tration with $KMnO_4$. The titer value corresponded to 0.286 g. of the oxalic acid per 1.5 g. of the ether ester, so that on molar basis 0.00405 mole of the ether ester gave 0.00227 mole of oxalic acid (yield 56%).

Glycol of the Methyl Ether of the Diolefinic Component.—The methyl ether ester (1 g.) was saponified to give 1-methoxy-2-carboxy-3-pentadecadienylbenzene (yield 0.7 g.). This on hydroxylation as in the case of the monoölefin yielded a sirupy liquid (0.5 g.) which, when kept at 0° for a day, set to a yellow waxy solid and on further purification with ether–petroleum ether mixture gave 0.40 g. of a yellowish amorphous solid without a sharp m.p.

Anal. Calcd. for $C_6H_3(OCH_3)(COOH)C_{15}H_{27}(OH)_4$: C, 64.80; H, 8.99. Found: C, 64.80; H, 9.01.

On decarboxylation, the diolefinic acid gave the corresponding monophenol whose methyl ether (b.p. 186° (1 mm.), $n^{30}\text{D}$ 1.5028) on oxidation with permanganate in acetone at 0° gave butyric, oxalic and ω-(3-methoxyphenyl)-caprylic acids.

Oxidation of the Triolefinic Component.—A 2-g. sample of the acid was oxidized with 21 g. of powdered permanganate at −20°. The steam-volatile portion gave a qualitative test for formic acid. The non-volatile portion gave azelaic (0.4 g.) and oxalic acids as in the previous case. A separate oxidation was conducted in order to estimate formic acid quantitatively by its conversion into CO_2 by mercuric acetate[13] and absorption of the gas by standard alkali. A 1-g. sample of the triolefin gave CO_2 corresponding to 0.0177 g. or 0.00038 mole of formic acid (yield, 13%).

Dimethyl Ether Ester of the Triolefinic Component.—Prepared according to the previously described method, the ether had boiling point 214° (1 mm.) and $n^{31}\text{D}$ 1.5132. Oxidation of the ether ester, 2 g. in 50 cc. of acetone at −20° with 8 g. powdered permanganate gave formic, oxalic and ω-(2-carboxymethyl-3-methoxyphenyl)-caprylic acids.

Anal. Calcd. for $C_{17}H_{24}O_5$: C, 66.12; H, 7.87. Found: C, 66.30; H, 7.79.

Oxalic acid quantitatively estimated here as in the case of the diolefinic component was found to be 0.0058 mole of acid per 0.00537 mole of the ether ester. It may be noted that this molar proportion of oxalic acid is twice that in the case of the diolefinic acid.

Diene Value Determination.—A 0.5781-g. sample of the ether ester when heated in a sealed tube with 10 cc. of a 2% maleic anhydride solution in acetone at 90° for 20 hours, according to the procedure of Priest and Von Mikusch,[14] gave no evidence for the presence of conjugated double bonds.

Oxidation of the Methyl Ether of the Triolefinic Component.—The decarboxylated acid on methylation as before gave a liquid (b.p. 187° (1 mm.), $n^{28}\text{D}$ 1.5120). A 2-g. sample of this ether on oxidation with 11 g. of powdered potassium permanganate in acetone at −20° gave formic, oxalic and ω-(3-methoxyphenyl)-caprylic acids.

Acknowledgment.—The authors wish to express their sincere thanks to Professor Charles R. Dawson, Chemistry Department, Columbia University, for help in the revision of the manuscript of this paper; and to the Ministry of Education, Government of India, for a senior research scholarship to one of the authors (V. J. P.).

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(13) J. D. Reid and H. D. Weihe, *Ind. Eng. Chem., Anal. Ed.*, **10**, 271 (1938).

(14) G. W. Priest and J. D. von Mikusch, *Ind. Eng. Chem.*, **32**, 1314 (1940).

MADRAS, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Products of Addition of Sulfenyl Halides to Norbornene[1,2]

BY HAROLD KWART AND ROBERT K. MILLER

RECEIVED FEBRUARY 24, 1956

2,4-Dinitrobenzenesulfenyl chloride and bromide and *p*-toluenesulfenyl chloride have been treated with norbornene. The products of reaction have been identified by various degradative procedures. An effect on the product composition due to solvent medium of reaction has been observed. A general interpretation is proposed to explain the differences between sulfenyl halide addition and other addition reactions of the bicyclic double bond which have been studied previously.

Introduction.—The addition of several sulfenyl halides to norbornene (I) has been undertaken in extension of previous work[1] in this Laboratory investigating the nature of addition reactions of bicyclic olefins. Kharasch and his co-workers have studied[3] the addition of this class of double bond reagents and have observed normal *trans* addition in the case of aliphatic and alicyclic olefins. They have demonstrated,[4] further, that the addition proceeds predominantly according to Markownikov's rule when conducted in glacial acetic acid and that the results are consistent with a three-membered cyclic cationic intermediate formed by addition of 2,4-dinitrobenzenesulfenyl cation to the double bond. Further aspects of the stereospecificity of this reaction have been emphasized in the work of Kharasch and Havlik[5] and of Cram.[5]

In our previous work we have investigated and interpreted the unusual course (rearrangement) taken by such comparatively simple reactions as halogenation and hydroxylation in the bicyclic system. The present objective was to determine the influence of the reagent on the course of addition to bicyclic olefins.[6] The aromatic sulfenyl halides seemed to be ideal reagents from this point of view because of the considerably greater size and highly polar nature of addition fragments.

2,4-Dinitrobenzenesulfenyl Chloride.—The addition of 2,4-dinitrobenzenesulfenyl chloride (II) to norbornene in a variety of solvents yielded predominantly two products: a 1:1 adduct III and a

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(1) Paper VI in this series; for previous papers see THIS JOURNAL, **76**, 5400 (1954).

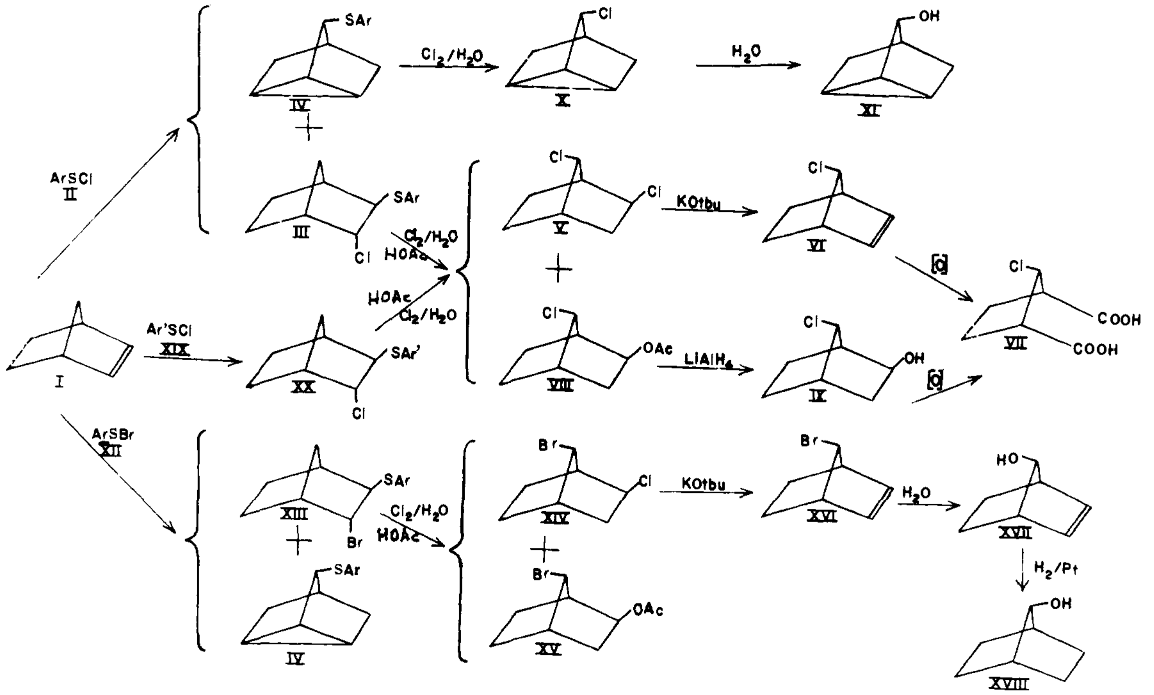
(2) Revised nomenclature reported by A. M. Patterson, *Chem. Eng. News*, **30**, 930 (1952).

(3) W. I. Orr and N. Kharasch, THIS JOURNAL, **78**, 1201 (1956), is paper XXIII in a series on sulfenyl halide chemistry and contains references to prior contributions.

(4) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

(5) (a) N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953), A. J. Havlik and N. Kharasch, *ibid.*, **78**, 1207 (1956); (b) D. J. Cram, *ibid.*, **71**, 3884 (1949).

(6) While our work was under way we became aware (through personal communication with Dr. S. J. Cristol) of a similar study being undertaken at the University of Colorado laboratories. These results have now been disclosed (see S. J. Cristol and G. D. Brindell, Abstracts of Papers, Am. Chem. Soc. Meeting, Cincinnati, Ohio, March 29–April 7, 1955, p. 35N).

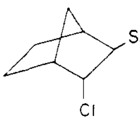


Reaction flowsheet Ar = 2,4-dinitrophenyl Ar' = *p*-tolyl

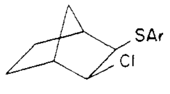
halogen free product IV. The ratio of the two and the ease of materials recovery was dependent on the nature of the solvent, its purity and the purity of the sulfenyl halide reagent. Thus, moisture in either reagent increased the yield of IV and caused oiliness in the character of the crude product mixture. Purified ethylene bromide, ethylene chloride and carbon tetrachloride were used as solvents with approximately the same results. The use of the considerably more polar acetic acid, described by Kharasch and co-workers as the most convenient medium for the reaction, resulted in a large decrease in the ratio of III to IV and a significant amount of oily residue of undetermined nature. Ordinarily III was obtained directly from the reaction mixture as an easily purified, excellently crystalline material in yields up to 70%. IV was separated from the mother liquors and purified by recrystallization.

The structure of III was demonstrated by its analysis and the fact (see flow sheet) that it can be converted to *anti*-7-*exo*-2-dichloronorbornane (V) by chlorinolysis in aqueous acetic acid solution.[7] The structure of V was proved by dehydrohalogenation to *anti*-7-chloronorbornene (VI), followed by oxidation to *trans*-2-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid (VII). Both VI and VII are known and direct infrared and melting point comparison of the latter with an authentic sample[8] was possible. The dipole moment of the dichloride V also confirms the assignment of the *anti* configuration to the 7-chlorine atom and provides further substantiation for the structure assigned to *syn*-7-*exo*-2-dichloronorbornane, first characterized by Roberts, Johnson and Carboni.[9] The moment found for V is 2.25 *D;* those calculated for *anti*-7-*exo*-2- and *syn*-7-*exo*-2-dichloronorbornanes are 2.40 and 4.29 *D*, respectively, assuming tetrahedral bond angles and a carbon–chlorine bond moment of 2.18 *D*.[10]

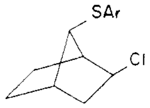
The structure III given in the flow sheet was deduced from the following considerations. Based on earlier observations of addition to norbornene,[1,9] a 1 : 1 adduct with sulfenyl halide would be expected to have either the 2,3-*trans*- (A), the 2,3-*cis*- (B) or the *syn*-7-*exo*-2- (C) structure.



A



B



C

Structure B can be eliminated at once since, without an unprecedented rearrangement, chlorinolysis would not convert it to a dichloride with the *anti*-7-chloro configuration proved for V. It is conceivable that either A or C might yield V; A through a Wagner–Meerwein rearrangement of conventional character among norbornane derivatives[1] and C through rearward displacement of the carbon–sulfur bond by chloride ion or its equivalent.

Fortunately, the occurrence of a by-product of the chlorinolysis reaction permitted a choice be-

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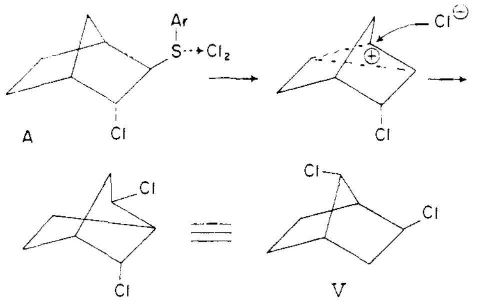
(7) Aspects of the mechanism and stereochemistry of this reaction, knowledge of which was necessary to the establishment of some of the structures deduced here, will be discussed in a future publication. In brief, the reaction has been found to follow the course generalized by the equation

$$\mathrm{RSAr} \xrightarrow[\mathrm{H_2O/HOAc}]{\mathrm{Cl_2}} \left\{ \begin{matrix} \mathrm{RCl} \\ \mathrm{ROAc} \end{matrix} \right. + \mathrm{ArSO_2Cl}$$

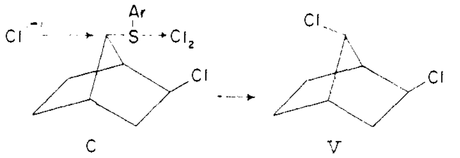
(8) We are obliged to Dr. J. D. Roberts of the California Institute of Technology for this sample.

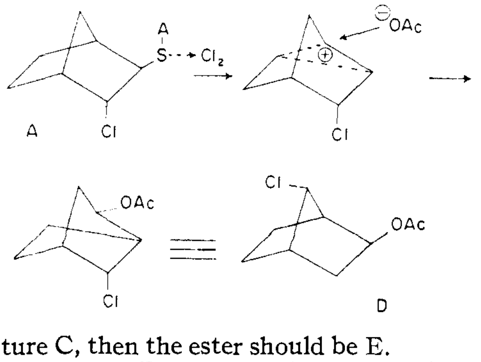
(9) J. D. Roberts, F. O. Johnson and R. A. Carboni, THIS JOURNAL, **76**, 5692 (1954).

(10) M. T. Rogers and M. B. Panish, *ibid.*, **77**, 4230 (1955).

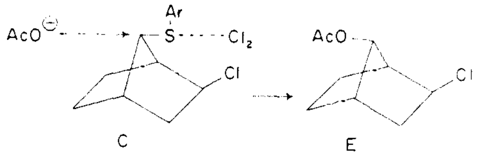


tween possibilities A and C. In the chlorinolysis of alkyl aryl sulfides in acetic acid solution a certain amount of acetoxy compound always accompanies the alkyl chloride product.[7] The chlorinolysis of III yielded, in addition to V, a chloroacetoxy compound (VIII). The identity of VIII was established by its elemental analysis and through the isolation and characterization of simple degradation derivatives (see flow sheet). The ester VIII is a primary product of the chlorinolysis reaction since V strongly resists acetolysis and can be recovered essentially unchanged from long heating in acetic acid, conditions that are much more severe than exist during the chlorinolysis reaction. VIII does not result from reaction of nortricyclyl chloride with acetic acid, since it does not appear among the products of chlorinolysis of nortricyclyl 2,4-dinitrophenyl sulfide (see below). One may, therefore, make the reasonable assumption, based on observations of many similar reactions,[11] that VIII has resulted from a reaction in which acetate (or its equivalent) has replaced chloride ion and consequently the products V and VIII will have an entirely analogous steric relationship of acetoxy and chloro groups. Therefore if the adduct III were A, the ester VIII should be *anti*-7-chloro-*exo*-norbornyl acetate (D), but if the adduct had the structure C, then the ester should be E.





The structure D proved to be correct, since VIII yielded the known *anti*-7-chloro-*exo*-norborneol (IX) by treatment with lithium aluminum hydride.[12] In the interest of additional positive characterization IX was oxidized to the same dicarboxylic acid (VII) obtainable in the degradation series leading from V.



The second product of the reaction between 2,4-dinitrobenzenesulfenyl chloride and norbornene was identified readily as nortricyclyl 2,4-dinitrophenyl sulfide (IV) by (1) its elemental analysis, (2) the fact that its infrared spectrum showed no alicyclic unsaturation bands but did show strong absorption in the region of $12.3\ \mu$,[13] and (3) chlorinolysis to nortricyclyl chloride (X). The latter was readily characterized by infrared comparison with an authentic spectrum and by hydrolysis to the crystalline derivative 3-hydroxynortricyclene (XI).

A by-product of the chlorinolysis of IV was an ester, presumably nortricyclyl acetate. Its infrared spectrum had all the features to be expected of a compound of that structure and both its refractive index and infrared were distinctly different from those of VIII. This is significant in that it demonstrates VIII cannot result from the acetolysis of nortricyclyl chloride during chlorinolysis of III.

2,4-Dinitrobenzenesulfenyl Bromide.—This reagent was added to norbornene to ascertain whether any change in the course of addition would result from variation in the halogen. XII reacted smoothly with norbornene to give an excellent yield of 1:1 adduct XIII, along with a bromine-free product which proved to be identical with IV isolated previously from the reaction of I and II. The structure of the adduct XIII followed from its elemental analysis and the fact that on chlorinolysis a good yield of XIV is obtained. XIV was established to be *anti*-7-bromo-*exo*-2-chloronorbornane by means of several lines of evidence: (1) the dipole moment of XIV, 2.24 *D*, eliminates *syn*-7-bromo-*exo*-2-chloronorbornane; (2) dehydrohalogenation of XIV with potassium *t*-butoxide gave an unsaturated bromide XVI which on hydrolysis and reduction resulted in the known compound XVIII, 7-hydroxynorbornane. The infrared spectrum of XVIII proved to be identical with that of an authentic sample.[14] Applying the same line of reasoning by which structure V was established for the dinitrobenzenesulfenyl chloride adduct, XIV clearly arises from the sulfenyl bromide adduct *via* rearrangement during chlorinolysis, and thus the adduct is *endo*-3-bromo-*exo*-norbornyl 2′,4′-dinitrophenyl sulfide (XIII).

Difficulty was encountered in the dehydrohalogenation of XIV due to the removal of both chlo-

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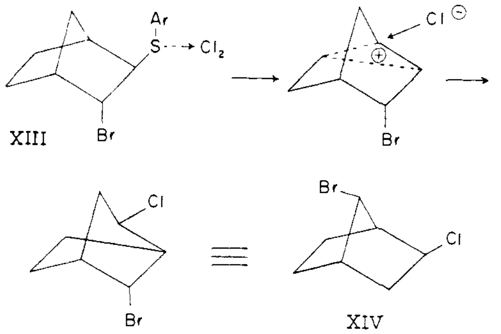
[11] See, for examples, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1956, pp. 660 ff.

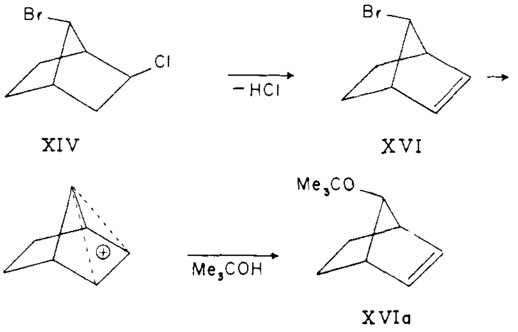
[12] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948), have shown this reagent to be very unreactive toward alicyclic halogen.

[13] J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[14] This sample was kindly provided by Mr. V. Rolleri of these laboratories. The synthesis of this compound by an independent method will appear in a forthcoming publication.



rine and bromine and formation of a product (probably *anti*-7-*t*-butoxynorbornene, XVIa), which could be separated from the unsaturated bromide only with difficulty. It was clear, however, that the chlorine in XIV is not situated on C$_7$ since in the dehydrohalogenation reaction almost all the chlorine (92%) is recovered as KCl while only 39% of the bromine appears as bromide ion. In view of the inertness, under these conditions, of the 7-bromine in *syn*-7-*exo*-2-dibromonorbornane[15] and the recently reported[16] unusual reactivity of *anti*-7-norbornenyl derivatives, these results must be regarded as evidence in favor of the assigned structure. The side reaction probably takes the course

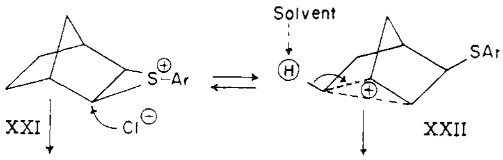


The hydrolysis product of XVI has been assigned the structure of the *anti*-7-hydroxynorbornene in consonance with the reported[16] retention of configuration associated with the 7-norbornenyl cation intermediate. This compound was free of any carbonyl impurity detectable either by infrared or by qualitative analysis with carbonyl reagents. This observation seems important in that it indicates that the dehydrohalogenation of XIV has not resulted in any vinylic halide and, thus, that XIV could not contain any significant amount of 2,3-dihalonorbornane impurity.

As in the previous case some bromoacetoxy compound was formed along with the main product of chlorinolysis of XIII. The structure *anti*-7-bromo-*exo*-norbornyl acetate (XV) has been assigned to this compound entirely by analogy.

***p*-Toluenesulfenyl Chloride.**—To determine the extent of generality of this mode of addition of arylsulfenyl halides to norbornene, addition of *p*-toluenesulfenyl chloride (XIX) also was tried. Reaction in carbon tetrachloride solution gave only one product, a liquid. It was identified by analysis of its sulfone, a solid, as the 1:1 adduct. Chlorinolysis yielded the same dichloride and the same chloroester as obtained by chlorinolysis of III. Hence, this adduct is probably *endo*-3-chloro-*exo*-norbornyl *p*-tolyl sulfide (XX). This is in agreement with the conclusions of Cristol and Brindell[6] concerning the structure of this adduct.

Interpretation.—The results of the present work are, at first glance, somewhat surprising. Yet, with the exception of 2,7-rearranged product (corresponding to C), sulfenyl halide addition leads to each of the products analogous to those observed to form in the bromination of norbornene, though in different proportions. The failure to observe Wagner–Meerwein rearrangement here as in the bromination and hydroxylation reactions of norbornene, however, may not be attributed to any lessening of the ionic character of the addition reagent.[17] The formation of a cyclic sulfonium ion XXI by electrophilic attack from the *exo* side of the bicyclic double bond is in agreement with the "rule of *exo* addition" and other observations on the stereochemistry of addition at positions of alicyclic unsaturation.[18] The predominant reaction product in non-polar solvents appears to be the result of a preference for attack by chloride at the *endo* side of the sulfonium ion (XXI) as indicated.



There is no reason to doubt (again by analogy to bromination) that anchimeric[19] assistance is afforded by delocalization of the neighboring σ-bond, as represented in XXII. Unlike the bromination reaction, however, the ion XXII does not lead to the formation of the Wagner–Meerwein rearrangement product.

The extraordinary tendency to form the *endo* is made understandable by an examination of scale models. Models I and II shown in two views also provide some perspective on the nature of this hindrance to rearrangement. The numbering corresponds to the norbornane skeleton carbons, S and H, respectively, to sulfur and hydrogen atoms, and the planar hexagon represents an unsubstituted benzene ring in proportion. It will be seen that the aryl group effectively shields C$_3$ and C$_4$ and encounters the hydrogen atom at C$_3$ in many

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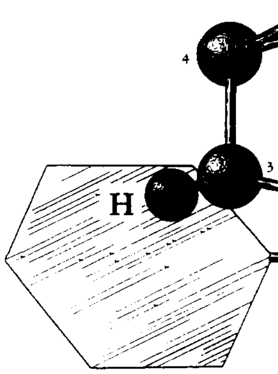
[15] H. Kwart and L. Kaplan, THIS JOURNAL, **76**, 4072 (1954).

[16] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

[17] N. Kharasch, C. M. Buess and W. King, *ibid.*, **75**, 6035 (1953), have even demonstrated that ArSCl is measurably dissociated in certain media and considerable evidence exists in other papers from this school (see reference 3) contributing to the impression of strong ionic character of the sulfur–chlorine bond in sulfenyl halides.

[18] See reference 1 for further discussion on this point. As is evident in the work of D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953), and D. H. R. Barton and N. J. Holness, *ibid.*, 78 (1952), this generalization should rather be stated "Attack at a point of alicyclic unsaturation occurs from the least hindered side of the molecule" where the point of unsaturation is an exocyclic olefin, endocyclic olefin or carbonyl carbon.

[19] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).



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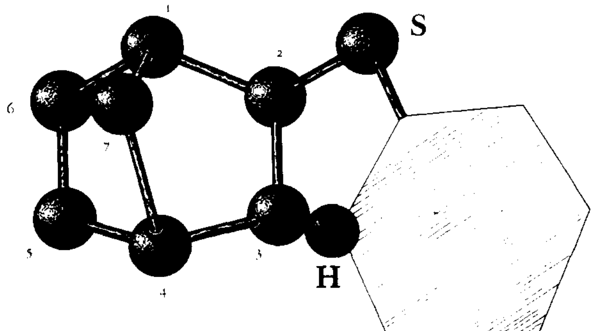

II

of its conformations.[20] An *o*-nitro group actually prevents the attainment of some conformations of the benzene ring due to interference with C_3 and C_4. As a consequence of the shielding, halide ion cannot attack C_4 in ion XXII; since ion XXI has no electron deficiency at C_4, no route is open for formation of 2,7-rearranged product.

The formation of nortricyclyl product, which is promoted by ionic solvents, is shown to occur in the bridged ion XXII. Chloride is probably associated with the solvent and is consequently too bulky to readily attack the sulfonium ion XXI from the *endo* side where strong non-bonded interaction with axial hydrogen atoms exists. Though screened from reaction at the C_3 and C_4 positive centers, the bridged ion may readily stabilize itself by proton loss to solvent, as indicated. Highly polar and more strongly ionizing solvents also possess the ability to foster the deep-seated rearrangements which have been interpreted to develop from the formation of nortricyclonium ions.[21] This latter effect may very well explain the suppression of the 2,3-*trans* product, the enhancement of the nortricyclyl product and the observation of other products that attend the use of the highly polar solvent, acetic acid.

Experimental

Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Norbornene. (a) ***endo*-3-Chloro-*exo*-norbornyl 2′,4′-Dinitrophenyl Sulfide.**—Ethylene bromide was the most satisfactory solvent. The best yield of the 1:1 adduct (64.7%) was obtained using this solvent. Norbornene (50 g., 0.53 mole) in 70 ml. of freshly distilled ethylene bromide was stirred while a solution of the sulfenyl chloride (92.2 g., 0.393 mole) in 320 ml. of solvent was added over a period of 20 minutes. Ice-bath cooling was used to keep the temperature below 50°. The mixture, which fumed strongly at the end of the addition, was stirred for another 45 minutes, and then allowed to stand for about a day. After cooling to about 6° (incipient freezing of the solvent), the precipitate was filtered off, washed with carbon tetrachloride until the filtrate came through practically colorless, and then air-dried. The light yellow *endo*-3-chloro-*exo*-norbornyl 2′,4′-dinitrophenyl sulfide weighed 83.5 g., and had m.p. 165–166°.

Repeated recrystallization from a variety of solvents never gave a product with a higher melting point than that of the analytical sample: 166–167° (from benzene–carbon tetrachloride).

Anal. Calcd. for $C_{13}H_{13}O_4N_2SCl$: Cl, 10.78. Found: Cl, 10.64, 10.78.

(b) **Nortricyclyl 2,4-Dinitrophenyl Sulfide.**—The filtrate from the 1:1 adduct was evaporated to dryness in a stream of air and then allowed to stand until practically all norbornene odor had dissipated. The dark brown residue was taken up in 300 ml. of hot benzene, boiled with a large amount of activated carbon, and filtered through Celite. The light yellow filtrate, when allowed to evaporate slowly, deposited a crop of large, well formed yellow rhombs. These crystals were large enough to allow their separation by simply pouring off the mother liquor and washing with small amounts of benzene by decantation. The decantate was heated until completely clarified. Further solvent evaporation yielded a second crop of these crystals. The two crops of crystals (15.0 g., 9.7%), on recrystallization from benzene, easily yielded pure nortricyclyl 2,4-dinitrophenyl sulfide, m.p. 141.5–143.5°. The compound contains no chlorine. Its infrared spectrum[22] shows no olefinic character, but does show a strong absorption at 12.3 μ, characteristic of nortricyclene derivatives.[18]

The analytical sample had m.p. 142.8–144° after repeated recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{12}O_4N_2S$: C, 53.40; H, 4.14. Found: C, 53.42; H, 4.47.

Further evaporation of the benzene solution yielded a mixture of the 1:1 adduct and the nortricyclyl sulfide. The above process of separation of the nortricyclyl compound was very slow, and systematic fractional crystallization proved laborious. Fortunately the two products crystallize separately, and a process of flotation was developed for the separation. The mother liquor from the preparation of the 1:1 adduct was evaporated to dryness, taken up in benzene, and treated with activated carbon. Addition of about 2 volumes of methanol to the filtered solution gave, on slow, undisturbed cooling, a crystalline mass consisting of pale yellow needles and darker yellow, denser rhombs. By stirring the mixture well and rapidly decanting the suspension of the needles, a moderately good separation was obtained. Combination of the dense crystals from several runs and recrystallization from benzene gave enough pure nortricyclyl 2,4-dinitrophenyl sulfide for identification by chlorinolysis.

Chlorinolysis of *endo*-3-Chloro-*exo*-norbornyl 2′,4′-Dinitrophenyl Sulfide. (a) ***anti*-7-*exo*-2-Dichloronorbornane.**—The crude (m.p. 165–166°) adduct (92.2 g., 0.280 mole) was suspended in a mixture of 500 ml. of glacial acetic acid and 25 ml. of water by vigorous stirring. A fairly rapid stream of chlorine was passed in while the mixture was kept just cool to the hand with an ice–water-bath. In about 45 minutes chlorine absorption had virtually ceased, and after a further 10 minutes the chlorine flow was stopped and the mixture permitted to stand at room temperature for an additional 3 hours. The resulting clear yellow solution was mixed with about 500 g. of crushed ice, which resulted in the formation of a yellow, crystalline precipitate of 2,4-dinitrobenzenesulfonyl chloride, m.p. 101–102°. After the ice had melted the entire mixture was extracted repeatedly with a total of about a liter of low boiling petroleum ether. The extracts were washed with half-saturated sodium bicarbonate until carbon

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[20] D. J. Cram, THIS JOURNAL, **74**, 2129 (1952), discusses a bridged-ion pair intermediate in connection with Wagner–Meerwein rearrangement. In the ion pair, corresponding to XXII, hindrance to rearrangement is viewed as the result of insulation of the positive charge centers at C_3 and C_4 on the ring against electrostatic interaction with the chloride gegenion.

[21] J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).

[22] All infrared spectra referred to in this paper are reproduced in the Ph.D. dissertation of R. K. Miller, available at the University of Delaware Library.

dioxide was no longer evolved, then washed with several portions of water, and dried over calcium chloride.

After stripping off petroleum ether at atmospheric pressure, the residue was distilled quickly at reduced pressure through a short Skinner–Noyes column. After residual solvent was removed, 40.1 g. of distillate was obtained boiling between 60° (12 mm.) and 95° (6 mm.). This material was distilled slowly through an 8″ Widmer column to give 2.4 g. of forecut ($n^{20}_{\rm D}$ 1.4898; corresponding very well with the properties of nortricyclyl chloride) and 21.7 g. of *anti*-7-*exo*-2-dichloronorbornane, b.p. 70–90° (12 mm.). Refractionation gave 1.7 g. with b.p. 77–79° (10 mm.), $n^{20}_{\rm D}$ 1.5048, and the remainder distilling 79–81° (10 mm.) with constant refractive index: $n^{20}_{\rm D}$ 1.5070 ± 0.0002; total recovery 21.0 g.

Anal. Calcd. for $C_7H_{10}Cl_2$; Cl, 42.96. Found: Cl, 43.31, 43.23.

The infrared spectrum of the product showed a small amount of carbonyl impurity, probably ester. A redistillation reduced the amount of this absorption and gave a product of slightly higher refractive index: $n^{20}_{\rm D}$ 1.5086.

(b) ***anti*-7-Chloro-*exo*-norbornyl Acetate.**—The residue from the distillation of the dichloride through the Widmer column had refractive index $n^{20}_{\rm D}$ 1.4890. Infrared analysis indicated the presence of an ester. *Anal.* Cl, 24.35.

Assuming this material to be a mixture of dichloride and a chloronorbornyl acetate, the analysis indicates the presence in the residue of 12.3 g. (23.2% yield) of ester.

Residues from this and another chlorinolysis were combined and repeatedly distilled to obtain a pure sample of the ester. The final product had b.p. 44.0–44.8° (0.40–0.45 mm.), $n^{20}_{\rm D}$ 1.4850–1.4841, and was obtained in 4.2% yield.

Anal. Calcd. for $C_9H_{13}O_2Cl$: Cl, 18.8; $MR_{\rm D}$, 45.9. Found: Cl, 20.0; $MR_{\rm D}$, 45.7.

Infrared analysis of the purified product showed that the residue from the dichloride preparation contains only dichloride and chloroester, and that the ester obtained here was identical with the ester which was the by-product of the chlorinolysis of the *p*-toluenesulfenyl chloride adduct (XX).

To determine whether this ester could be a secondary product of the chlorinolysis, the dichloride V (15.3 g., $n^{20}_{\rm D}$ 1.5081–1.5087) was heated at 80° for 14 hours in a mixture of 155 ml. of acetic acid and 32 ml. of concentrated hydrochloric acid. The mixture was worked up in the manner of the chlorinolysis work-ups, and the final distillation yielded, after a forecut of about 0.9 g. ($n^{20}_{\rm D}$ 1.5063; the low refractive index is probably due to some residual extraction solvent), 13.6 g. of dichloride, $n^{20}_{\rm D}$ 1.5086–1.5090. A special effort was made to find high boiling material of low refractive index by flaming the pot and column so as to force over all distillable material, but the final refractive index is just about equivalent to that of the ester-free dichloride, and it can be seen that the procedure, in fact, purified the dichloride.

***anti*-7-Chloronorbornene.**—*anti*-7-*exo*-2-Dichloronorbornane (17.5 g., 0.106 mole) was refluxed for 19 hours with a solution prepared by dissolving 5.2 g. of potassium metal in 140 ml. of *t*-butyl alcohol. The cooled reaction mixture was poured into 400 ml. of water and extracted repeatedly with a total of 700 ml. of petroleum ether (30–60°). The extracts were dried over calcium chloride and most of the solvent removed by distillation at atmospheric pressure. Vacuum distillation then yielded, after removal of residual solvent, 7.1 g. (55.5%) of *anti*-7-chloronorbornene, b.p. 64–65° (44 mm.), $n^{20}_{\rm D}$ 1.4920–1.4933 (lit.[9] value $n^{25}_{\rm D}$ 1.4927). The infrared spectrum agrees very well with that given in the literature.[9]

The material balance is partly accounted for by high boiling liquid (2.5 g., 15–19%), $n^{20}_{\rm D}$ 1.4930–1.5069, which is probably a mixture of olefin and unreacted dichloride.

***trans*-2-Chloro-*cis*-cyclopentane-1,3-dicarboxylic Acid.** (a) **Oxidation of *anti*-7-Chloronorbornene.**[23]—*anti*-7-Chloronorbornene (5.1 g., 0.04 mole) was dissolved in 200 ml. of acetone, and the solution stirred and cooled while sodium permanganate (30.1 g. of the trihydrate made up to 100 ml. with water) was added dropwise. After the addition of 70.6 ml. of the oxidant solution, the permanganate color was no longer discharged. The addition required an hour, and the temperature was maintained in the vicinity of 10° during this time. The cooling was continued while 25 ml. of 1:4 sulfuric acid was added, followed by sodium bisulfite to remove permanganate and manganese dioxide. Dilution with 400 ml. of water was required for the bisulfite to react readily with the last of the manganese dioxide. The resulting clear solution was extracted with a total of 800 ml. of diethyl ether, the extracts dried over sodium sulfate, and most of the ether boiled off on the steam-bath. Overnight evaporation of the residual ether caused crystallization of 4.0 g. (51.8%) of crude *trans*-2-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid. The crude product was taken up in fresh anhydrous ether, stirred with activated carbon, and filtered through Celite. Evaporation of the ether and crystallization from hot benzene–ether gave a white product of m.p. 153–154.5°, mixed m.p. with authentic[8] acid, 153–154°. The neut. equiv. found was 94.7 (calcd. for $C_5H_7Cl(COOH)_2$, 96.3).

(b) **Oxidation of *anti*-7-Chloro-*exo*-norborneol.**—The procedure of Roberts, *et al.*,[9] was followed exactly in this experiment. The oxidation of the chlorohydrin (7.05 g., 0.048 mole) yielded 7.3 g. (78.8%) of crude acid which, on recrystallization from hot benzene–diethyl ether, had m.p. 155–156°.

***anti*-7-Chloro-*exo*-norborneol.**—Three ester-rich fractions from several runs on chlorinolysis of *endo*-3-chloro-*exo*-norbornyl 2′,4′-dinitrophenyl sulfide were used in this experiment. The refractive indices, $n^{20}_{\rm D}$ 1.4840–1.4846, indicate that the material used contained about 95% chloroester. The ester (7.3 g., about 0.037 mole as pure ester) dissolved in 100 ml. of anhydrous ether was added dropwise, over a period of 15 minutes, to a large excess (2.9 g.) of lithium aluminum hydride in 125 ml. of ether. After 2 hours at room temperature, water was added carefully to the stirred mixture until the white precipitate agglomerated. The mixture was then filtered with suction and the residue washed with an additional 500 ml. of ether. The ether solution was dried over sodium sulfate and most of the solvent stripped off at atmospheric pressure. Heating the residue to 92° at 10 mm. and cooling gave 5.1 g. of crude, solid *anti*-7-chloro-*exo*-norborneol. Vacuum sublimation of this residue gave 5.0 g. (about 93%) of chlorohydrin, m.p. 70–78°. Further purification was not attempted, but instead the product was identified by converting part of it to the α-naphthylurethan, m.p. 138–139° (lit.[9] m.p. 138–139°), and oxidizing part of it to *trans*-2-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid.

Chlorinolysis of Nortricyclyl 2,4-Dinitrophenyl Sulfide, (a) **Nortricyclyl Chloride.**—Following the technique described for the chlorinolysis of the 1:1 adduct III, chlorinolysis of the tricyclene derivative (IV, 38.8 g., 0.133 mole) in 250 ml. of glacial acetic acid and 10 ml. of water gave 5.5 g. (32.3%) of nortricyclyl chloride, b.p. 75–85° (38.6 mm.), $n^{15.5}_{\rm D}$ 1.4972 (lit.[13] b.p. 60.4–61.0° at 32 mm., $n^{25}_{\rm D}$ 1.4948). It was identified by its infrared spectrum[13] which showed several per cent. carbonyl impurity, and by hydrolysis (see below). The material balance is partly accounted for by 5.5 g. of a product of b.p. 92–95° (12 mm.), $n^{20}_{\rm D}$ 1.4778, which gives a positive hydroxamic acid test and shows strong infrared absorption at 5.75–5.85 and 12.3 μ. This by-product is probably nortricyclyl acetate, but no effort was made to identify it more conclusively.

(b) **3-Hydroxynortricyclene.**—The product from the above chlorinolysis (5.30 g., 0.041 mole) was refluxed with 7.0 g. of lithium carbonate and 200 ml. of water for 80 hours. The cooled reaction mixture was extracted repeatedly with a total of about 800 ml. of ether, and the extracts dried over sodium sulfate. Most of the solvent was removed by distillation, and the remainder was allowed to evaporate by stirring and warming in a gentle air stream. The residue gave 3.49 g. of oily crystals which were quickly pressed free of oil on a clay plate to give 2.74 g. (60.3%) of tan, waxy solid. Part of this solid was converted to the phenylurethan, m.p. 145.2–147.0°, after recrystallization from benzene–petroleum ether (lit.[13] m.p. 146–147.5°), and the remainder was repeatedly sublimed. The sublimation entailed considerable loss and was not exceptionally effective in the purification of this compound; the 3-hydroxynortricyclene had m.p. 98–105° (sealed tube) (lit.[13] m.p. 107.8–108.8). The infrared spectrum of the sublimed product was identical with the published spectrum[13] of this alcohol.

Addition of 2,4-Dinitrobenzenesulfenyl Bromide to Norbornene. (a) ***endo*-3-Bromo-*exo*-Norbornyl 2′,4′-Dinitrophenyl Sulfide.**—A solution of 2,4-dinitrobenzenesulfenyl bromide (130 g., 0.466 mole) in 400 ml. of dry ethylene chloride was added dropwise to a stirred solution of norbornene (50 g., 0.532 mole) in 50 ml. of the same solvent. The tem-

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[23] S. F. Birch, W. J. Oldham and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

perature was maintained at 15–20° by ice-bath cooling, and the addition was made during 5 hours. The precipitate was filtered off and washed with 200 ml. of carbon tetrachloride. After air drying, 142 g. (81.4%) of 1:1 adduct, m.p. 170–173°, was obtained. Repeated crystallization from ethylene chloride gave an analytical sample with m.p. 173.8–174.8.

Anal. Calcd. for $C_{13}H_{13}O_4N_2SBr$: Br, 21.42. Found: Br, 21.51.

Additional crude yield of the product was obtained by concentrating the filtrate, dissolving the residue in 150 ml. of hot benzene, charcoaling and filtering, and diluting the resulting solution to three times its volume with ethanol. Cooling gave 9.5 g. (5.5%) of less pure adduct melting in the range 167–172°.

(b) **Nortricyclyl 2,4-Dinitrophenyl Sulfide.**—The filtrate from the second crop of crude adduct yielded, on evaporation of solvent, a mixture. By applying the flotation method of separation, 5.8 g. (4.3%) of crude nortricyclene derivative, m.p. 139–142°, could be obtained. Recrystallization from alcohol gave a good recovery of pure nortricyclyl 2,4-dinitrophenyl sulfide, m.p. 143–144.5°. This melting point was undepressed by mixture with the purified by-product IV from the addition of 2,4-dinitrobenzenesulfenyl chloride to norbornene.

Chlorinolysis of *endo*-3-Bromo-*exo*-norbornyl 2′,4′-Dinitrophenyl Sulfide. (a) ***anti*-7-Bromo-*exo*-2-Chloronorbornene.**—*endo*-3-Bromo-*exo*-norbornyl 2′,4′-dinitrophenyl sulfide (128.1 g., 0.343 mole) dissolved in 500 ml. of glacial acetic acid and 22 ml. of water was chlorinolyzed in the usual way. Vacuum distillation of the product (using a Skinner–Noyes column) gave 4.8 g. (8.1%) of nortricyclyl bromide, b.p. 41° (0.7 mm.), n^{25}_{D} 1.5282 (lit.[14] b.p. 81.5–82.2° at 30 mm., n^{25}_{D} 1.5269), identified by its infrared spectrum,[14] and 26.6 g. (36.9%) of *anti*-7-bromo-*exo*-2-chloro-norbornane, b.p. 40–42° (0.65 mm.), n^{25}_{D} 1.5317–1.5332. Repeated redistillation of this compound gave indication of an impurity of low refractive index, but the bulk of the material always boiled in the range 38–40° (0.6–0.7 mm.), n^{25}_{D} 1.5328–1.5333. The analytical sample had n^{25}_{D} 1.5330; its total halogen was calculated on the assumption that the ratio of chlorine to bromine in the sample was exactly 1:1.

Anal. Calcd. for $C_7H_{10}ClBr$: C, 40.13; H, 4.81; halogen, 55.08; MR_{D}, 42.8. Found: C, 40.22; H, 4.77; halogen, 54.94; MR_{D}, 42.6.

The infrared spectrum of the analytical sample showed freedom from ester impurity.

(b) ***anti*-7-Bromo-*exo*-norbornyl Acetate.**—After distillation of the dihalide fraction there was a sharp rise in the head temperature and 25.7 g. (32.1%) of distillate was obtained, b.p. 61–67° (0.6 mm.), n^{25}_{D} 1.5098–1.5071. These cuts gave a strong hydroxamic acid test. They were combined with high boiling fractions from another run and redistilled. Early cuts apparently were contaminated with much dihalide, n^{20}_{D} 1.5162–1.5108, but the last half of the distillate had practically constant refractive index: n^{20}_{D} 1.5089–1.5076. The cut with n^{20}_{D} 1.5076 was carefully redistilled into four approximately equal cuts. The last three cuts were pure *anti*-7-bromo-*exo*-norbornyl acetate, b.p. 44–46° (0.10–0.2 mm.), n^{20}_{D} 1.5067–1.5064.

Anal. Calcd. for $C_9H_{13}O_2Br$: C, 46.37; H, 5.62; Br, 34.28; MR_{D}, 48.8. Found: C, 46.50; H, 5.55; Br, 33.90; MR_{D}, 48.7.

The infrared spectrum shows strong carbonyl absorption at 5.6–6.0 μ.

Dehydrohalogenation of *anti*-7-Bromo-*exo*-2-chloronorbornane. (a) ***anti*-7-Bromonorbornene.**—The optimum conditions for this reaction were the following: *anti*-7-bromo-*exo*-2-chloronorbornane (27 g., 0.129 mole) was refluxed for 11 hours with a solution of potassium *t*-butoxide prepared from 0.129 g. at. of potassium and 170 ml. of *t*-butyl alcohol. The charge was then poured into 250 ml. of distilled water and the mixture extracted with a total of 750 ml. of low boiling petroleum ether. The extracts were combined, washed three times with 50-ml. portions of distilled water, separated carefully, and dried over calcium chloride. Solvent was then removed by distillation at atmospheric pressure, and the residue distilled at reduced pressure through a Skinner–Noyes column to give, after removal of residual solvent, 14.8 g. of distillate, b.p. 84–93° (37 mm.). This contained a considerable amount of unreacted dihalide, but the unsaturated bromide obtained, when redistilled, gave a series of cuts within a relatively narrow refractive index range. No further attempt was made to obtain olefin bromide of any greater purity. Cuts with refractive indices equal to or greater than 1.4988 were used in the conversion to alcohol.

(b) **7-Hydroxynorbornane.**—A sample of the above unsaturated bromide (10.7 g.), 350 ml. of water and 10 g. of calcium carbonate were refluxed for 38 hours. Ether extraction and evaporation of the dried solution yielded 4.2 g. of oily crystals which gave a negative 2,4-dinitrophenylhydrazine test. The sublimed product also showed no carbonyl absorption in the infrared, melted at 107–113° (sealed tube) and rapidly decolorized bromine in carbon tetrachloride. All the material was dissolved in 100 ml. of ethyl acetate, 10–20 mg. of platinum oxide was added, and the solution was shaken under 50 lb. of hydrogen for three hours. Filtration and distillation left a dark residue which, on sublimation, gave 2.1 g. of white, waxy 7-hydroxynorbornane, m.p. 137–141°. This product did not decolorize bromine in carbon tetrachloride. A portion was converted to the α-naphthylurethan, m.p. 152.5–153.5° (from carbon tetrachloride), and the remainder was recrystallized from small volumes of low boiling petroleum ether. Three recrystallizations gave a product of m.p. 150.5–151.5° (lit.[16] m.p. 150–151). The infrared spectrum of this alcohol compares favorably with that of a sample of 7-hydroxynorbornane prepared by a different method.[14]

Addition of *p*-Toluenesulfenyl Chloride to Norbornene. (a) ***endo*-3-Chloro-*exo*-norbornyl *p*-Tolyl Sulfide.**—Norbornene (70 g., 0.744 mole) in 200 ml. of carbon tetrachloride was added dropwise to a stirred, cooled solution of *p*-toluenesulfenyl chloride (97.5 g., 0.615 mole) in 200 ml. of carbon tetrachloride. The addition was carried out over a period of 35 minutes while the temperature was held below 20°. After standing several days the resulting solution had yielded no precipitate and the solvent was largely removed by distillation at the water-pump. The residual oil could not be induced to crystallize, and approximately 45 g. of it was distilled. After removal of the last trace of solvent, 42.7 g. of the product distilled entirely in the range 129–133° (0.7 mm.), n^{20}_{D} 1.5801–1.5833. A residue of 1.2 g. of viscous black oil remained. The infrared spectra of the first and last cuts were obtained and compared. They were identical, indicating the absence of any large amount of second product. A sample of the adduct prepared by Cristol and Brindell[6,24] by a slightly different method was compared with these cuts. The infrared spectra were all identical.

(b) ***endo*-3-Chloro-*exo*-norbornyl *p*-Tolyl Sulfone.**—*endo*-3-Chloro-*exo*-norbornyl *p*-tolyl sulfide, n^{20}_{D} 1.5808 (6.24 g., 0.025 mole), was dissolved in 200 ml. of glacial acetic acid. Hydrogen peroxide (41 ml., 30–35%) was added and the mixture heated on the steam-bath for two hours, filtered from a slight flocculent precipitate, and let stand for 17 hours. Mixing the solution with four times its volume of water yielded a white precipitate which, after filtration and vacuum desiccation, weighed 6.6 g. (93.8% yield) and had the m.p. 112.5–114°. The product was best recrystallized from carbon tetrachloride–petroleum ether mixture: m.p. 115–117°, white coarsely crystalline solid.

Anal. Calcd. for $C_{14}H_{17}O_2SCl$: C, 59.04; H, 6.02; Cl, 12.45; Found: C, 59.00; H, 6.10; Cl, 12.30.

The mixed melting point of the analytical sample with the compound prepared by Cristol and Brindell[6,24] was 114.5–117°.

Chlorinolysis of *endo*-3-Chloro-*exo*-norbornyl *p*-Tolyl Sulfide.—(a) ***anti*-7-*exo*-2-Dichloronorbornane.**—The adduct (125.7 g., 0.497 mole) in 500 ml. of acetic acid and 25 ml. of water was treated with chlorine and the mixture worked up in the usual manner. In this case, since *p*-toluenesulfonyl chloride is soluble in low boiling petroleum ether, the products were more difficult to purify than usual. Solvent was removed at aspirator pressure, and the residue then rapidly distilled at about 1.5 mm. pressure to free the products from the bulk of the sulfonyl chloride; 73.9 g. of distillate was obtained. Redistillation through a Skinner–Noyes column gave 3.6 g. (5.7%) of fairly pure nortricyclyl chloride, n^{25}_{D} 1.4920–1.4942, which was identified by its infrared spectrum (the spectrum showed a small amount of carbonyl impurity), followed by 30.5 g. (37.2%) of crude *anti*-7-*exo*-2-dichloronorbornane, b.p. 70–82° (6.6 mm.), n^{20}_{D} 1.5059–1.5068. Redistillation of this product through a 6″ Widmer column

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(24) Sample kindly provided by Dr. Cristol.

gave the pure dichloride, b.p. 58–60° (5.7 mm.), $n^{20}D$ 1.5090–1.5094. Its infrared spectrum showed no carbonyl and identified it with the dichloride obtained on chlorinolysis of the 2,4-dinitrobenzenesulfenyl chloride adduct.

The molar refraction and dipole moment of the dichloride were measured on the product from this run since it is the purest sample obtained; MR_D: calcd., 39.9; found, 39.7.

(b) *anti*-7-Chloro-*exo*-norbornyl Acetate.—The residue from the distillation of the dichloride was distilled through the 6" Widmer to give 20.5 g. of distillate, $n^{20}D$ 1.5051–1.4868. These cuts were systematically refractionated in the manner described previously. 3.3 g. of practically pure chloroacetate, b.p. 40.3° (0.2 mm.), $n^{20}D$ 1.4842, was obtained. The infrared spectrum of this cut showed it to be identical with the chloroester previously obtained.

Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Norbornene in Acetic Acid.—To a stirred solution of norbornene (20 g., 0.213 mole) in 50 ml. of glacial acetic acid was added, dropwise, a solution of 2,4-dinitrobenzenesulfenyl chloride (45.0 g., 0.192 mole) in 600 ml. of acetic acid. The addition was made during 4 hours, to keep the temperature low (26°). A yellow precipitate was filtered off and washed with hot carbon tetrachloride to give 3.2 g. (5.0%) of product of m.p. 164–166°, mixed m.p. with known *endo*-2-chloro-*exo*-norbornyl 2,4-dinitrophenyl sulfide, 164.5–167°.

The filtrate was stirred into 2 l. of water; the oily mass which separated was extracted repeatedly with about 2 l. of benzene. The benzene extract, after washing with water, sodium carbonate solution, and again with water, was concentrated to 300 ml. The remainder of the benzene was allowed to evaporate. The orange oil which was obtained in that way failed to crystallize on long standing. When recrystallization from hot ethanol was attempted, it was found that an oil separated as the solution cooled, and then a solid appeared after long standing. The entire mass was then extracted repeatedly with ethanol by boiling, cooling, decanting the clear solution, and allowing crystallization to proceed. This lengthy process gave 35.3 g. of product in four crops with long, indefinite melting ranges, *ca.* 80–140°. The oil was discarded.

A portion of the yellow solid was crystallized repeatedly from hot carbon tetrachloride to give, in minute quantity, a solid with constant m.p. of 191.5–192.5°. The amount of this product was too small to warrant further work.

Another portion of the yellow solid was chromatographed on an 18 × 1000 mm. column of alumina. Benzene elution, followed by evaporation of solvent, gave, from 1.0 g. of starting mixture, 0.9 g. of a mixture with the m.p. 115–130°. Purification by the flotation and recrystallization method previously described gave nortricyclyl 2,4-dinitrophenyl sulfide, m.p. 142–144°, mixed m.p. with an authentic specimen, 142.5–143.5°, and a small amount of the high melting (185–190° after three recrystallizations) compound. Analysis of the crude first fraction from another chromatogram showed 0.91% chlorine, indicating that the nortricyclyl compound is the main constituent of the yellow solid. The last fraction from the chromatography was an oil; it contained no chlorine at all, as evidenced by a negative Beilstein test, and is therefore probably an unsaturated sulfide.

NEWARK, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Terpenoids. XXV.[1] The Structure of the Cactus Triterpene Dumortierigenin[2,3]

BY CARL DJERASSI, C. H. ROBINSON[4] AND D. B. THOMAS[5]

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Degradative evidence coupled by a direct conversion to erythrodiol has led to the structure elucidation of dumortierigenin, a hexacyclic triterpene isolated from the Mexican cactus *Lemaireocereus dumortieri*. Dumortierigenin is the 28 → 15-lactone of 15β,22α-dihydroxyoleanolic acid and attention is called to the pronounced shielding effect of the lactone ring upon the 12–13 double bond.

The preliminary characterization of dumortierigenin, a triterpenoid lactone isolated from the Mexican cactus *Lemaireocereus dumortieri*, has already been reported in an earlier paper.[6] No definite decision could be made at that time[6] between the empirical formulas $C_{30}H_{46}O_4$ and $C_{30}H_{48}O_4$, but it will now be shown that the former is correct. The four oxygen atoms were demonstrated to be present as a five-membered lactone ring and as two secondary hydroxyl groups. Evidence was also adduced that both alcoholic functions are equatorially oriented and attached to six-membered rings and that one of them is almost certainly present as the conventional 3β-hydroxyl group. The relative accessibility of this cactus[6] has permitted the isolation of adequate amounts of this triterpene and the present communication is concerned with its structure elucidation.

The probable presence of a double bond in dumortierigenin was indicated[6] by the high terminal ultraviolet absorption[7] and by a weak coloration with tetranitromethane observed with certain dumortierigenin derivatives (though not with the parent lactone). The absence of any perceptible reaction[6] with perbenzoic acid did not shed any further light on this point since triterpenes of the α-amyrin series react only very slowly under those conditions.[8] Direct proof for the presence of the typical 12–13 double bond was provided by the course of the chromium trioxide oxidation of dumortierigenin diacetate which led to an α,β-unsaturated ketone. It should be noted that the ultraviolet absorption maximum (241 mμ) occurred at a lower wave length than is usually observed (*ca.* 250 mμ) for 11-keto-Δ^{12}-triterpenes[9] and this suggested the influence of some additional structural feature upon this chromophore.[10] Dumortierigenin diacetate did not react with selenium dioxide in glacial acetic solution under conditions

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[1] Paper XXIV, C. Djerassi, J. A. Henry, A. J. Lemin, T. Rios and G. H. Thomas, THIS JOURNAL, **78**, 3783 (1956).

[2] We are indebted to the National Science Foundation for financial support.

[3] Presented at the Symposium on Recent American Terpene Research at the Dallas A.C.S. Meeting, April 11, 1956.

[4] Postdoctorate research fellow, 1954–1955.

[5] Postdoctorate research fellow, 1955–1956.

[6] C. Djerassi, E. Farkas, A. J. Lemin, J. C. Collins and F. Walls, THIS JOURNAL, **76**, 2969 (1954).

[7] T. G. Halsall, *Chemistry & Industry*, 867 (1951).

[8] *Cf.* L. Ruzicka, H. Silbermann and M. Furter, *Helv. Chim. Acta*, **15**, 482 (1932).

[9] For leading references see C. R. Noller, THIS JOURNAL, **66**, 1269 (1944).

[10] 11-Keto-A_1-barrigenyl pentaacetate (A. R. H. Cole, D. T. Downing, J. C. Watkins and D. E. White, *Chemistry & Industry*, 254 (1955)) exhibits a maximum at 245 mμ.