product in crystalline form. A variety of solvents were tried for recrystallization without success, but it was found that treatment with methyl acetate or ethyl acetate gave a crystalline substance. These products contained solvent of crystallization and a constant analysis could not be obtained. The product from ethyl acetate (colorless plates, m.p. 225–257°) showed a carbonyl ester band in the infrared. The solvated products were not studied in greater detail. Acetylation of the non-crystalline product to yield acetylandromedotoxin was not successful.

Periodate Oxidation Studies.—A study of the periodate oxidation of andromedotoxin in buffered solution (acetic acid–sodium acetate) at *p*H 4.7 was carried out,[12] using 0.0885 g. of andromedotoxin with 50 ml. of 0.0100 *M* sodium metaperiodate solution.

A consumption of 0.61 mole of periodate per mole of compound resulted after 45 minutes. The oxidation stopped at 0.70 mole after 1.5 hours.

The same oxidation method was applied to the amorphous hydrolysis product of andromedotoxin and to acetylandromedotoxin, and in these cases the addition of ethanol was necessary. The hydrolysis product used 0.36 mole of periodate in 50 minutes, and the oxidation was complete at 0.70 mole after 4 hours. With acetylandromedotoxin, a consumption of 0.04 mole of periodate resulted after 22 hours.

Lead Tetraacetate Oxidation Studies.—The oxidation of andromedotoxin (0.1768 g.) in acetic acid solution (100 ml. of total volume) with lead tetraacetate solution (50 ml. of 0.1 *N* solution) was followed at 20°. The lead tetraacetate used in the oxidation was 0.65, 0.89, 0.93 and 1.1 moles for periods of 18 minutes, and 4, 18 and 29 hours, respectively.

Dehydrogenation Studies.—Catalytic dehydrogenation (Pd catalysts) under relatively mild conditions (up to about 250°) did not result in the formation of recognizable aromatic products. Selenium dehydrogenations at elevated temperatures gave low yields of non-crystalline material.

BETHESDA, MARYLAND

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[12] E. L. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 361.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

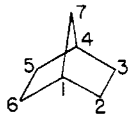
Some Chlorine Derivatives of Norbornane (Bicyclo[2.2.1]heptane)

BY JOHN D. ROBERTS,[1a] FREDERICK O. JOHNSON AND RUDOLPH A. CARBONI[1b]

RECEIVED APRIL 23, 1954

The *endo-cis* and *trans*-5,6-dichloronorbornenes were prepared by the respective additions of *cis*- and *trans*-dichloroethylene to cyclopentadiene. The stereochemical assignments were confirmed by dipole moment studies. The *cis*-dichloride was inert to hydrolysis while the *trans* isomer was hydrolyzed to 3,5-dihydroxynortricyclene. Hydrogenation of the dichloride isomers gave the *endo-cis*- and *trans*-2,3-dichloronorbornanes. Contrary to expectations based on preferential *trans*-elimination of hydrogen halide, the saturated *cis*-dichloride appeared to dehydrohalogenate somewhat less readily than the *trans* isomer, although the reaction was slow in both cases. Both isomers gave the same dehydrohalogenation product, 2-chloronorbornene, the structure of which was confirmed by oxidation to *cis*-cyclopentane-1,3-dicarboxylic acid and hydrolysis to norcamphor. Chlorination of norbornene at −75° gave nortricyclyl chloride and *syn*-7-*exo*-2-dichloronorbornane. The structure of the latter was assigned (in preference to *exo-cis*-2,3-dichloronorbornane) because of the compound's relative inertness to dehydrohalogenating reagents. *endo-cis*-2,3-Dichloronorbornane was not readily hydrolyzed, but *trans*-2,3-dichloronorbornane and *syn*-7-*exo*-2-dichloronorbornane hydrolyzed to *anti*- and *syn*-7-*exo*-2-norborneol, respectively. The *syn*-isomer also was obtained by addition of hypochlorous acid to norbornene. The structures of the chloro alcohols were inferred from their modes of formation and oxidation to chlorine-containing dicarboxylic acids which were presumed to be, respectively, *trans*- and *cis*-2-chloro-*cis*-cyclopentane-1,3-dicarboxylic acids. These acids were different from *trans*- and *cis*-4-chloro-*cis*-cyclopentane-1,3-dicarboxylic acids obtained by oxidation of *exo*- and *endo*-dehydronorbornyl chlorides, respectively. The chloro alcohols also were oxidized to the corresponding ketones, *anti*- and *syn*-7-chloronorcamphor. The assignments of the *syn* and *anti* configurations to the ketones were confirmed by dipole moment measurements. The *syn*- and *anti*-chlorohydrins were converted by pyrolysis of their carboxylic acid esters in low yield to *syn*- and *anti*-7-chloronorbornenes. Each of the latter substances on hydrogenation gave the same compound, 7-chloronorbornane.

Until recently, very little was known about the chemistry of vicinal-*cis*-alicyclic dihalides and the present research was concerned with the synthesis of such compounds by addition of appropriately substituted ethylenes to cyclopentadiene along lines laid out by Alder and Rickert.[2] It was planned originally to study the rates and mechanisms of elimination reactions of such compounds, but, in view of the recent elegant investigations of Professor Cristol and co-workers[3] on similar substances this objective has been abandoned in favor of a more general survey of the chemistry of chlorine-substituted norbornanes[4] (bicyclo[2.2.1]heptane derivatives, I).



I

Cyclopentadiene and *cis*-dichloroethylene at 190° for 17 hours in a steel bomb gave 8–11% yields of solid *endo-cis*-5,6-dichloronorbornene (II). Some (3–4%) of lower-boiling material was isolated and shown by its infrared spectrum to be *trans*-5,6-dichloronorbornene (III). Formation of III in this reaction was due presumably to partial conversion of *cis*- to *trans*-dichloroethylene. This isomerization is known to occur under the influence of heat[5] and free-radical catalysts.[6] None of the *trans*-adduct was formed when the addition was carried out in a sealed glass tube. *trans*-5,6-Dichloronorbornene (III) was prepared in 34% yield by heating cyclopentadiene and *trans*-dichloroethylene in a steel bomb with a glass liner at 190–195° for 24 hours. The assignment of the *endo* configuration to the *cis*-dichloride was made in accordance with the Alder

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[1] (a) Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, Calif.; (b) U. S. Rubber Company Predoctoral Fellow.

[2] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

[3] We are indebted to Professor S. J. Cristol for much helpful information in advance of publication.

[4] In this paper, we use the nomenclature suggested for bicyclo-[2.2.1]heptane by A. M. Patterson, *Chem. Eng. News*, **30**, 930 (1952).

[5] R. E. Wood and D. P. Stevenson, THIS JOURNAL, **63**, 1650 (1941).

[6] R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

rules.[7] The *cis*- and *trans*-chlorine configurations assigned to II and III were confirmed by dipole moment measurements (Table I). The experimental moment for the *endo-cis*-dichloride II was found to be substantially smaller than the calculated value. The difference may be due to the same factors which have been used previously to account for the abnormally low dipole moments of other vicinal dihalides such as *o*-dichlorobenzene.[8]

TABLE I

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS (25°)

Substance	MR_D	P_∞	μ, debyes Exptl.	μ, debyes Calcd.
endo-cis-5,6-Dichloronorbornene	38.6	241.5	3.15	3.92[a]
trans-5,6-Dichloronorbornene	39.1	132.4	2.14	1.97[a]
syn-7-Chloronorcamphor	35.2	269.6	3.39	4.29[b]
anti-7-Chloronorcamphor	34.7	134.9	2.21	1.55[b]

[a] Calculated assuming tetrahedral angles and 2.08 *D* for the vector moment of the C–Cl bond as in cyclopentyl chloride.[18] [b] Calculated using Fig. 2 and values for vector moments as described in text.

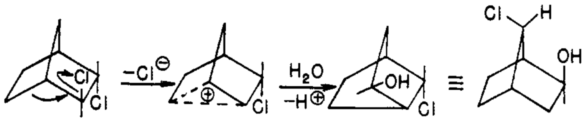
The *endo-cis*-dichloride II was not hydrolyzed by boiling water in 60 hours and liberated almost no halide ion on attempted dehydrohalogenation under reflux with 20% potassium hydroxide–80% absolute methanol for 24 hours. Hydrogenation of II gave a 90% yield of *endo-cis*-2,3-dichloronorbornane (IV). The saturated dichloride IV reacted with zinc in refluxing acetamide to give norbornene in 40% yield. No reaction was observed with zinc in refluxing ethanol. It may be inferred from this reaction that the *trans*-concerted mechanism[9] proposed for the elimination reactions of 1,2-dihalides with zinc is not required in this system.

The saturated dichloride IV did not hydrolyze when refluxed with water for three days but did undergo slow dehydrohalogenation when refluxed with 20% potassium hydroxide–80% methanol for 24 hours. A 9% yield of 2-chloronorbornene (V) was obtained. The structure of V was confirmed by oxidation to *cis*-cyclopentane-1,3-dicarboxylic acid and hydrolysis to norcamphor with water in a sealed tube at 250°. *trans*-5,6-Dichloronorbornene (III) with water at the reflux temperature for two days yielded 37% of a dihydroxy compound presumed to be 3,5-dihydroxynortricyclene (VI). The structure of VI was assigned on the basis of a negative 1,2-glycol test (periodic acid), infrared spectrum and elemental analyses. The formation of VI may be formulated by a mechanism similar to that proposed for the formation of nortricyclanol from dehydronorbornyl chloride.[10] Permanganate oxidation of the *trans*-dichloride III gave *trans*-4,5-dichloro-*cis*-cyclopentane-1,3-dicarboxylic acid,

Hydrogenation of the *trans*-dichloride III gave an 85% yield of *trans*-2,3-dichloronorbornane (VII). The saturated dichloride VII reacted with zinc in refluxing acetamide to give norbornene. No reaction occurred with zinc in refluxing ethanol. We detected no qualitative difference in the activity of the *cis*- and *trans*-vicinal dichloronorbornanes with zinc.

The saturated *trans*-2,3-dichloride VII was not dehydrohalogenated by refluxing quinoline in two hours. However, it did react with 20% potassium hydroxide–80% absolute ethanol at the reflux temperature and, after 30 hours, a 20% conversion to 2-chloronorbornene (V) occurred. Qualitatively, it appears that the *trans*-dichloride VII is dehydrohalogenated 2–3 times faster than its *endo-cis* isomer IV. This order of reactivity is anomalous with regard to the usual preference for *trans*-dehydrohalogenation in second-order alkaline elimination reactions of alicyclic halides.[11] However, analogous results have been obtained in the elimination reaction with *cis*- and *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes and rationalized by Cristol and Hause.[12]

The saturated *trans*-dichloride VII hydrolyzed slowly on boiling with water to give a solid chlorohydrin VIII. This chlorohydrin was clearly not *trans*-2-hydroxy-3-chloronorbornane since on oxidation with permanganate it gave a solid dicarboxylic acid whose neutral equivalent and elemental analysis were consistent for a chlorocyclopentanedicarboxylic acid. It is here assumed that the chlorohydrin VIII has the structure *anti*-7-chloro-*exo*-2-norborneol and is formed by way of a non-classical chlorine-substituted "norbornonium" cation[13] (IX) resulting from solvolysis of the *exo*-chlorine of VII as shown in the following sequence of reactions. Further evidence for the structure of VIII will be presented later.



VII IX VIII

Schmerling[14] has reported that norbornene reacts with chlorine in *n*-pentane at −75° to yield two products in the approximate ratio of 5 to 3. The lower-boiling product was presumed to be 2-chloronorbornene since, on hydrolysis, it gave norcamphor. The higher-boiling substance was a previously unknown saturated dichloride which was not assigned a definite structure. Schmerling's preparation was repeated as part of the present investigation to determine whether his products were the same as the 2-chloronorbornene and *trans*-2,3-dichloronorbornane obtained in the present work. The supposed "2-chloronorbornene" was found to be actually nortricyclyl chloride (X) and was identified by comparison of its infrared spectrum with that of an authentic sample.[15] The mechanism for formation of nortricyclyl chloride in the reaction of chlorine

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[7] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[8] See, for example, O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 489 (1947).

[9] *Cf.* W. G. Young, S. J. Cristol and T. Skei, THIS JOURNAL, **65**, 2099 (1943).

[10] J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950).

[11] S. J. Cristol, *ibid.*, **69**, 338 (1947).

[12] S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952).

[13] (a) S. Winstein and D. S. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952); (b) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); (c) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

[14] L. Schmerling, U. S. Patent 2,500,385; *C. A.*, **44**, 5391 (1950).

[15] J. D. Roberts and W. Bennett, THIS JOURNAL, **76**, 4623 (1954).

with norbornene may be similar to the ionic mechanism previously proposed for an analogous reaction which occurs in the bromination of norbornene.[16] Nortricyclyl chloride is hydrolyzed to nortricyclanol in 85% yield by boiling water. As reported by Schmerling,[14] the chloride X yields norcamphor when heated with water in a sealed tube at 250° for four hours. However, nortricyclanol also is converted to norcamphor with a trace of acid under similar conditions.

The higher-boiling product XI from the chlorination of norbornene was more difficult to identify. Its infrared spectrum (Fig. 1) clearly indicated that it was different from *trans*-2,3-dichloronorbornane and *endo-cis*-2,3-dichloronorbornane. The new dichloride was presumed to be either *exo-cis*-2,3- or *syn*-7-*exo*-2-dichloronorbornane since it behaved like a homogeneous substance. A possible mechanism for the formation of the latter two compounds in the chlorination of norbornene is given below, which is in accord with the behavior of the norbornyl system in other reactions.[10,13,16]

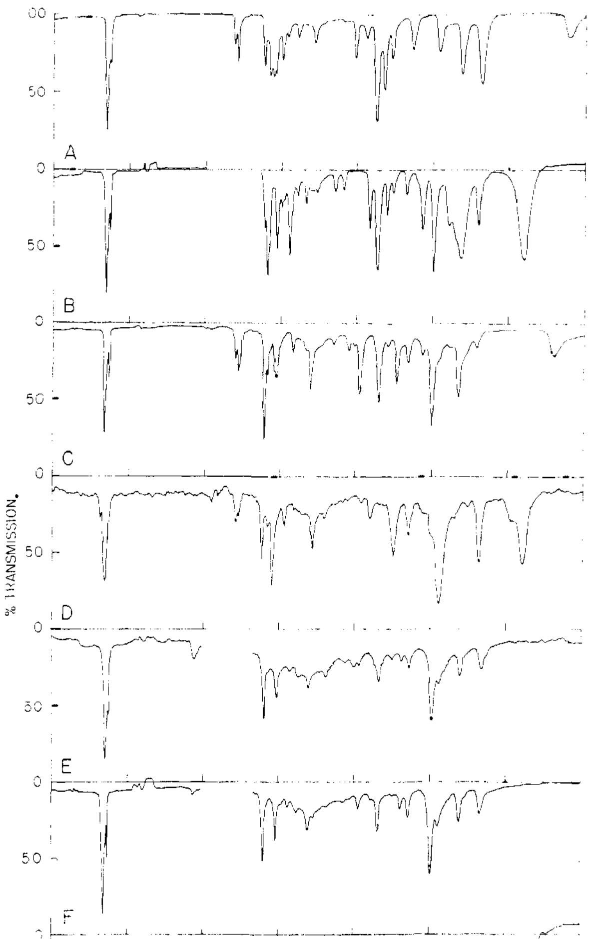
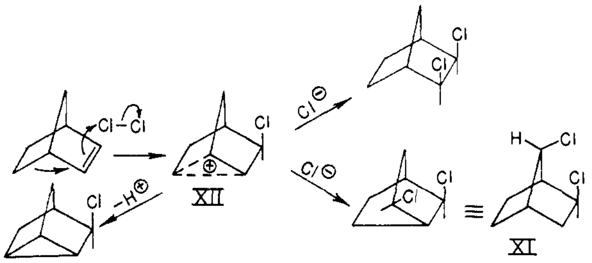


Fig. 1.—Infrared spectra: Baird spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of CS_2 except in the region 6.2–7.5 μ where CCl_4 was used as solvent: A, *endo-cis*-2,3-dichloronorbornane (IV); B, *trans*-2,3-dichloronorbornane (VII); C, *syn-exo*-2,7-dichloronorbornane (XI); D, *anti*-7-chloronorbornene (XVIII); E, 7-chloronorbornane (XX) from hydrogenation of XVIII; F, 7-chloronorbornene (XX) from hydrogenation of XIX; G, *syn*-7-chloronorbornene (XIX).



The chloronorbornyl cation XII is presumed to be formed in the slow step of the reaction and is here assigned the chlorine in the *exo* configuration since introduction of chlorine in this manner would facilitate the formation of the non-classical cation. Cation XII is a stereoisomer of IX. In accordance with the usual stereospecific behavior of the norbornyl cation, the second chloride ion in attacking C-1 or C-2 of XII is expected to assume the *exo* configuration.

Schmerling's dichloride XI was not easily dehydrohalogenated at the reflux temperature with 20% potassium hydroxide–80% methanol in 30 hours. Most of the starting dichloride was recovered and only a very small amount of unsaturated material appeared to be formed. The dichloride reacted with zinc in refluxing acetamide and, although some unsaturated material appeared to result, there was no evidence of norbornene in the reaction product. Since XI was not dehalogenated to norbornene with zinc and did not dehydrohalogenate to give a significant amount of 2-chloronorbornene, it was assigned the structure *syn*-7-*exo*-2-dichloronorbornane in preference to *exo-cis*-2,3-dichloronorbornane.

syn-7-*exo*-2-Dichloronorbornane (XI) hydrolyzed slowly to a chlorohydrin which was shown by its infrared spectrum and derivatives to be different from the hydrolysis product VIII of *trans*-2,3-dichloronorbornane (VII). The chlorohydrin XIII derived from the 2,7-dichloride was clearly not 2-hydroxy-3-chloronorbornane since it, like chlorohydrin VIII, gave on oxidation a chlorodicarboxylic acid which from its neutral equivalent, analysis and mode of formation was assigned the structure *cis*-2-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid. The acid was different from the chlorodicarboxylic acid derived from the oxidation of chlorohydrin VIII. The formation of a chlorohydrin XIII different from chlorohydrin VIII is to be expected in the hydrolysis of the dichloride XI if the non-classical cation XII is the first intermediate and subsequently reacts with water at the 2-position. Considerable support for this mechanism is afforded by the observation that chlorohydrin XIII is obtained

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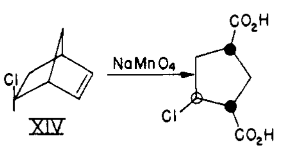
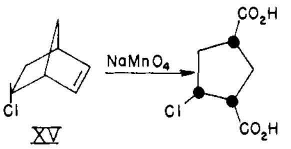
[16] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, This Journal, **72**, 3116 (1950).

directly by addition of hypochlorous acid to norbornene. The small possibility that the chlorines in chlorohydrins VIII and XIII were located at the 5- or 6-positions was ruled out completely by the demonstration that the chlorocyclopentanedicarboxylic acids obtained by oxidation of the chlorohydrins were different from *cis*- and *trans*-4-chloro-*cis*-cyclopentane-1,3-dicarboxylic acids prepared by oxidation of *exo*- and *endo*-dehydronorbornyl chlorides XIV and XV, respectively.

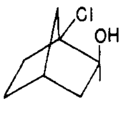


XIV

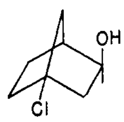


XV

The only remaining possibilities for the structures of the chlorohydrins are VIII, XIII, and the bridgehead chloronorborneols XVI and XVII. Clearly, the two chlorohydrins cannot *both* be identified with structures XVI and XVII since they are oxidized to *different* chlorocyclopentane-1,3-dicarboxylic acids. Thus, both chlorohydrins could have chlorine at the 7-position or one of them could have chlorine at the 1-position and the other at the 7-position. The latter alternative was ruled out in the following way. Pyrolysis of the 2-naphthoates of the chlorohydrins VIII and XIII gave two different chloronorbornenes (XVIII and XIX, respectively) (*cf.* Fig. 1), each of which was contaminated with a small amount of nortricyclyl chloride. Catalytic hydrogenation of the chloronorbornenes gave the *same* saturated chloronorbornane (XX) from each (see Fig. 1). The production of a single chloro compound by reduction of the two different chloronorbornenes is only possible if the chlorine is located at the 7-position of the norbornane ring system. The possibility of rearrangement in the pyrolysis of the naphthoates was ruled out completely for the *syn*-7-chloronorbornene (XIX) since, on oxidation, it yielded the same chlorocyclopentane-1,3-dicarboxylic acid as was produced by oxidation of the parent chlorohydrin XIII.



XVI



XVII

Confirmation of the *syn* and *anti* configurations assigned to the above series of compounds was obtained from dipole moment studies of the chloroketones XXI and XXII derived, respectively, from chlorohydrins XIII and VIII. The dipole moments were measured at 25° in benzene solutions (Table I) and, in accord with the assigned structures, the *syn*-chloro ketone XXI has a substantially larger dipole moment than the corresponding *anti* compound XXII. Theoretical values for the dipole moments of the chloro ketones were calculated from the diagram (Fig. 2) using 2.95 D (camphor)[17] and 2.08 D (cyclopentyl chloride)[18] as the respective carbonyl and carbon–chlorine vector moments from the formulas

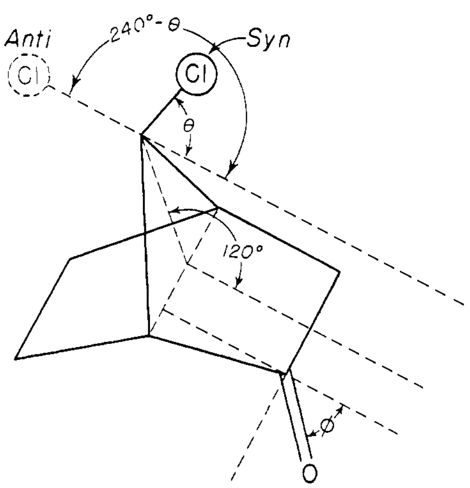


Fig. 2.—Diagram for calculation of the dipole moments of *syn*- and *anti*-7-chloronorcamphor.

$$\mu_{\text{calcd.}}\ (syn) = [(2.08)^2 + (2.95)^2 + 2(2.08)(2.95) \cos \phi \cos \theta]^{1/2}$$

$$\mu_{\text{calcd.}}\ (anti) = [(2.08)^2 + (2.95)^2 + 2(2.08)(2.95) \cos \phi \cos (240 - \theta)]^{1/2}$$

If ϕ and θ are taken to be 30 and 60°, respectively, the calculated moments of the *syn*- and *anti*-ketones are 4.29 and 1.55 D, respectively. These values are not in very good agreement with the experimental figures given in Table I which are substantially closer together. The discrepancy reasonably arises from the values assumed for ϕ and θ. Steric hindrance between the 7-chlorine and the carbon and hydrogens of the ring is certain to make θ somewhat greater than the 60° expected for a tetrahedral carbon. Furthermore, ring-strain at the 2-position will make ϕ substantially greater than 60°. Increases in θ and/or ϕ over the values assumed in the calculations tend to make the computed moments closer together and in better agreement with the experimental figures.

Solvolytic reactivities of many of the compounds here reported will be presented in detail in a later paper. Preliminary results indicate that *syn*-7-chloronorbornene (XIX) and 7-chloronorbornane (XX) are *exceptionally unreactive* compared to cyclopentyl chloride in 80% ethanol. The lack of reactivity may be attributed to steric inhibition of hyperconjugation of a cationic carbon at the 7-position with the 1- and 4-hydrogens (such resonance would involve forms violating Bredt's rule) and/or increase in angle strain in going from chloride to cation.

A flow sheet for the various reactions discussed is given in Fig. 3.

Experimental Part

***endo-cis*-5,6-Dichloronorbornene.**—A mixture of 180 g. (2.7 moles) of cyclopentadiene, 400 g. (4.2 moles) of *cis*-dichloroethylene and 0.1 g. of hydroquinone was heated in a steel bomb at 190° for 17 hours. Distillation of the crude product gave 245 g. of low-boiling liquid, 95 g. of b.p. 50–115° (23 mm.), and 130 g. of dark viscous residue. Fractional distillation of the intermediate material through a vacuum-jacketed Vigreux column gave 30 g. of material,

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(17) H. L. Donle and G. Volkert, *Z. physik. Chem.*, **8B**, 60 (1930).

(18) M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

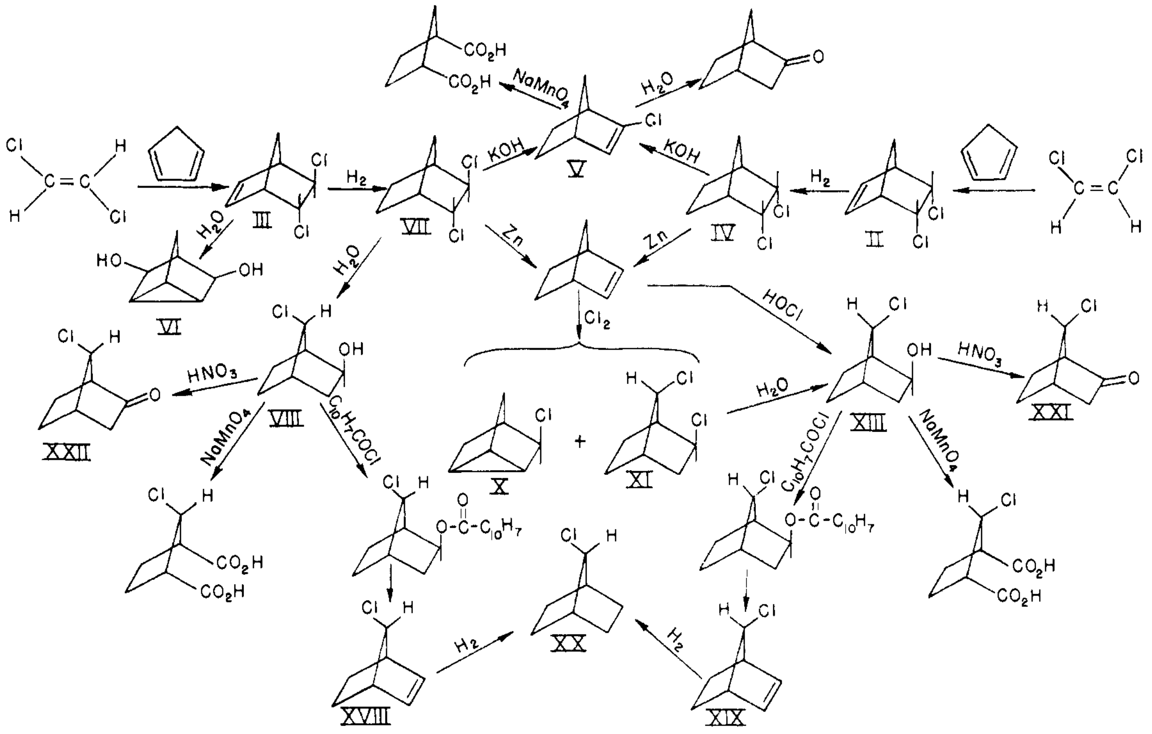

Fig. 3.—Reaction flowsheet.

b.p. 69–104° (23 mm.). The distillation residue solidified on cooling and on sublimation afforded 35 g. (8% based on cyclopentadiene) of *endo-cis*-5,6-dichloronorbornene, m.p. 70–72°. Refractionation of the forerun from the second distillation yielded 14 g. of *trans*-5,6-dichloronorbornene, b.p. 67–70° (11 mm.).

In other preparations the product was recrystallized from hexane at −75° and had m.p. 72–74°. The analytical sample was boiled with water to remove more reactive chlorides and then recrystallized from hexane, m.p. 76–77°.

Anal. Calcd. for $C_7H_8Cl_2$: C, 51.53; H, 4.91; Cl, 43.56. Found: C, 51.53; H, 4.94; Cl, 43.61.

endo-cis-5,6-Dichloronorbornene did not undergo significant dehydrohalogenation when heated under reflux with 20% potassium hydroxide in absolute methanol for 24 hours. About 85% of the starting material was recovered after boiling the *cis*-dichloride with a suspension of lithium carbonate in water for 60 hours.

endo-cis-2,3-Dichloronorbornane.—*endo-cis*-5,6-Dichloronorbornene (18 g., 0.11 mole) and 0.25 g. of platinum oxide in 100 ml. of ethyl acetate were shaken with hydrogen at 15 p.s.i. The theoretical amount of hydrogen was absorbed within 0.5 hour. The solution was filtered, most of the solvent removed under reduced pressure and the products distilled through a 10-cm. Vigreux column. The yield of *endo-cis*-2,3-dichloronorbornane, b.p. 98–105° (13–14 mm.), m.p. 74–77°, was 16.5 g. (90%). The infrared spectrum is shown in Fig. 1.

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.91; H, 6.06; Cl, 43.03. Found: C, 51.06; H, 6.19; Cl, 43.02.

endo-cis-2,3-Dichloronorbornane was not hydrolyzed readily by water and only starting material was recovered after heating the dichloride with a suspension of lithium carbonate in water for three days.

Dehalogenation of *endo-cis*-2,3-Dichloronorbornane.—A mixture of 3.5 g. (0.02 mole) of *endo-cis*-2,3-dichloronorbornane, 2 g. (0.03 gram atom) of zinc dust and 15 g. of acetamide was refluxed for 12 hours. After about 15 minutes, a white solid began to collect in the lower part of the reflux condenser and was removed from time to time. Sublimation of the solid product gave 0.8 g. (40%) of chlorine-free material which was shown by its infrared spectrum to be norbornene.

Dehydrohalogenation of *endo-cis*-2,3-Dichloronorbornane.—*endo-cis*-2,3-Dichloronorbornane (8 g., 0.05 mole) and 90 ml. of a filtered 20% potassium hydroxide–80% absolute methanol solution were heated under reflux at 85° for 25 hours. During the first five hours of the reaction, only a little chloride ion was formed. The reaction mixture was diluted with water and extracted continuously with ether for seven hours. The extract was dried over magnesium sulfate, the ether removed under reduced pressure, and the residue distilled through a semi-micro column.[19] The yield of 2-chloronorbornene was 0.9 g. (9%), b.p. 50–54° (41 mm.), $n^{25}\text{D}$ 1.4875. Sublimation of the distillation residue gave 2 g. of solid starting material.

***trans*-5,6-Dichloronorbornene.**—A mixture of 90 g. (1.35 moles) of cyclopentadiene and 210 g. (2.15 moles) of *trans*-dichloroethylene was heated in a steel bomb with a glass liner at 190–195° for 24 hours. The products of three such runs were combined and distilled through a 20-cm. vacuum-jacketed Vigreux column with a Claisen head. In addition to 340 g. of low-boiling material, 45 g. of intermediate fractions and 235 g. of high-boiling residue, there was obtained 225 g. (34% based on cyclopentadiene) of *trans*-5,6-dichloronorbornene, b.p. 76–78° (18 mm.), $n^{25}\text{D}$ 1.5101, d^{25}_4 1.2467.

Anal. Calcd. for $C_7H_8Cl_2$: C, 51.53; H, 4.91; Cl, 43.56. Found: C, 51.89; H, 5.00; Cl, 43.28.

Hydrolysis of *trans*-5,6-Dichloronorbornene.—A mixture of 14 g. (0.09 mole) of *trans*-5,6-dichloronorbornene and a suspension of 7 g. of lithium carbonate in 100 ml. of water was heated under reflux for 51 hours. Sublimation of the crude solid product gave 4.2 g. (37%) of a saturated, colorless solid, m.p. 161–163° after crystallization from benzene. The product gave a negative 1,2-glycol test with periodic acid and was presumed to be 3,5-dihydroxynortricyclene. Except for analysis, it was not further characterized.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.62; H, 7.99. Found: C, 66.56; H, 7.82.

***trans*-2,3-Dichloronorbornane.**—Low-pressure hydrogenation of 150 g. of *trans*-5,6-dichloronorbornene in 300 ml. of 99% ethyl acetate over 1.8 g. of platinum oxide proceeded rapidly and the reaction had to be stopped occasionally to prevent overheating. When the theoretical amount of hydrogen had been absorbed, the mixture was filtered and the ethyl acetate removed under reduced pressure. The product was distilled through a vacuum-jacketed Vigreux

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[19] C. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

column and in addition to 10 g. of forerun, b.p. 82–84° (18 mm.), there was obtained 130 g. (85%) of *trans*-2,3-dichloronorbornane, b.p. 85–86° (18 mm.), n^{25}D 1.5015. The infrared spectrum is given in Fig. 1.

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.91; H, 6.06; Cl, 43.03. Found: C, 50.84; H, 6.23; Cl, 43.08.

Dehalogenation of *trans*-2,3-Dichloronorbornane.—The procedure was similar to that described for the corresponding *cis*-dichloride and 10 g. of *trans*-2,3-dichlornorbornane refluxed with 4.7 g. of zinc dust and 15 g. of acetamide for 4 hours yielded 1.75 g. (31%) of norbornene (identified by infrared spectrum).

Dehydrohalogenation of *trans*-2,3-Dichloronorbornane.—*trans*-2,3-Dichloronorbornane (50 g., 0.30 mole) and 325 ml. of a filtered 20% potassium hydroxide–80% absolute methanol solution were stirred and heated under reflux at 85° for 30 hours. The mixture was diluted with water and extracted continuously with ether. The extract was dried over magnesium sulfate, the ether removed and the residue distilled through a vacuum-jacketed Vigreux column. The yield of 2-chloronorbornene, b.p. 64–66° (52 mm.), n^{25}D 1.4880, was 8.2 g. (21%).

The structure of the dehydrohalogenation product as 2-chloronorbornene was established as follows. The material was unsaturated (Baeyer test) and showed a strong infrared absorption band at 6.3 μ suggestive of an unsymmetrically-substituted double bond. Sodium permanganate oxidation yielded a solid chlorine-free organic acid, m.p. 118–120°, which did not depress the melting point of an authentic sample of *cis*-cyclopentane-1,3-dicarboxylic acid, m.p. 119–120°. Hydrolysis of 8 g. of 2-chloronorbornene in 75 ml. of water in a sealed glass tube at 250° for 4 hours yielded 3.7 g. (55%) of a waxy solid, m.p. 90–94°, identified as norcamphor by its infrared spectrum. The analytical sample of 2-chloronorbornene had n^{25}D 1.4875.

Anal. Calcd. for C_7H_9Cl: C, 65.37; H, 7.00; Cl, 27.63. Found: C, 65.01; H, 7.16; Cl, 27.36.

Hydrolysis of *trans*-2,3-Dichloronorbornane.—A mixture of 200 g. (1.20 moles) of *trans*-2,3-dichloronorbornane, 75 g. (1.0 mole) of lithium carbonate and 2.5 l. of water was heated under reflux for 5 days and then extracted continuously with ether. The extract was dried over magnesium sulfate, the ether removed and the dark-brown residue distilled through a 10-cm. Vigreux column with a Claisen head. After 60 g. of forerun, b.p. 35–112° (25 mm.), there was obtained 96 g. (55%) of crude chlorohydrin, b.p. 112–128° (25 mm.), m.p. 79–83°. The elemental analysis indicated that the crude material was somewhat contaminated with products of further hydrolysis.

Anal. Calcd. for $C_7H_{11}ClO$: C, 57.34; H, 7.51; Cl, 24.23. Found: C, 58.54; H, 7.67; Cl, 23.15.

The chlorohydrin was satisfactorily characterized as the **α-naphthylurethan**, m.p. 138–139° after recrystallization from benzene–hexane, and the ***p*-phenylazobenzoate**, m.p, 137.5–139° after crystallization from ethanol–water.

Anal. Calcd. for $C_{18}H_{18}ClNO_2$ (urethan): C, 68.46; H, 5.71; Cl, 11.25; N, 4.44. Found: C, 68.37; H, 5.86; Cl, 11.13; N, 4.56. Calcd. for $C_{20}H_{19}ClN_2O_2$ (phenylazobenzoate): C, 67.70; H, 5.36; Cl, 10.01; N, 7.90. Found: C, 67.76; H, 5.43; Cl, 9.65; N, 7.72.

The liquid forerun from the distillation of the chlorohydrin contained some ketonic material and yielded an unidentified 2,4-dinitrophenylhydrazone, m.p. 96–97.5° after crystallization from ethanol–water. The hydrazone was unsaturated and chlorine free.

Anal. Calcd. for $C_{12}H_{14}N_4O_4$: C, 53.79; H, 4.83; N, 19.31. Found: C, 53.93; H, 4.94; N, 19.13.

***trans*-2-Chloro-*cis*-cyclopentane-1,3-dicarboxylic Acid.**—*anti*-7-Chloro-*exo*-norborneol (15 g., 0.10 mole), 40 ml. of *n*-pentane, 7 g. (0.13 mole) of potassium hydroxide and 200 ml. of water were placed in an ice-cooled flask equipped with mechanical stirrer and dropping funnel. To the stirred mixture was added 66 g. (0.34 mole) of sodium permanganate trihydrate and 9 g. (0.16 mole) of potassium hydroxide dissolved in 475 ml. of water over a period of 20 minutes. After an additional 30 minutes, sulfur dioxide was passed in to reduce the excess permanganate and manganese dioxide. The solution was acidified to *p*H 2–3 with 50% sulfuric acid and extracted with ten 50-ml. portions of ether. The combined extracts were dried over magnesium sulfate, most of the ether was removed in an air stream and the residue heated to 50° (1 mm.) to remove volatile impurities. The crude *trans*-2-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid amounted to 8 g. (40%) and had m.p. 154–155.5° after crystallization from ether–pentane.

Anal. Calcd. for $C_7H_9ClO_4$: C, 43.64; H, 4.68; Cl, 18.44; neut. equiv., 96.6. Found: C, 43.90; H, 4.91; Cl, 18.01; neut. equiv., 94.7.

The acid was further characterized as the **di-*p*-bromophenacyl ester**, m.p. 214–216° after crystallization from acetone.

Anal. Calcd. for $C_{23}H_{19}O_6ClBr_2$: C, 47.06; H, 3.24. Found: C, 47.02; H, 3.53.

***anti*-7-Chloronorcamphor.**—A mixture of 15 g. (0.11 mole) of *anti*-7-chloro-*exo*-norborneol and 75 ml. of 65% concentrated nitric acid–35% water was heated under reflux on a steam-cone for 10 minutes. The reaction was vigorous and was accompanied by evolution of oxides of nitrogen. The mixtures from three such runs were combined and extracted with ether. The ethereal extracts were washed with water, sodium hydroxide solution, water and dried over magnesium sulfate. The ether was removed and the residue distilled through a 10-cm. Vigreux column. The yield of crude *anti*-7-chloronorcamphor, b.p. 95–104° (13 mm.), was 15 g. (32%). For purification, the ketone was converted to the semicarbazone, recrystallized from ethanol–water, and regenerated by steam distillation from an oxalic acid solution. The steam distillate was extracted with ether and the ethereal extract dried over magnesium sulfate. After removal of the ether, the residue was sublimed at atmospheric pressure to give *anti*-7-chloronorcamphor as a waxy white solid.

Anal. Calcd. for C_7H_9ClO: C, 58.13; H, 6.23; Cl, 24.57. Found: C, 58.00; H, 6.44; Cl, 24.36.

The analytical sample of the **semicarbazone** had m.p. 185.5–187° after crystallization from ethanol–water.

Anal. Calcd. for $C_8H_{12}ClN_3O$: C, 47.64; H, 5.96; Cl, 17.62; N, 20.84. Found: C, 47.52; H, 5.73; Cl, 17.32; N, 20.58.

The **2,4-dinitrophenylhydrazone** had m.p. 143.5–145° after crystallization from ethanol.

Anal. Calcd. for $C_{13}H_{13}ClN_2O_4$: C, 48.07; H, 4.01; Cl, 10.94; N, 17.26. Found: C, 47.85; H, 4.16; Cl, 10.82; N, 17.28.

The **trimethylenemercaptol of *anti*-7-chloronorcamphor** was prepared by the method of Hauptman[20] and recrystallized from acetone–hexane at −75°. The yield was 70% of material having m.p. 81.5–83°.

Anal. Calcd. for $C_{10}H_{15}ClS_2$: C, 51.17; H, 6.40; Cl, 15.14; S, 27.29. Found: C, 51.15; H, 6.37; Cl, 15.07; S, 27.49.

Chlorination of Norbornene.—Chlorine, dried with concentrated sulfuric acid was bubbled into a stirred solution of 150 g. of norbornene in 400 ml. of *n*-pentane, cooled in a Dry Ice-bath. When no further chlorine was absorbed, the mixture was allowed to warm to room temperature. The products of four similar runs were combined, most of the *n*-pentane evaporated on a steam-cone and the residue distilled through a glass-helix packed column. After a forerun of 53 g., b.p. 64–67° (29 mm.), n^{25}D 1.4888, there was obtained 330 g. (43%) of almost pure nortricyclyl chloride, b.p. 64–65° (27 mm.), n^{25}D 1.4911. This material was identified by comparison of its infrared spectrum with that of an authentic sample.[15] The balance of the distillation of the chlorination products afforded 100 g. of intermediate fractions, b.p. 58–115° (22 mm.), n^{25}D 1.5055, and 368 g. (37%) of crude solid *syn*-7-*exo*-2-dichloronorbornane, b.p. 97–110° (11 mm.). The dichloride had m.p. 36–38° after trituration with *n*-pentane and sublimation. The infrared spectrum (Fig. 1) was identical with that of a sample kindly provided by Dr. L. Schmerling and prepared in a similar manner.[14]

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.88; H, 6.12; Cl, 43.00. Found: C, 50.90; H, 6.11; Cl, 43.20.

As reported by Schmerling,[14] nortricyclyl chloride is converted to norcamphor on high temperature hydrolysis. It was found also that nortricyclanol heated at 250° with a 5% solution of acetic acid in water was converted largely to norcamphor in 4 hours. In these experiments, the norcamphor

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[20] H. Hauptmann and M. M. Campos, THIS JOURNAL, **72**, 1405 (1950).

was identified as its 2,4-dinitrophenylhydrazone, m.p. 130–131.5° after crystallization from aqueous ethanol. The saturated dichloride reacted with zinc dust in refluxing acetamide but no norbornene could be detected in the resulting complex mixture of chlorine-containing unsaturated materials.

***syn*-7-Chloro-*exo*-norborneol.**—*syn*-7-*exo*-2-Dichloronorbornane (300 g.) was refluxed with a suspension of 112 g. of lithium carbonate in 3 l. of water for six days. The dark-brown solution was extracted continuously with ether, the extract was dried over magnesium sulfate, and most of the ether removed on a steam-cone. The residue was distilled through a 20-cm. vacuum-jacketed Vigreux column with passage of steam through the condenser to prevent the higher-boiling distillate from solidifying until it reached the receiver. Besides 11 g. of forerun, b.p. 25–116° (48 mm.), $n^{25}\text{D}$ 1.3677–1.5029, there was obtained 200 g. (75%) of crude *syn*-7-chloro-*exo*-norborneol, b.p. 116–140° (48 mm.). The material had m.p. 90–91.5° (with some softening at 75°) after crystallization from pentane at −75°.

Anal. Calcd. for $C_7H_{11}ClO$: C, 57.34; H, 7.51; Cl, 24.23. Found: C, 57.18; H, 7.40; Cl, 25.46.

The **α-naphthylurethan** of the chlorohydrin had m.p. 136–137° after crystallization from benzene–hexane.

Anal. Calcd. for $C_{18}H_{18}ClNO_2$: C, 68.46; H, 5.71; Cl, 11.25. Found: C, 68.43; H, 5.81; Cl, 11.22.

The **p-phenylazobenzoate** had m.p. 106–108° after recrystallization from ethanol–water.

Anal. Calcd. for $C_{20}H_{19}ClN_2O_2$: C, 67.70; H, 5.36; Cl, 10.01; N, 7.90. Found: C, 67.75; H, 5.53; Cl, 9.65; N, 7.86.

syn-7-Chloro-*exo*-norborneol was obtained also by the reaction of norbornene with hypochlorous acid. The hypochlorous acid solution was prepared by the method of Soper[21] or that of Coleman and Johnstone.[22] With the former procedure, the hypochlorous acid solution was distilled under reduced pressure from freshly prepared mercuric oxide.

A total of 42 g. (0.45 mole) of norbornene and the calculated volume of hypochlorous acid solution were added alternately in four portions each to an ice-cooled reaction flask equipped with an efficient mechanical stirrer. The reaction temperatures were about 10–20°. Fresh portions of the reactants were added when periodic tests of portions of the reaction mixture with acidified potassium iodide solution indicated the absence of hypochlorous acid. Stirring was continued for 0.5 hour after the addition was complete and the mixture was then extracted with six 200-ml. portions of ether. The combined ethereal extracts were shaken with aqueous bisulfite solution, water and finally dried over anhydrous sodium sulfate. After evaporation of the ether at the atmospheric pressure, the residual oil was distilled under reduced pressure and yielded 15.4 g. (30%) of nortricyclyl chloride, b.p. 60–70° (20 mm.), $n^{25}\text{D}$ 1.4940. Short-path distillation of the boiler residue at 1 mm. afforded 32.3 g. (51%) of colorless waxy *syn*-7-chloro-*exo*-norborneol, m.p. 89–90°. The product gave no m.p. depression on admixture with a sample prepared by hydrolysis of *syn*-7-*exo*-2-dichloronorbornane.

***syn*-7-Chloronorcamphor.**—The nitric acid oxidation procedure for the preparation of *anti*-7-chloronorcamphor with 30 g. of *syn*-7-chloro-*exo*-norborneol yielded 16 g. (55%) of crude waxy *syn*-7-chloronorcamphor, b.p. 105–112° (13 mm.). The ketone was purified through the **semicarbazone**, m.p. 183.5–185° after crystallization from ethanol–water.

Anal. Calcd. for C_7H_9ClO (ketone): C, 58.13; H, 6.23; Cl, 24.57. Found: C, 58.01; H, 6.44; Cl, 24.58.

Anal. Calcd. for $C_8H_{12}ClN_3O$ (semicarbazone): C, 47.64; H, 5.96; N, 20.84. Found: C, 47.66; H, 6.25; N, 20.49.

The **2,4-dinitrophenylhydrazone** had m.p. 192.5–193.5° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{13}H_{13}ClN_4O_4$: C, 48.07; H, 4.01; Cl, 10.94; N, 17.26. Found: C, 48.20; H, 4.18; Cl, 10.75; N, 17.20.

The **trimethylenemercaptol** of *syn*-7-chloronorcamphor was prepared by the method of Hauptmann[20] and had m.p. 54–55.5°.

Anal. Calcd. for $C_{10}H_{15}ClS_2$: C, 51.17; H, 6.40; Cl, 15.14; S, 27.29. Found: C, 51.13; H, 6.52; Cl, 15.05; S, 27.40.

***cis*-2-Chloro-*cis*-cyclopentane-1,3-dicarboxylic Acid.**—Permanganate oxidation of *syn*-7-chloro-*exo*-norborneol by the procedure described above for the corresponding *anti*-isomer gave a 20% yield of *cis*-2-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid, m.p. 186–187° dec. after recrystallization from ether–pentane.

Anal. Calcd. for $C_8H_9ClO_4$: C, 43.64; H, 4.68; Cl, 18.44; neut. equiv., 96.3. Found: C, 43.76; H, 4.86; Cl, 18.47; neut. equiv., 93.7.

The acid was further characterized as the **di-p-bromophenacyl ester**, m.p. 217–219° after crystallization from acetone. This derivative did not depress the melting point of the derivative of the corresponding *trans*-2-chloro-*cis*-dicarboxylic acid.

Anal. Calcd. for $C_{23}H_{19}Br_2ClO_6$: C, 47.06; H, 3.24. Found: C, 47.11; H, 3.40.

***cis*-4-Chloro-*cis*-cyclopentane-1,3-dicarboxylic Acid.**—Oxidation of *endo*-dehydronorbornyl chloride[10] with sodium permanganate by a procedure similar to that used for the oxidation of norbornene[23] gave a 24% yield of *cis*-4-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid, m.p. 177.5–178.5° after recrystallization from ether–pentane.

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN BENZENE (25°)

f_2	ϵ	d^{25}_4	$n^{25}\text{D}$	P_2
endo-cis-5,6-Dichloronorbornene				
0.00000	2.273	0.87246	1.49728	(P_1 26.66)
.00328	2.315	.87414		227.7
.00655	2.366	.87664		241.3
.00993	2.409	.87838		233.6
.01695	2.502	.88259		227.4
.02890	2.659	.88984	1.49868	219.7
.03938	2.804	.89596	1.49907	216.5
.05283	2.977	.90373	1.49960	209.1
trans-5,6-Dichloronorbornene				
0.00000	2.272	0.87235		(P_1 26.67)
.00343	2.295	.87464		133.6
.00696	2.317	.87616		132.0
.01052	2.339	.87850		129.6
.01754	2.383	.88229		129.3
.02965	2.458	.88870		128.5
.04164	2.541	.89529		129.4
.05603	2.623	.90292		125.7
anti-7-Chloronorcamphor				
0.00000	2.2638	0.87286	1.49704	(P_1 26.52)
.00276	2.279	.87420		112.1
.00497	2.295	.87519		126.87
.00735	2.312	.87626		130.2
.01026	2.334	.87776		133.0
.01752	2.389	.88101	1.49713	135.0
.01997	2.402	.88216	1.49713	129.5
.03743	2.477	.89014	1.49728	115.9
syn-7-Chloronorcamphor				
0.00000	2.2638	0.87286	1.49704	(P_1 26.52)
.00270	2.303	.87417		246.6
.00687	2.372	.87629		261.0
.01083	2.438	.87819		263.7
.01917	2.579	.88228		261.2
.02377	2.658	.88448	1.49738	258.2
.03556	2.860	.89019	1.49752	252.3
.05170	3.133	.89717	1.49776	243.9

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(21) G. C. Israel, J. K. Martin and F. G. Soper, *J. Chem. Soc.*, 1282 (1950).

(22) G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 158.

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

Anal. Calcd. for $C_7H_9ClO_4$: C, 43.64; H, 4.68; Cl, 18.44; neut. equiv., 96.3. Found: C, 43.72; H, 4.70; Cl, 18.22; neut. equiv., 96.6.

trans-4-Chloro-*cis*-cyclopentane-1,3-dicarboxylic Acid.—A similar oxidation procedure using *exo*-dehydronorbornyl chloride[10] gave a 30% yield of *trans*-4-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid, m.p. 95.5–97.5° after crystallization.

Anal. Calcd. for $C_7H_9ClO_4$: C, 43.64; H, 4.68; Cl, 18.44; neut. equiv., 96.3. Found: C, 44.29, 44.18; H, 4.90, 5.08; Cl, 18.40; neut. equiv., 95.5.

syn-7-Chloronorbornene.—The following procedure gave the best results of the several which were investigated for conversion of the chlorohydrin to the corresponding chloronorbornene. To 5 g. (0.026 mole) of 2-naphthoyl chloride was added a solution of 4 g. (0.027 mole) of *syn*-7-chloro-*exo*-norborneol in dry pyridine. The reaction mixture became warm and was cooled in an ice-bath. The mixture was allowed to stand overnight and was then poured with stirring into ice-water. The solid ester was collected, washed in cold water, taken up in ether and the ethereal solution washed with dilute acid, dilute sodium carbonate solution, and water and dried over sodium sulfate. *syn*-7-Chloro-*exo*-norbornyl 2-naphthoate was obtained by removal of the ether and recrystallization of the residue from pentane–ether. The yield was 70% of material with m.p. 93–94°.

Anal. Calcd. for $C_{18}H_{17}O_2Cl$: C, 71.87; H, 5.70; Cl, 11.79. Found: C, 71.63; H, 5.89; Cl, 11.75.

The 2-naphthoate ester (10 g., 0.033 mole) was placed in a flask fitted with a 15-cm. Vigreux column and heated at 280° (60–150 mm.) for seven hours in a Woods metal-bath. The distillate was dissolved in pentane and shaken with bicarbonate solution, water and finally dried over sodium sulfate. The ether was evaporated and the residue distilled through a semimicro column.[19] The yield of *syn*-7-chloronorbornene, b.p. 45° (50 mm.), $n^{25}D$ 1.4920, was 1.40 g. (30%).

Anal. Calcd. for C_7H_9Cl: C, 65.37; H, 7.05. Found: C, 65.20; H, 7.19.

The infrared spectrum (Fig. 1) of the material prepared in the above manner indicated the presence of 10–20% of nortricyclyl chloride.

anti-7-Chloronorbornene was prepared from *anti*-7-chloro-*exo*-norbornyl 2-naphthoate, m.p. 92–93° (ether–pentane), as described above.

Anal. Calcd. for $C_{18}H_{17}O_2Cl$: C, 71.87; H, 5.70; Cl, 11.79. Found: C, 72.28; H, 5.78; Cl, 12.05, 11.98.

Pyrolysis of the naphthoate ester gave a 28% yield of *anti*-7-chloronorbornene, $n^{25}D$ 1.4927. The infrared spectrum of the product is given in Fig. 1 and indicates the presence of 10–20% of nortricyclyl chloride.

7-Chloronorbornane.—*syn*-7-Chloronorbornene (0.250 g.) was dissolved in 20 ml. of ether and shaken with hydrogen over platinum oxide at atmospheric pressure for two hours at 10°. Hydrogen uptake ceased after one mole had been absorbed. The catalyst was separated, the ether removed and the residue distilled without fractionation to yield 7-chloronorbornane, $n^{25}D$ 1.4878.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.36; H, 8.50; Cl, 27.15. Found: C, 64.94; H, 8.16; Cl, 26.85.

The infrared spectrum of the material obtained above was essentially the same as that of a sample obtained by hydrogenation of *anti*-7-chloronorbornene (see Fig. 1).

Dipole moments were determined by the method described previously.[24] The data are presented in Tables I and II.

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[24] J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, THIS JOURNAL, **71**, 843 (1949).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Additions to Bicyclic Olefins. *p*-Thiocresol and Norbornylene

BY STANLEY J. CRISTOL AND GORDON D. BRINDELL

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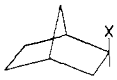
The addition of *p*-thiocresol to norbornylene gave pure *exo*-norbornyl *p*-tolyl thioether, as shown by conversion of the reaction mixture to pure *exo*-norbornyl *p*-tolyl sulfone, in excellent yield, and without contamination with measurable amounts of either the *endo* isomer or of the anticipated rearrangement product, 7-*p*-thiocresoxynorcamphane. The *endo* and *exo* sulfones have been prepared by several straightforward syntheses. The free-radical nature of the addition process has been demonstrated, and the relative reactivity of the *p*-thiocresoxy radical toward norbornylene and cyclohexene has been measured. The question of carbon-bridged mesomeric free radicals in this and analogous systems has been discussed.

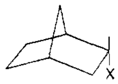
The mechanistic details of the addition of mercaptans to olefins *via* free-radical intermediates are well established.[1,2] As part of a program of study of additions to bicyclic olefins, we undertook the present research, the purpose of which was to elaborate the stereochemistry of addition of *p*-thiocresol to (2,2,1)-bicyclo-2-heptene (norbornylene, I)

I

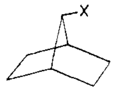
and to determine whether or not rearrangements of the intermediate substituted norbornyl radical occurred. The products of addition without rearrangement might be *exo*-norbornyl *p*-tolyl thioether (IIa) or the *endo* analog (IIIa); the rearrangement product, based upon analogy with ionic rearrangements, would be anticipated to be 7-*p*-thiocresoxynorcamphane (IVa),



II



III



IV

a, X = $SC_6H_4CH_3$-*p*
b, X = $SO_2C_6H_4CH_3$-*p*
c, X = $OSO_2C_6H_4Br$-*p*

This system is of particular interest in consideration of radical-rearrangement processes, as ionic additions to analogous systems are generally accompanied by Wagner–Meerwein rearrangements.[3] Thus, for example, rearrangements have been observed in the addition of strong acids to *endo*-dicyclopentadiene and in the acid-catalyzed solvation of *endo*-

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[1] M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry and Industry*, 752 (1938).

[2] S. O. Jones and E. E. Reid, THIS JOURNAL, **60**, 2452 (1938).

[3] For a general review of such ionic rearrangements, see P. D. Bartlett in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 55–70.