{-1}, respectively. Recent work on the structural elucidation of the products from the reaction of **3a** with the chlorosulfonic acids provides further support for the strucure of **4b**.[7] With chlorosulfonic acid, **3b** yields the corresponding ester, **4a**. Sulfur trioxide, which will effect the synthesis of **4c** from **3a**,[8] cannot be substituted for fluoro- or chlorosulfonic acid in the reaction with hexabromocyclopentadiene. Apparently, bromide ion is formed in the reaction and oxidized by the sulfur trioxide and complete decomposition of the starting material is observed.



Hydrate **5** of the title compound was prepared from either **4a** or **4b**. From the fluorosulfate ester **4b**, aqueous alkali is required to effect the hydrolysis, whereas chlorosulfate ester **4a** is hydrolyzed readily by dissolution in 10% aqueous acetone.[9,10] Ketone hydrate **5** is readily dehydrated at elevated temperatures and reduced pressure to the title compound **1b**. The dehydration may be followed by the disappearance of the hydroxyl stretching modes in the 3600-cm^{-1} region of the infrared spectrum and by the appearance of the strong carbonyl stretching mode at 1798 cm^{-1}, a reasonable frequency for the caged ketone.[11] Hemiketal **6** was prepared from either dissolution of **1b** in methanol or by recrystallization of **5** from methanol containing a trace of mineral acid.

Experimental Section

Infrared spectra were obtained with a Beckman IR-9 spectrometer. The mass spectra were obtained on a CEC-21-110B (Direct Probe) instrument. The isotope peaks observed match the relative abundances calculated for the naturally occurring isotopes.

Hexabromocyclopentadiene (3b) was prepared by the method of Straus.[12] Recrystallization from hexane or methanol yielded a product melting at 86.5–88°.

Fluorosulfonic Acid, Undecabromopentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$decan-5-yl Ester (4b).—Hexabromocyclopentadiene (25 g, 0.046

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[1] To whom inquiries should be addressed.

[2] K. V. Scherer, Jr., G. A. Ungefug, and R. S. Lunt, III, *J. Amer. Chem. Soc.* **88**, 2859 (1966).

[3] W. L. Dilling, H. P. Braendlin, and E. T. McBee, *Tetrahedron*, **23**, 1211 (1967).

[4] R. H. Earle, Jr., Ph.D. Thesis, Purdue University, June 1957.

[5] C. W. Roberts and M. B. Chenoweth, U. S. Patent 3,212,973 (1965).

[6] P. T. Kwitowski and R. West, *J. Amer. Chem. Soc.*, **88**, 4541 (1966); **90**, 4697 (1968).

[7] (a) Y. Okaya and A. Bednowitz, *Acta Cryst.*, **22**, 111 (1967); (b) R. G. Pews, *Can. J. Chem.*, in press.

[8] E. E. Gilbert and S. L. Giolito, U. S. Patents 2,616,825 and 2,616,928 (1952).

[9] The facile hydrolysis of **4a** compared to **4b** is in good agreement with the order of reactivity of toluenesulfonyl halides with nucleophilic reagents. The order of reactivity toward diethylamine in benzene at 25° is I > Br > Cl ≫ F.[10]

[10] L. M. Litvinenko, A. F. Popov, and A. M. Borovenski, *Reaktsii Sposobnost. Organ. Soedin., Gos. Univer.*, **3**, 93 (1966); *Chem. Abstr.*, **66**, 115190 (1966).

[11] The carbonyl stretching mode of the caged ketone **1a** in KBr is 1810 cm^{-1}: G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964).

[12] F. Straus, L. Kollek, and W. Heyn, *Ber.*, **63B**, 1868 (1930).

mol) and fluorosulfonic acid[13] (200 ml) were stirred overnight in 500-ml round-bottomed flask equipped with condenser and drying tube. The reaction mixture was heated to 80° and maintained at that temperature for 2 hr, cooled and poured onto cracked ice with vigorous stirring. The product was filtered, washed with water and then dissolved in methylene chloride. After drying the methylene chloride solution with $MgSO_4$ the solvent was evaporated and the product recrystallized from ether–methanol to give 12 g (48%) of product, mp >310°. At temperatures above 200° the material darkens and continues this color change to ~310°. At this temperature decomposition takes place with the evolution of bromine. Thus the melting point cannot be used as a criterion of purity. The infrared spectrum showed the antisymmetric and symmetric –S=O stretching modes at 1458 and 1259 cm^{-1}, respectively. The molecular weight by mass spectroscopy was found to be 1088 (^{79}Br). The ^{19}F nmr gave a singlet a −51.2 ppm from $CFCl_3$ in good agreement with the proposed structure.

Anal. Calcd for $C_{10}Br_{11}SO_3F$: C, 10.93; H, 0.00; Br, 80.04; S, 2.92; F, 1.73; O, 4.38. Found: C, 11.00; H, <0.30; Br, 80.00; S, 2.95; F, 1.66; 0O, 4.00.

Chlorosulfonic Acid, Undecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]-decan-5-yl Ester (4a).—Hexabromocyclopentadiene (50 g, 0.0925 mol) and chlorosulfonic acid (250 g) were placed in a 500-ml round-bottom flask equipped with magnetic stirrer, condenser, and drying tube. The reaction mixture was heated with vigorous stirring for 2 hr at 50°. The reaction mixture was cooled to ice bath temperature and the white precipitate that formed during the reaction and cooling process was removed by filtration through a sintered glass filter. After slurrying with carbon tetrachloride, filtering, and drying, 40 g (78%) of the crude chlorosulfate ester was obtained. Attempts to purify the crude chlorosulfate resulted in decomposition as evidenced by the disappearance of the SO_2 stretching vibrations at 1429 and 1205 cm^{-1}, respectively, in the infrared and the formation of –OH stretching bands in the 3300-cm^{-1} region.

Decabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (1b). Procedure A.—The fluorosulfate ester (3.0 g, 0.0027 mol) was dissolved in tetrahydrofuran (30 ml) and 30 ml of 0.4 *N* potassium hydroxide was added to the solution. The reaction mixture was stirred for 20 min, diluted with water (75 ml) and acidified with concentrated hydrochloric acid. The acidified solution was extracted with methylene chloride and the extract dried (Na_2SO_4) and evaporated to give a 70% yield of the crude ketone hydrate. The ketone monohydrate was obtained by the addition of hexane to a benzene acetone (2:1) solution of the crude hydrate. Purified hydrate **5** was vacuum dried at ~125° and 10 mm pressure to give the anhydrous ketone **1b,** mp >330°. The mass spectrum showed a molecular ion peak at *m/e* 926 (calcd for $C_{10}Br_{10}O$, *m/e* 926), ir (split mull) 1798 cm^{-1} (C=O).

Anal.[14] Calcd for $C_{10}Br_{10}O$: C, 12.82; H, 0.00; Br, 85.47. Found: C, 13.30; H, <0.2; Br, 85.1.

Procedure B.—The chlorosulfate ester (10 g) was dissolved in 10% aqueous acetone (10 ml). The dissolution and/or reaction of the ester resulted in a mild exothermic reaction. After cooling to room temperature, the nearly colorless solution was poured onto ice–water and the precipitate filtered and dried. Recrystallization and drying as described above gave pure anhydrous ketone.

Methyl Hemiketal of Decabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]-decan-5-one (6).—Hydrate **5** was recrystallized from anhydrous methanol containing a trace of mineral acid to give product mp >330°: ir (split mull) 2950–2850 and 1450–1435 (CH_3), 3512 cm^{-1} (OH); nmr ($CDCl_3$) δ 3.66 (s, 3, OCH_3), 2.98 (s, 1, OH). The mass spectrum showed a molecular ion peak at *m/e* 958 (calcd for $C_{11}H_4Br_{10}O_2$, *m/e* 928).

Anal. Calcd for $C_{11}H_4Br_{10}O_2$: C, 13.64; H, 0.42; Br, 82.64. Found: C, 13.80; H, 0.60; Br, 82.5.

Registry No.—**1b,** 19581-67-0; **4b,** 19581-66-9; **6,** 19613-61-7.

Acknowledgment.—The authors are grateful to Dr. J. Heeschen for the ^{19}F nmr experiment, to Mr. R. Nyquist for determining the infrared spectra, and to Dr. L. Shadoff for the mass spectral data. We are indebted to Mr. L. Swim and his associates for the elemental analyses reported herein.

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[13] CAUTION: The addition of fluorosulfonic acid to water is a violent reaction. The decomposition must be carried out in a hooded area with adequate facial protection, etc. It should also be noted that skin burns resulting from contact with fluorosulfonic acid are often reluctant to heal!

[14] All attempts to obtain acceptable analyses for **1b** or **5** were unsuccessful, presumably due to the facile hydration and dehydration reactions.

A Calculation of the Optical Activity of a Trefoil Knot

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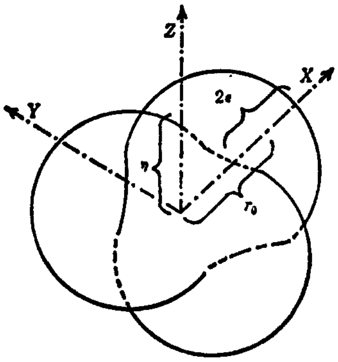
The optical activity of a trefoil, a ring which contains a simple overhand knot, is a property of the structure which distinguishes it from the unknotted ring.[3] To obtain some feeling for the magnitude and sign of rotation expected we have carried out a straightforward Kirkwood calculation[4] of the activity expected for a polymethylene trefoil $(CH_2)_m$.

A particular conformation of the knot of absolute configuration I may be represented by the parametric



I

equations[5]

$$r = r_0 + \epsilon \cos\left(\frac{3}{2}\theta\right)$$

$$z = \eta \sin\left(\frac{3}{2}\theta\right) \qquad (1)$$

with

$$0 \leq \theta \leq 4\pi, \quad 0 < |\epsilon| < r_0, \quad \eta > 0$$

The chain was divided into n segments (n = 10, 25, or 50) and the fragments were treated as the individually polarizable groups characteristic of the Kirkwood

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[3] H. L. Frisch and E. Wasserman, *J. Amer. Chem. Soc.*, **83**, 3789 (1961).

[4] J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937). Note correction in sign in W. W. Wood, W. Fickett, and J. G. Kirkwood, *ibid.*, **20**, 561 (1952), footnote 2.

[5] We wish to thank Dr. F. H. Stillinger for a discussion on this point.