case of aromatic iodides it is possible that the complex ions may be stabilized by resonance forms as pictured above in which iodine accommodates ten electrons in its valence shell. Since the other halogen atoms probably cannot readily accommodate more than the normal octet of valence electrons, it is not too surprising that the other halobenzenes do not form the silver ion-halogen type complex.

Undoubtedly the K_1 values for the iodo compounds measure in part the reaction in which silver ion bonds to the aromatic ring. In forming Ag_2Ar^{++} from iodobenzene it is probable that one silver ion bonds to the iodine atom and the other to the aromatic nucleus. The K_2 value for *p*-diiodobenzene probably measures equilibria for the formation of several different structures of the type Ag_2Ar^{++}

Summary

Argentation constants for a variety of mono- and disubstituted benzene derivatives have been obtained by measurement of the solubilities of the aromatic substance in aqueous silver nitrate at 25°. The relative magnitudes of the constants have been discussed in terms of Hammett's ρ,σ substituent constants. The structures of the silver-aromatic complexes have been discussed and are suggested as being similar to those of intermediates in aromatic substitution reactions.

Evidence has been presented that iodo- and *p*-diiodobenzene form complexes with silver ion in which the metallic ion coördinates with the iodine atoms of the organic molecules.

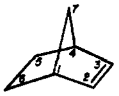
DAVIS, CALIFORNIA RECEIVED OCTOBER 31, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY OF NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Reaction of Norbornylene with N-Bromosuccinimide. Nortricyclene and its Derivatives[1,2]

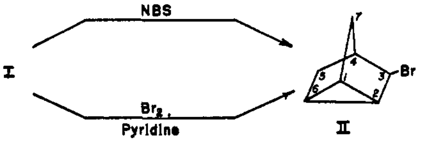
BY JOHN D. ROBERTS, E. R. TRUMBULL, JR., WINIFRED BENNETT AND ROSE ARMSTRONG

N-Bromosuccinimide (NBS) reacts with camphene, a compound whose only allyl hydrogen atom is located at a bridgehead of a bicyclic ring system, to give principally 8-bromocamphene,[3] a vinyl bromide derivative. In order to determine the scope of this abnormal bromination[4] the reaction of NBS with norbornylene (bicyclo-[2.2.1]-2-heptene, I) was investigated.



I

The reaction of I with NBS in the presence of benzoyl peroxide in boiling carbon tetrachloride was about twice as fast as that of camphene with NBS,[3] being complete in four hours. Hydrogen bromide appeared to be an effective catalyst and in one experiment using carbon tetrachloride saturated with dry hydrogen bromide the reaction was complete in fifteen minutes. The yield of monobromide (II) ranged from 27-40%. II, b. p. 70-74° (19 mm.), reacted rapidly with alcoholic silver nitrate and absorbed very little hydrogen over platinum oxide.[5] The elemental analysis was satisfactory for C_7H_9Br, a monosubstitution product of I. The saturated character and analysis of II are suggestive of a tricyclic ring system, while the facile reaction with silver nitrate indicates that the halogen atom is not located at a bridgehead position.[6] From these inferences and consideration of possible modes of reaction between I and NBS (*vide infra*) the most likely structure for II appears to be 3-bromonortricyclene (3-bromotricyclo[2.2.1.$0^{2,6}$]-heptane).



The conversion of I to II is not unique to NBS. The reaction of I with bromine in carbon tetrachloride was found to give mono- and dibromide fractions. The monobromide fraction consisted of about equal quantities of II and of norbornyl bromide resulting from the addition of hydrogen bromide to I. When excess pyridine was added to the reaction mixture to combine with the hydrogen bromide formed by the substitution reaction, the monobromide fraction was essentially

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[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

[2] Presented in part at the St. Louis Meeting of the American Chemical Society, Sept. 7, 1948.

[3] Roberts and Trumbull, THIS JOURNAL, **71**, 1630 (1949).

[4] *Cf.* Djerassi, *Chem. Revs.*, **43**, 271 (1948), for discussion of the usual course of the reaction.

[5] Most of the preparations of II contained sufficient quantities of an isomeric unsaturated bromide to react with dilute alcoholic potassium permanganate solution. This fact led to the supposition that II was in reality an unsaturated bromide and that on attempted hydrogenation the catalyst was rapidly poisoned by impurities. II was previously assigned the structure, 7-bromonorbornylene (*cf.* Abstracts of St. Louis Meeting of the American Chemical Society, September, 1948, p. 43L.)

[6] Bartlett and Knox, THIS JOURNAL, **61**, 3184 (1939).

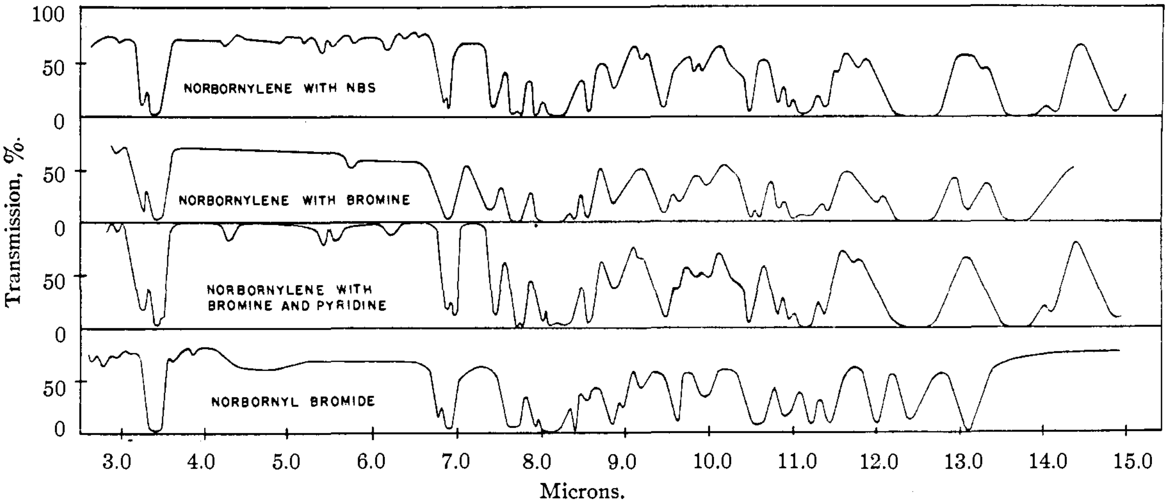
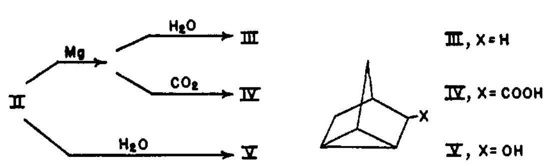
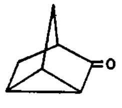


Fig. 1.—Infrared spectra: Perkin–Elmer spectrograph with NaCl prism, 0.1 mm. samples (no solvent).

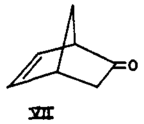
the same as that obtained from the reaction of I with NBS. The products of these reactions were identified by their infrared spectra (Fig. 1).

The Grignard reagent corresponding to II was found to be converted to (a) a saturated solid hydrocarbon (III) by hydrolysis and (b) a saturated carboxylic acid (IV) with carbon dioxide. With boiling water in the presence of lithium carbonate, II was hydrolyzed to a saturated alcohol (V). The crude products of each of the foregoing reactions contained some unsaturated materials as shown by permanganate test and quantitative hydrogenation (from 5–10% absorption of the theoretical quantity of hydrogen calculated for isomeric monounsaturated impurities). The unsaturated contaminants were removed on purification and were not identified. III, IV and V are considered to have the same ring system as II on the basis of their saturated character and a prominent infrared absorption band at 12.4–12.5 μ which appears to be characteristic of these substances (as well as II) and their derivatives (Fig. 2).[7] Indication of the nortricyclene ring system was gained by the conversion of V with chromic acid to the corresponding ketone (nortricyclanone, VI). The absorption maximum (365 mμ) of the 2,4-dinitrophenylhydrazone of VI was definitely closer to the visible than that of the derivative of dehydronorcamphor (VII) and the magnitude of the shift was, within experimental error, equal to the difference in λ_{max} (4 mμ) between the 2,4-dinitrophenylhydrazones of cyclopropyl methyl ketone and cyclopentanone.[8]



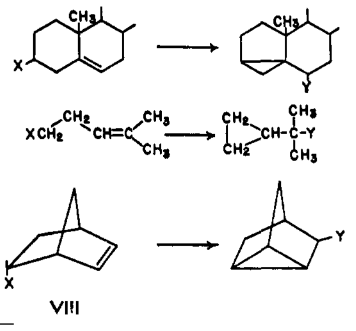


VI



VII

Further indication of the nortricyclene ring structures assigned to hydrocarbon III, acid IV, and alcohol V was the formation of each of these substances, by reactions similar to those used starting with II, from *endo*-dehydronorbornyl halides[9] (VIII) prepared by the addition of vinyl bromide or chloride to cyclopentadiene. The formation of V from VIII is suggested to be analogous to the production of *i*-sterols from cholesterol derivatives[10] and of cyclopropylmethyl com-



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[7] Swann and Cripwell, *Ind. Chemist.*, **24**, 573 (1948), have described a similar very strong absorption band at 12.3μ in the infrared spectrum of tricyclene.

(8) Roberts and Green, THIS JOURNAL, **68**, 214 (1946).

(9) The *endo*-configurations were assigned to these substances in consideration of the work of Alder and Rickert, *Ann.*, **543**, 1 (1939). It should be noted that this type of diene-addition reaction is by no means as stereospecific as implied by Alder and Rickert. It has been found repeatedly in the present investigation that mixtures of products are obtained with cyclopentadiene and adducts such as vinyl acetate and acrylic acid. In each case, however, the *endo*-isomer predominates to the extent of 85% or more.

(10) *Cf.* Fieser and Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 256–261, for many references.

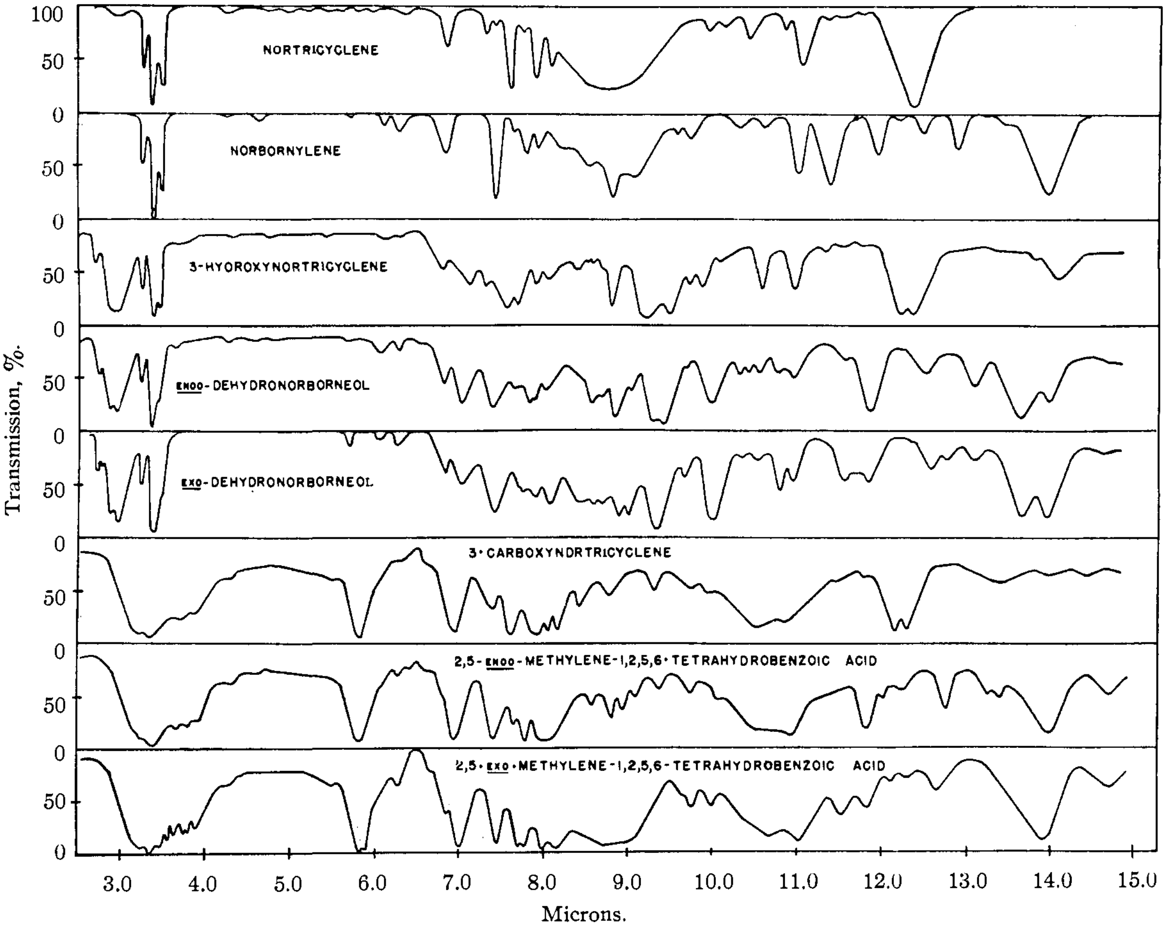

Fig. 2.—Infrared spectra: Baird spectrometer with NaCl prism, 10% solutions in carbon disulfide except in the regions 4.2–5.0μ and 6.2–7.2μ where carbon tetrachloride was used as solvent.

pounds from suitably constituted allylcarbinyl derivatives,[11] *i. e.* as shown in the formulas just given. While the formation of tricyclic products in the reactions of VIII does not in itself constitute proof of the structures assigned to III, IV and V, it is felt that the above formulation, rather than some more deep-seated skeletal rearrangement, best explains the character and ease of the transformations of VIII which as written are akin to the well known allylic rearrangement reactions. More positive indication of the structure of III has been obtained from a detailed study of its infrared and Raman spectra by Drs. R. C. Lord, Jr., and E. R. Lippincott. Their spectroscopic data (to be published separately) are completely consistent with the proposed nortricyclene structure.

The tendency for ring closure in the reactions of the halides VIII is notably greater than *i*-sterol formation in the reactions of cholesteryl compounds. Thus, while *i*-sterols have been reported from many of the reactions of cholesteryl *p*-toluenesulfonate, the reactions of cholesteryl chloride[10,12a] appear to be generally (if not exclusively) normal[13] and no *i*-sterol derivatives have been reported from the reactions of the cholesteryl Grignard reagent.[12b,c] The differences in ease of ring closure may possibly be ascribed either to a special stability of the tricyclene structure[14] or a particularly favorable orientation of reactive centers as a consequence of the geometry of the rigid bicyclic ring system. It is interesting to note that the reversal of the ring closure reaction (where X = Y) should be substantially exothermic (see (1)). That this process is also normally exergonic is shown by the facile conversion of (a) *i*-cholesteryl acetate to the normal acetate by heating with a catalytic amount

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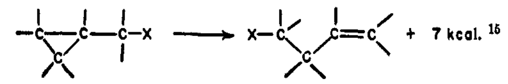
[11] Favorskaya and Fridman, *J. Gen. Chem.* (USSR), **15**, 421 (1945).

[12] (a) Shoppee, *J. Chem. Soc.*, 1032 (1948); (b) Baker and Squire, This Journal, **70**, 1487 (1948); (c) Marker, Oakwood and Crooks, *ibid.*, **58**, 481 (1936).

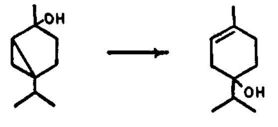
[13] The possibility exists, as suggested by Winstein and Adams, This Journal, **70**, 838 (1948), that the first product formed in the acetolysis of cholesteryl chloride studied by Shoppee (ref. 12a) was actually *i*-cholesteryl acetate which subsequently rearranged in the acidic medium to the normal acetate. However, a similar sequence in the reactions of cholesteryl Grignard reagent is unlikely.

[14] Note, however, that Lipp, *Ber.*, **80**, 165 (1947), has reported that 10-hydroxytricyclene is converted to 6-bromocamphene by phosphorus pentabromide.

(1)



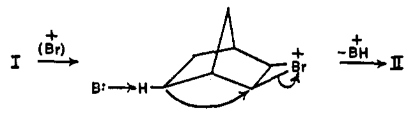
of sulfuric acid in acetic acid and (b) of sabinene hydrate (IX) to terpinen-4-ol (X) with dilute acid.[16] With the dehydronorbornyl–nortricyclyl



IX X

system the free energy change accompanying Reaction (1) seems to be considerably more positive.[17] Thus, in the preparation of the halides VIII by reaction of vinyl chloride or bromide at 195 and 160°, respectively, with cyclopentadiene in a *steel* vessel about half of the reaction products were nortricyclyl halides formed by rearrangement. The fact that no substantial amount of rearrangement was observed when the reactions were carried out in glass containers would indicate that traces of metal salts catalyze the rearrangement.[18] A number of attempts were made to isomerize alcohol V, *endo*-dehydronorborneol (XI) and *exo*-dehydronorborneol (XII) to an equilibrium mixture with aqueous sulfuric acid at room temperature by the method used by Young, Nozaki and Warner[19] for the isomerization of allylic alcohols. With each alcohol and 30–35% aqueous sulfuric acid some of the starting material was recovered along with solid glycols resulting from addition of water to the cyclopropane ring of V or the double bonds of XI or XII. The same glycol, m. p. 171°, was obtained from V, XI and XII, which indicates that rearrangement probably takes place in the hydration of at least one of the alcohols. The structure of the glycol has not yet been established. For the isomerization experiments, XII was prepared from XI by the elegant stereochemical equilibration technique of Doering and Aschner.[20]

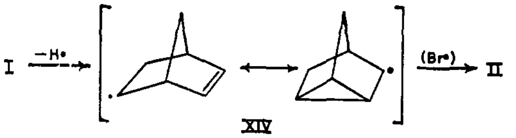
The mechanism of the formation of II in the reaction of NBS or bromine with I is uncertain. However, the fact that NBS and bromine are both effective agents suggests that the initial phase of the reaction involves the donation of Br⊕ (or possibly electrophilic bromine when bromine is used)[21] to the double bond of I.[22] The resulting bromonium ion (XIII) may lose a proton directly to a suitable acceptor (B:) and yield II. That the double bond takes an important role in the



XIII

reaction of I with NBS is shown by the very slow rate of reaction between norbornylane and NBS. However, the bicyclic ring system is also an essential feature since *t*-butylbenzene (which has a center of unsaturation in the same relative position to its methyl groups as that of I to its methylene groups) does not react with NBS in boiling carbon tetrachloride.

It is also possible that the reaction of I with NBS proceeds *via* a free-radical intermediate (XIV) analogous to that postulated for the customary allylic bromination[4] and stabilized by resonance structures similar to those proposed for the stabilization of the cholesteryl-*i*-cholesteryl-carbonium ion.[12a,23,24,25] XIV might be expected



XIV

to be unusually stable for an intermediate of this type because of the favorable orientation of orbitals in the rigid bridged-ring system.[26] Against this interpretation is the marked hydrogen bromide catalysis of the reaction and the necessity for having to postulate a separate mechanism for the formation of the same final product from I and bromine.

In order to determine whether *exo*-dehydronorbornyl bromide (XV) could be an intermediate in the formation of bromide II attempts were made to synthesize XV and the corresponding chloride from *endo*-dehydronorborneol (XI). Reaction of XI with thionyl chloride in the presence of pyridine gave a mixture of chlorides which from its

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(15) This value was obtained from the difference between the heats of combustion of cyclopropane and propylene using the data given by Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929).

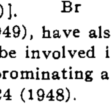
(16) Wallach, *Ann.*, **357**, 65 (1907); **360**, 94 (1908).

(17) The small difference in heat of combustion (data taken from Kharasch, ref. 15) between camphene (1467.6 kcal./mole), cyclofenchene (1469.3 kcal./mole) and tricyclene (1467.3 kcal./mole) suggests that the heat of Reaction (1) in bicyclic compounds is practically negligible.

(18) Lane, Fentress and Sherwood, THIS JOURNAL, **66**, 545 (1944), have shown that cuprous chloride is an effective isomerization catalyst for crotyl and α-methylallyl chlorides.

(19) Young, Nozaki and Warner, *ibid.*, **61**, 2564 (1939).

(20) Doering and Aschner, *ibid.*, **71**, 838 (1949).

(21) While Nozaki and Ogg, *ibid.*, **64**, 697, 704, 709 (1942), have shown in several instances that the simple bromonium intermediate proposed by I. Roberts and Kimball, *ibid.*, **59**, 947 (1937), for the bromination of olefins is not consistent with the marked bromide ion catalysis, it is possible that the intermediate is actually an olefin-bromine complex of the type  $\underset{\substack{|\\ \mathrm{Br}}}{\overset{>\mathrm{C}---\mathrm{C}<}{\mathrm{Br}}}$ [*cf.* White and Robertson, *J. Chem. Soc.*, 1509 (1939)].

(22) Braude and Wright, *Nature*, **164**, 241 (1949), have also suggested that bromonium ion intermediates may be involved in certain olefin reactions where NBS functions as a brominating agent.

(23) Dodson and Riegel, *J. Org. Chem.*, **13**, 424 (1948).

(24) Pearson, Subluskey and King, THIS JOURNAL, **70**, 3479 (1948).

(25) Winstein and Schlesinger, *ibid.*, **70**, 3528 (1948).

(26) An alternative viewpoint would direct attention to the expectation (*cf.* ref. 17) that the resonance forms of XIV would be more energetically equivalent than those contributing to the stabilization of a simple allylcarbinyl free radical and hence that resonance would be more important in stabilizing XIV than an allylcarbinyl free radical.

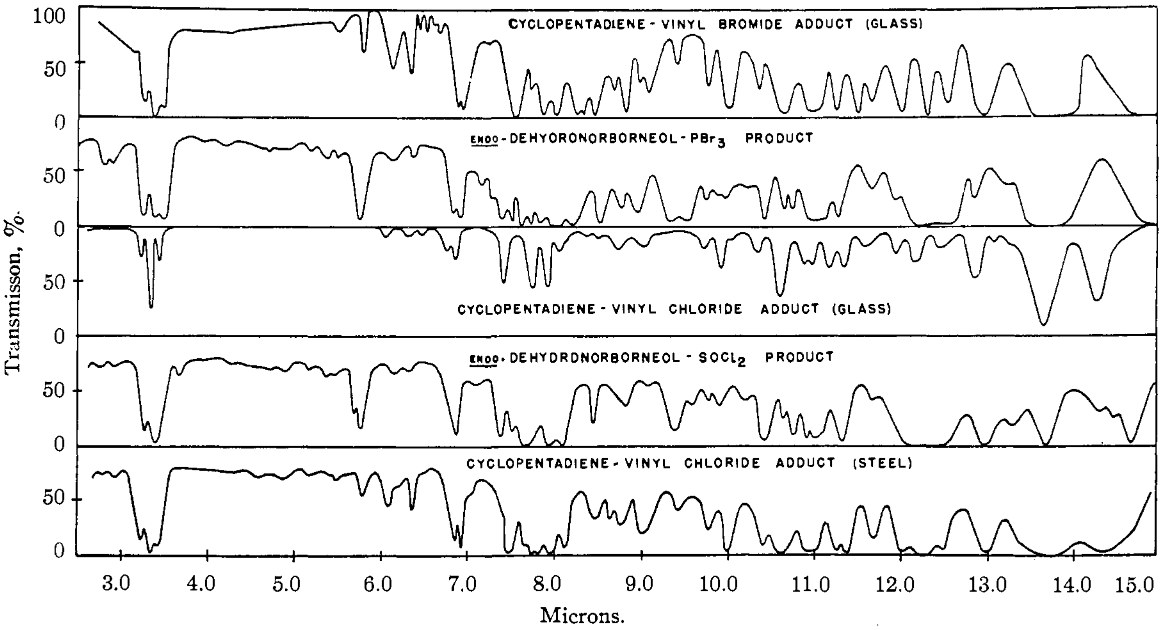
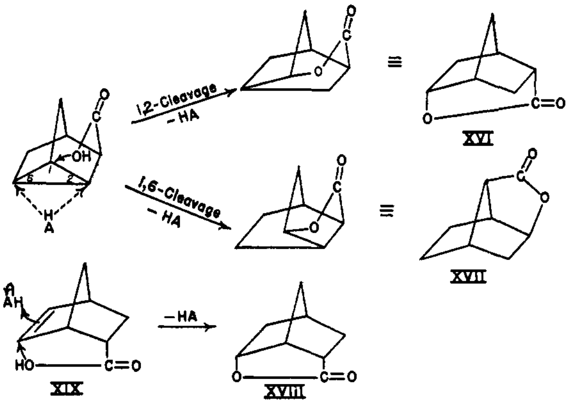


Fig. 3.—Infrared spectra: all except cyclopentadiene–vinyl chloride adduct (glass) determined with Perkin–Elmer spectrograph with NaCl prism, 0.1 mm. samples (no solvent). Cyclopentadiene–vinyl chloride adduct (glass) spectrum determined with Baird spectrometer with NaCl prism, 10% solutions in carbon disulfide except in the regions 4.2–5.0μ and 6.2–7.2μ where carbon tetrachloride was used as solvent.

infrared spectrum (Fig. 3) and predominantly saturated character was judged to be largely 3-chloronortricyclene. XI with phosphorus tribromide gave a similar result in that the infrared spectrum (Fig. 3) indicated that the major product was II admixed with some bromide VIII although a number of absorption bands were found in the spectrum which may have been due to XV. If XV was actually present in this material it seems unlikely that XV could rearrange to II easily enough for it to be a precursor of II in the reaction of I with NBS or bromine.

The acid-catalyzed formation from IV of a solid lactone (XVI or XVII) different from the lactone (XVIII) obtained from *endo*-2,5-methylene-1,2,5,6-tetrahydrobenzoic acid (XIX) by Alder and co-workers[27] is to be expected on the basis of the nortricyclene ring system of IV. The carboxyl group of IV is so located on the rigid ring structure that the only sterically favorable point for attack of the carboxyl group on the three-membered ring in lactone formation is at C-1. The proton of the catalyzing acid (HA) may be added at either C-6 resulting in cleavage between C-1 and C-2 or at C-2 resulting with cleavage between C-1 and C-6. In either case the product is not expected to be identical with XVIII and the only simple way that XVIII may be formed from IV is by a sterically unfavorable attack of the carboxyl at C-6. It has not been determined whether the structure of the lactone is best represented by XVI or XVII.



In the early phases of the investigation it was considered possible that IV might be *exo*-2,5-methylene-1,2,5,6-tetrahydrobenzoic acid (XX) and an unsuccessful attempt was made to prepare XX by decarboxylation of the malonic acid derivative obtained from the hydrolysis of the adduct of diethyl methylenemalonate and cyclopentadiene. XX was finally prepared by isomerization of methyl *endo*-2,5-methylene-1,2,5,6-tetrahydrobenzoate (XXI) with sodium methoxide to the methyl ester of XX which was then saponified. XXI was obtained by the addition of methyl acrylate to cyclopentadiene.

Acknowledgment.—We are indebted to Dr. R. C. Lord, Jr., Miss B. J. Fax, and Mr. R. S. McDonald for many of the infrared spectra.

[27] Alder, Stein, Liebmann and Rolland, *Ann.*, **514**, 197 (1934).

Experimental

Reaction of N-Bromosuccinimide with Norbornylene.—In a 1-l. three-necked flask equipped with stirrer and reflux condenser were placed 50 g. (0.53 mole) of norbornylene, 95 g. (0.53 mole) of N-bromosuccinimide, 1 g. of benzoyl peroxide and 250 ml. of carbon tetrachloride. The mixture was heated to reflux, stirred and irradiated with a General Electric RS Sunlamp for four hours at the end of which time all of the solid material in the flask floated on the carbon tetrachloride when the stirrer was stopped.[4] The solid was filtered, the washings were combined and the bulk of the carbon tetrachloride removed through a short Vigreux column. The residue was distilled under reduced pressure with no attempt at fractionation until the temperature reached 122° (37 mm.). The crude product (43.2 g.) was fractionated through a 1.0 × 30 cm. Vigreux column. The yield of II was 32.2 g. (35%); b. p. 70–74.5° (19 mm.), $n^{25}{}_D$ 1.5269, $d^{25}{}_4$ 1.4609. The infrared spectrum of the product is shown in Fig. 1.

II gave an immediate precipitate with alcoholic silver nitrate solution (89% of the theoretical quantity of silver bromide was found) and reacted with potassium permanganate in acetone. The proportion of unsaturated material was small since on quantitative hydrogenation only about 10% of the theoretical amount of hydrogen was absorbed in glacial acetic acid using a platinum oxide catalyst.

Anal. Calcd. for C_7H_9Br: C, 48.58; H, 5.24. Found: C, 48.86; H, 5.31.

Reaction of Bromine with Norbornylene.—In a 500-ml. three-necked flask equipped with stirrer, dropping funnel and thermometer was placed 50 g. (0.53 mole) of norbornylene dissolved in 110 ml. of carbon tetrachloride. The contents of the flask were cooled to −4° with an ice-salt-bath and a solution of 74 g. (0.46 mole) of bromine in 50 ml. of carbon tetrachloride was added with stirring at such a rate that the temperature did not rise above −1°. Most of the solvent was distilled at atmospheric pressure and the residue was separated into two fractions, b. p. 77–130° (19 mm.) and b. p. 130° (19 mm.)–120° (5 mm.), respectively. The first fraction (46 g.) was redistilled through a 1.0 × 30 cm. Vigreux column giving a 20.4 g. yield of monobromides; b. p. 67° (15 mm.), $n^{25}{}_D$ 1.5222, $d^{25}{}_4$ 1.4252. The infrared spectrum of the monobromide product (Fig. 1) indicates that this is a mixture of II and norbornyl bromide.[28] The structures of the dibromides formed in the addition of bromine to I are under investigation.

A sample of II, free of norbornyl bromide, was prepared by the following procedure. To a mixture of 20 g. (0.21 mole) of I and 17 g. (0.21 mole) of pyridine in 100 ml. of carbon tetrachloride was added dropwise 34 g. (0.21 mole) of bromine over a period of two hours. During the addition the mixture was stirred and cooled in an ice-bath. The mixture was filtered and the filtrate washed with water, 6 *N* hydrochloric acid, and dried over calcium chloride. The carbon tetrachloride was distilled and the residue fractionated through a 1.0 × 35 cm. Vigreux column. The yield of II, b. p. 81.5–82.2° (30 mm.) was 3.5 g. (10%); $n^{25}{}_D$ 1.5269. Higher-boiling fractions amounted to 32 g. The infrared spectrum of the monobromide is shown in Fig. 1.

Preparation of *exo*-Norbornyl Bromide.—A mixture of 50 g. (0.53 mole) of norbornylene and 180 g. (excess) of 48% hydrobromic acid was stirred and heated at 50–65° for two and a half hours. The organic layer was separated, washed with water and dried over calcium sulfate. The product was distilled through a short Vigreux column. The yield of crude product, b. p. 84–87° (31 mm.), was 72.0 g. (77%). For the infrared spectrum (Fig. 1) the material was fractionated through a 1.5 × 35 cm. Vigreux column and 67 g. of pure *exo*-norbornyl bromide, b. p. 82° (29 mm.), was obtained; $n^{25}{}_D$ 1.5126, $d^{25}{}_4$ 1.3808.

Insufficient data are available to determine whether this bromide is identical with the product obtained by Komppa and Beckmann[29] (b. p. 81–83° at 30 mm.) from the reaction of β-norborneol with phosphorus tribromide.

Preparation of *endo*-Dehydronorbornyl Halides (VIII).—The general procedure of Alder and Rickert[9] for the addition of vinyl compounds to cyclopentadiene was used. Products uncontaminated with nortricyclyl halides were obtained in sealed glass tubes. In a steel hydrogenation bomb considerable amounts of rearrangement products were obtained, probably as a result of catalysis by iron salts. The following experiments are illustrative.

(a) **Dehydronorbornyl Bromide (VIII).**—A mixture of 32.2 g. (0.30 mole) of vinyl bromide and 13.2 g. ((0.20 mole) of freshly-distilled cyclopentadiene was heated in a sealed glass tube at 165° overnight. The products were distilled through a 1.0 × 30 cm. Vigreux column and 19.1 g. (55%) of dehydronorbornyl bromide was obtained; b. p. 63–65.5° (15 mm.), $n^{25}{}_D$ 1.5231, $d^{25}{}_4$ 1.4108. On the quantitative hydrogenation the material absorbed 94% of the theoretical quantity of hydrogen in glacial acetic acid over platinum oxide. The infrared spectrum of the adduct is given in Fig. 3.

Anal. Calcd. for C_7H_9Br: C, 48.58; H, 5.24; Br, 46.18. Found: C, 49.60; H, 5.43; Br, 46.01.

(b) **Cyclopentadiene with Vinyl Bromide in Steel Bomb.**—A mixture of 169 g. (1.58 moles) of vinyl bromide and 92 g. (1.38 moles) of freshly-distilled cyclopentadiene was heated overnight at 160° in a steel hydrogenation bomb. The products of the reaction were distilled giving 103 g. of crude adduct, b. p. 62–64° (12 mm.) and 87 g. of high-boiling residue. On redistillation, the bulk of the crude adduct (83 g.) boiled at 63° (11.5 mm.) and had $n^{25}{}_D$ 1.5249. The refractive index of this material was considerably higher than that obtained in (a) and assuming that II is the only other reaction product the index indicated 45% of II and 55% of bromide VIII. Several experiments confirmed the presence of II in the adduct to the extent of about 50%.

On hydrogenation the adduct absorbed about 50% of the theoretical amount of hydrogen in ethyl acetate over platinum oxide. The hydrogenation product, b. p. 70° (15 mm.), did not react with potassium permanganate in acetone and had $n^{25}{}_D$ 1.5198 which if only II and the expected *endo*-norbornyl bromide ($n^{25}{}_D$ 1.5131, *vide infra*) were assumed to be present corresponded roughly to an equimolal mixture. Hydrolysis of the hydrogenated adduct by boiling with a suspension of lithium carbonate in water for two days gave a solid product which after crystallization from ligroin had m. p. 102.8–105.5°. The infrared spectrum of the product showed all of the characteristic bands of V.

(c) **Dehydronorbornyl Chloride.**—A mixture of 18 g. (0.27 mole) of freshly distilled cyclopentadiene and 24 g. (0.38 mole) of vinyl chloride was heated in a glass tube at 170° for fourteen hours. Distillation of the products of two such runs gave 6.4 g. (9%) of dehydronorbornyl chloride; b. p. 50° (19 mm.); $n^{25}{}_D$ 1.4922. This material absorbed 102% of the theoretical amount of hydrogen over platinum oxide in ethyl acetate. The infrared spectrum of the product is given in Fig. 3.

(d) **Cyclopentadiene and Vinyl Chloride in Steel Bomb.**—A 500-ml. steel hydrogenation bomb was cooled with Dry Ice and 100 g. (1.51 moles) of freshly distilled cyclopentadiene and 163 g. (2.60 moles). of liquid vinyl chloride added. The bomb was closed and heated at 195° for twelve hours. Distillation of the reaction products through a 1.5 × 35 cm. Vigreux column gave 95.1 g. (48%) of adduct, b. p. 48.5–50.5° (13 mm.) (lit., 46–47° (12 mm.)[9]) which had $n^{25}{}_D$ 1.4938. The strong band at 12.3 μ in the infrared spectrum (Fig. 3) of this material indicates a substantial portion of 3-chloronortricyclene in the reaction products and on quantitiative hydrogenation only 57% of the theoretical quantity of hydrogen was absorbed in ethyl acetate over platinum oxide.

Preparation of Nortricyclene (III).—Several runs were made using II and dehydronorbornyl halides all of which

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[28] Assuming only II and norbornyl bromide to be present the refractive index indicates proportions of 60 and 40%, respectively.

[29] Komppa and Beckmann, *Ann.*, **512**, 172 (1934).

gave substantially the same results. Only the largest run employing dehydronorbornyl chloride will be described. A mixture of 25 g. (0.19 mole) of dehydronorbornyl chloride and 7.6 g. (0.05 mole) of *n*-amyl bromide was added dropwise with stirring to 6.0 g. (0.25 gram atom) of magnesium turnings in 200 ml. of anhydrous ether. A nitrogen atmosphere was maintained throughout. After the addition was complete (thirty minutes), the Grignard solution was refluxed for two hours and then an excess of dilute hydrochloric acid was run in. The ethereal layer was separated, dried over anhydrous magnesium sulfate and distilled. The yield of crude III, b. p. 104–107°, was 10.3 g. (57%). The material of b. p. 104–106° (7.6 g.) contained some unsaturated contaminant which could be removed by shaking with aqueous permanganate. Pure III, b. p. 106–107° (2.7 g.), showed m. p. 56° (sealed capillary). The infrared spectrum of the product is given in Fig. 2.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.31; H, 10.70.

3-Nortricyclenecarboxylic Acid (IV).—A solution of 52.7 g. (0.304 mole) of II in 50 ml. of anhydrous ether was added with stirring over forty-five minutes to 8.0 g. (0.33 mole) of magnesium turnings and 200 ml. of anhydrous ether. A nitrogen atmosphere was maintained throughout the formation of the Grignard reagent. The reaction mixture was refluxed for an hour and then cooled by means of an ice-salt mixture. Carbon dioxide was bubbled through the cooled mixture for two hours. Dilute hydrochloric acid was added and the ethereal layer separated. The aqueous residue was extracted with ether and the combined ether solution shaken with five 50-ml. portions of 10% sodium carbonate solution. The carbonate extracts were combined, acidified with dilute hydrochloric acid and extracted with ether. The ether extracts were combined and dried over calcium sulfate. The ether was removed through a short Vigreux column and the residue subjected to evaporative distillation at 6 mm. The crude acid amounted to 19 g. (47%); m. p. 48–50°. The product was recrystallized from pentane (Skau tube), m. p. 49–50.6°. This material depressed the m. p. of acid XIX. The infrared spectrum is given in Fig. 2.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.46; H, 7.35.

The acid has also been obtained as a lower-melting crystalline modification, m. p. 43–45°, which on long standing or seeding changes to the higher melting form. Purified IV gave only a slight test for unsaturation with potassium permanganate in acetone and was not hydrogenated over platinum oxide in glacial acetic acid.

Nortricyclenecarboxamide was prepared by treatment of 1.1 g. of IV with 5 ml. of thionyl chloride and then with 20 ml. of cold concentrated ammonia solution. After successive crystallizations from water and benzene–petroleum ether the material had m. p. 187.5–189°.

Anal. Calcd. for $C_8H_{11}ON$: C, 70.03; H, 8.09. Found: C, 70.22; H, 8.19.

The ***p*-bromo-** and ***p*-phenylphenacyl esters** of IV were made in the usual way.[30] The *p*-bromophenacyl ester was recrystallized successively from methanol–water and hexane, m. p. 83.8–84.8°.

Anal. Calcd. for $C_{16}H_{15}BrO_3$: C, 57.33; H, 4.51. Found: C, 57.35; H, 4.34.

The *p*-phenylphenacyl ester was recrystallized from alcohol, m. p. 118.4–119.2°.

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.49; H, 6.07. Found: C, 79.01; H, 6.09.

Nortricyclenecarboxanilide was prepared from the reaction of the Grignard reagent of II with phenyl isocyanate. The reaction products were treated with dilute hydrochloric acid and the solid remaining after evaporation of the ethereal portion was recrystallized from benzene-ligroin, m. p. 144–145°. The anilide could not be hydrogenated in methanol over platinum oxide catalyst.

Anal. Calcd. for $C_{14}H_{15}ON$: C, 78.83; H, 7.09. Found: C, 78.68; H, 7.74.

Bromide VIII formed a Grignard reagent as described for II which on treatment (a) with carbon dioxide gave IV and (b) with phenyl isocyanate gave the anilide of IV. The identities of the products were established by m. p., mixed m. p.'s and comparison of the infrared spectra of the acids and *p*-phenylphenacyl esters.

Treatment of IV (2.0 g.) with 20 ml. of 50% sulfuric acid at room temperature for seventeen hours gave a low yield of the solid **lactone** XVI or XVII which was isolated by ether extraction and separation of the acidic material with sodium carbonate solution. The lactone was recrystallized from petroleum ether and then sublimed, m. p. 119–120°.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 68.93; H, 7.30.

The sodium salt of IV in aqueous solution containing excess sodium bicarbonate reacted slowly with bromine to give largely water-soluble products. From 1.0 g. of IV was obtained 0.062 g. of an insoluble oil which could not be crystallized.

***endo*-2,5-Methylene-1,2,5,6-tetrahydrobenzoic Acid (XIX).**—XIX was prepared as described by Alder.[27] The crude product, b. p. 118.5–120.5 (5.7 mm.), had $n^{25}\text{D}$ 1.4931 and was obtained in 85% yield. This material was liquid at room temperature and was shown by its infrared spectrum to contain 5–10% of the *exo*-isomer, XXI. Pure XIX was obtained by crystallization of the crude product from *n*-pentane, m. p. 44.1–45.0° (lit., 39°).[27] The infrared spectrum of pure XIX is given in Fig. 2.

Lactone XVIII was prepared by treatment of XIX with 50% sulfuric acid. The yield was 20% and the m. p. 154.2–155.2° (lit. 155–156°)[27] after crystallization from pentane and sublimation.

XIX (1.0 g.) was dissolved in a solution of 3.0 g. of sodium bicarbonate in 45 ml. of water and treated with 0.37 ml. of bromine. During the addition of the bromine the flask was cooled in an ice-bath. A light yellow oil separated which was extracted with ether. Evaporation of the ether gave the crude **bromolactone** which after several crystallizations from benzene–hexane amounted to 0.39 g. (25%); m. p. 64.8–65.9°. The bromolactone did not react visibly with a boiling solution of silver nitrate in alcohol.

Anal. Calcd. for $C_8H_9O_2Br$: C, 44.26; H, 4.18. Found: C, 44.33; H, 4.14.

The **anilide** of XIX was prepared by conversion of XIX to the acid chloride with thionyl chloride and subsequent reaction with excess aniline in dry benzene. The crude product was crystallized from benzene; m. p. 146.4–147.2°.

Anal. Calcd. for $C_{14}H_{15}ON$: C, 78.84; H, 7.09. Found: C, 79.24; H, 6.99.

The anilide of XIX did not depress the m. p. (144–145°) of nortricyclenecarboxanilide. The two compounds are easily distinguished since the former is typically unsaturated and absorbed 102% of the theoretical quantity of hydrogen to give *endo*-2,5-methylenehexahydrobenzanilide, m. p. 149.0–150.0° (lit., 151–152°)[27] after crystallization from methanol–water.

The ***p*-bromophenacyl ester**[30] of XIX was prepared and crystallized from methanol–water and hexane; m. p. 83.8–84.8°.

Anal. Calcd. for $C_{16}H_{15}O_3Br$: C, 57.33; H, 4.51. Found: C, 57.35; H, 4.34.

The ***p*-phenylphenacyl ester**[30] of XIX was crystallized from ethanol; m. p. 131.5–132.2°.

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.49; H, 6.07. Found: C, 79.24; H, 6.19.

Methyl *endo*-2,5-Methylene-1,2,5,6-tetrahydrobenzoate (XXI).—Freshly-distilled cyclopentadiene (89.2 g.,

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(30) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

1.35 moles) was added dropwise with stirring to an ice-cooled solution of 130.3 g. (1.51 moles) of methyl acrylate (b. p. 79–80°) and 1 g. of hydroquinone in 100 ml. of anhydrous ether. The addition was carried out over two hours and after another hour the ice-bath was removed and the mixture allowed to warm to room temperature. The ether was distilled and the residue fractionated giving 185.1 g. (90%) of XXI, b. p. 63.5° (5.2 mm.), $n^{25}\text{D}$ 1.4718.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.73; H, 7.97.

***exo*-2,5-Methylene-1,2,5,6-tetrahydrobenzoic Acid (XX)**.—A mixture of 25 g. (0.17 mole) of XXI, 15 g. (0.28 mole) of sodium methoxide and 35 g. of anhydrous methanol was heated on a steam-bath for forty-eight hours. The methanol was distilled, 20 ml. of water added and the mixture refluxed for twenty hours. The methanol formed in the hydrolysis of the ester was fractionated off through a Vigreux column and the residue extracted with ether. The aqueous alkaline solution was acidified with dilute sulfuric acid and extracted with ether. The ethereal extract was dried over calcium chloride and distilled. The yield of XX, b. p. 103.5–104° (2.2 mm.), was 16.2 g. (69%). The product was semisolid at room temperature and for the infrared spectrum (Fig. 2) a sample was recrystallized from pentane, m. p. 32.5–35°. This material depressed the melting point of IV.

The *p*-phenylphenacyl derivative of XX was prepared[30] and recrystallized twice from ethanol; m. p. 127.8–129.8°. This derivative depressed (10°) the m. p. (131.5–132.2°) of the corresponding ester of IV.

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 79.49; H, 6.07. Found: C, 79.14; H, 6.10.

5,5-Dicarbethoxybicyclo[2.2.1]2-heptene.—To 20.2 g. (0.31 mole) of freshly-distilled cyclopentadiene dissolved in 100 ml. of anhydrous ether was added over twenty minutes 52.7 g. (0.31 mole) of freshly-distilled diethyl methylenemalonate.[31] During and for two hours after the addition the reaction mixture was stirred and cooled in an ice-bath. The ether was distilled and the residue fractionated. The yield of ester was 49.2 g. (68%); b. p. 109–111.5° (2 mm.), $n^{25}\text{D}$ 1.4645.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.71. Found: C, 65.62; H, 7.76.

5,5-Dicarboxybicyclo[2.2.1]2-heptene was obtained by saponification of the diester with alkali and ether extraction of the acidified reaction mixture. The crude material was recrystallized from benzene–hexane. The m. p. of the solid depended somewhat on the rate of heating; customarily, melting began at 110–112° with gas evolution at 112–115° and extensive decomposition at higher temperatures.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.53. Found: C, 59.48; H, 5.53.

Several attempts to decarboxylate the diacid by heating alone or in solvents were unsuccessful. In each instance either no reaction or extensive decomposition occurred.

3-Hydroxynortricyclene (V).—A mixture of 10 g. (0.058 mole) of II, 10 g. (0.14 mole) of lithium carbonate and 100 ml. of water was refluxed for two days and then extracted with ether. The ethereal solution was dried over magnesium sulfate. The ether was distilled and the residue sublimed under reduced pressure. The crude product, m. p. 60–96°, amounted to 4.2 g. (66%) and gave a test for unsaturation with potassium permanganate in acetone. On quantitative hydrogenation the crude material absorbed 9% of the theoretical quantity of hydrogen.

Pure V, m. p. 107.8–108.8°, was obtained by crystallization of the crude material from pentane (Skau tube) followed by sublimation. The infrared spectrum of pure V is shown in Fig. 2.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found C, 76.26; H, 9.16.

The phenylurethan of V was prepared by the reaction of V with phenyl isocyanate and recrystallized from benzene–hexane; m. p. 146–147.5°.

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59. Found: C, 73.2; H, 6.64.

The reaction of V with *p*-phenylazobenzoyl chloride in pyridine gave the *p*-phenylazobenzoate of V, m. p. 120.9–121.5°, after crystallization from ethanol–water.

Anal. Calcd. for $C_{20}H_{18}O_2N_2$: C, 75.45; H, 5.70. Found: C, 75.07; H, 5.52.

Hydrolysis of bromide VIII by a procedure similar to that described for II gave crude V, m. p. 102.5–104.4°, which after two crystallizations from pentane and sublimation had m. p. 107.0–108.2°. This material was further characterized by its phenylurethan, m. p. 147.0–148.1°, and its infrared spectrum which was identical with that of V obtained from the hydrolysis of II.

Hydrolysis of chloride VIII by boiling with excess lithium carbonate and water for five days also gave crude V, m. p. 101.5–104°, in 72% yield. The product was characterized by the *p*-phenylazobenzoate which had m. p. 120.5–121° after crystallization from ethanol–water.

Nortricyclanone (VI).—To a solution of 1.1 g. (0.010 mole) of V in 5 ml. of acetic acid was added slowly 0.6 g. (0.006 mole) of chromium trioxide dissolved in 5 ml. of 80% acetic acid. The mixture was allowed to stand at room temperature for three hours and then neutralized with 10% sodium carbonate solution. The ketone was steam-distilled and isolated as the **2,4-dinitrophenylhydrazone** which after two crystallizations from ethanol had m. p. 188.2–189.6°. The ultraviolet absorption spectrum of the 2,4-dinitrophenylhydrazone of VI in 95% ethanol had a prominent maximum at 365 mμ (ϵ = 24,000).

Anal. Calcd. for $C_{13}H_{12}O_4N_4$: C, 54.16; H, 4.20. Found: C, 54.24; H, 4.51.

***endo*-Dehydronorborneol (XI).**—*endo*-Dehydronorbornyl acetate was prepared by the reaction of vinyl acetate with cyclopentadiene as previously described.[9] The yields in 1–3 mole runs were 41–43%; b. p. 72° (10 mm.), $n^{25}\text{D}$ 1.4668. Judging from the nature of the products obtained on hydrolysis of the adduct (*vide infra*) it appears that the material is largely but not completely the *endo*-isomer.

XI was prepared by hydrolysis of the adduct with sodium hydroxide or *via* ester interchange with methanol using sodium methoxide as a catalyst; m. p. 109.4–110.8° (lit., 108–109°)[9] after sublimation and two crystallizations from pentane (Skau tube). The infrared spectrum of the product is shown in Fig. 2. The purity of even the highest melting samples of XI is open to some question since on treatment with phenyl isocyanate a mixture of phenylurethans was produced which on extensive fractional crystallization from hexane gave the **phenylurethan** of XI, m. p. 129.4–129.9° and a small quantity of the corresponding derivative of the *exo*-isomer XII, m. p. 149.2–151.8°. None of the impurity in XI could be V since XI absorbed the theoretical amount of hydrogen in ethyl acetate over platinum oxide.

Anal. Calcd. for $C_{14}H_{15}O_2N$ (phenylurethan of XI): C, 73.34; H, 6.59. Found: C, 73.49; H, 6.59.

The structure of the phenylurethan of XI was established by hydrogenation in ethyl acetate over platinum oxide to the phenylurethan of α-norborneol; m. p. 157.4–158.2° (lit., 159–160°)[29] after crystallization from hexane.

The infrared spectra (Fig. 2) of the *endo*- and *exo*-isomers of dehydronorborneol were quite similar and the absence of strong characteristic bonds made analysis of mixtures difficult.

Reaction of XI with *p*-phenylazobenzoyl chloride in pyridine gave XI **p-phenylazobenzoate**; m. p. 112.4–113.6° after several crystallizations from ethanol–water.

Anal. Calcd. for $C_{20}H_{18}O_2N_2$: C, 75.45; H, 5.70. Found: C, 75.31; H, 5.61.

Oxidation of XI by the procedure described for V gave dehydronorcamphor VII which was isolated as the **2,4-dinitrophenylhydrazone**; m. p. 173.8–175.0° after several

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[31] Bachmann and Tanner, *J. Org. Chem.*, **4**, 500 (1939).

crystallizations from ethanol. The ultraviolet absorption spectrum of the 2,4-dinitrophenylhydrazone of VII in 95% ethanol had a prominent maximum at 361 mμ (ϵ = 23,400).

Anal. Calcd. for $C_{13}H_{12}O_4N_4$: C, 54.16; H, 4.20. Found: C, 54.44; H, 4.36.

Treatment of 12.8 g. (0.12 mole) of XI dissolved in 10 g. of pyridine at 0° with 14.0 g. (0.12 mole) of thionyl chloride gave 2.8 g. (19%) of a chloride, b. p. 47.5–48.5° (11 mm.) which had $n^{25}D$ 1.4932. The chloride appeared to be largely 3-chloronortricyclene on the basis of its infrared spectrum (Fig. 3) which showed very strong absorption at 12.2–12.8 μ. On quantitative hydrogenation in ethyl acetate the material absorbed 19% of the theoretical quantity of hydrogen for a dehydronorbornyl chloride.

The reaction at 0° of 11 g. (0.10 mole of XI dissolved in 50 ml. of ether containing 5 g. of dry pyridine with 12.4 g. (0.046 mole) of phosphorus tribromide gave 3.2 g. (19%) of a monobromide, b. p. 63–67° (14.3 mm.), with $n^{25}D$ 1.5210. The infrared spectrum (Fig. 3) of the product indicates that it is largely II since all the strong absorption bands of II are present. A number of bands correspond fairly well to bromide VIII although the absorptions at 5.8, 7.2, 9.0, 9.6 and 12.9 μ do not appear in the spectra of either II or bromide VIII and may be due to *exo*-dehydronorbornyl bromide (XV) which has not as yet been obtained as a pure substance. The reaction product may be largely II and XV or a mixture of II, VIII and XV.

Preparation of *exo*-Dehydronorborneol (XII).—The method was adapted from the work of Doering and Aschner.[20] A mixture of 5 g. of crude XI, 10 ml. of dry toluene, 0.1 g. of fluorenone and a small piece of sodium was refluxed for seventeen hours. The reaction products were poured into water and the organic layer separated and dried over magnesium sulfate. The toluene was evaporated under reduced pressure and the residue sublimed. The crude product was recrystallized from pentane (Skau tube); yield 1.8 g. (36%), m. p. 97.5–99.2°.

XII reacted with phenyl isocyanate to give the phenylurethan; m. p. 152.4–153.6° after several crystallizations from hexane.

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59. Found: C, 73.55; H, 6.82.

The structure of the urethan was established by hydrogenation in ethyl acetate over platinum oxide to the phenylurethan of β-norborneol; m. p. 140.6–141.4° (lit., 139–140°)[29] after crystallization from hexane.

The infrared spectrum of XII is shown in Fig. 2.

Attempted Isomerization of 3-Hydroxynortricyclene (V), *endo*- and *exo*-Dehydronorborneols (XI and XII).—One to two gram samples of the alcohols were shaken with 10 ml. of aqueous 25–50% sulfuric acid at room temperature for sixteen hours. Water was added and the mixture extracted with ether. The ethereal extract was shaken with dilute sodium hydroxide solution, then with water and finally dried over magnesium sulfate. The ether was distilled and the residue fractionally sublimed. In each case, the first fraction was alcohol while the second fraction was glycol. The alcohol fractions were analyzed by their infrared spectra in carbon disulfide solutions. With 25% acid only unchanged alcohol was recovered. With 30–35% acid the starting material and considerable glycol were obtained while using 40% acid only glycol was isolated. With 50% acid no solid products were obtained. The glycol from V, XI and XII had m. p. 169.5–171°.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.73; H, 9.53.

***t*-Butylbenzene and Norbornylane with N-Bromosuccinimide.**—A mixture of 15 g. (0.112 mole) of *t*-butylbenzene, 15 g. (0.085 mole) of N-bromosuccinimide, 0.1 g. of benzoyl peroxide and 100 ml. of carbon tetrachloride was stirred and refluxed under a General Electric RS Sunlamp for twenty-eight hours. The solution became dark but on filtration 13.8 g. (92%) of the N-bromosuccinimide was recovered.

A mixture of 10 g. (0.104 mole) of bicycloheptane, 19 g. (0.106 mole) of N-bromosuccinimide, 0.1 g. of benzoyl peroxide, and 50 ml. of carbon tetrachloride was stirred and refluxed under an ultraviolet lamp for two hours. Only a 4% yield of an impure bromide, b. p. 86–90° (45 mm.), was obtained.

Summary

The reaction of norbornylene with N-bromosuccinimide, bromine, or bromine and pyridine was found to give 3-bromonortricyclene.

3-Bromonortricyclene was converted to the corresponding hydrocarbon, alcohol, and carboxylic acid. The *endo*-dehydronorbornyl halides appear to isomerize at 160–195° in steel containers to 3-halonortricyclenes. The *endo*-dehydronorbornyl halides give the same reaction products as 3-bromonortricyclene *via* hydrolysis or the Grignard reagents.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY—NAVAL STORES DIVISION]

Nopol. II. Syntheses in the Apocamphane Series. The Preparation of Optically Pure *l*-Camphene

BY JOSEPH P. BAIN, ALBERT H. BEST, BURT L. HAMPTON, GEORGE A. HAWKINS AND LELAND J. KITCHEN

There was recently described[1] the preparation and certain reactions of nopol (I), (6,6-dimethylbicyclo[3.1.1.]2-heptene-2-ethanol), the bicyclic alcohol produced by the condensation of β-pinene with formaldehyde. Since β-pinene occurs only in the optically pure levo form and nopol produced under various conditions always possesses substantially the same optical rotation (−36.1° for 10-cm. tube) it is assumed that nopol is also an optically pure levo compound and is not readily racemized. It was shown that nopol possesses the α-pinene rather than the β-pinene structure, though it can be prepared only from β-pinene. Nopol and its esters undergo a number of reactions which have been applied to α-pinene. It is our purpose to describe here the reaction of nopyl acetate (II) with anhydrous hydrogen chloride to yield 2-chloro-1-apocamphane-β-ethyl acetate (III) and with hydrogen bromide to form the corresponding 2-bromo compound either of which may be converted to *l*-camphene by means of reactions to be described. It is considered that the addition of hydrogen

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[1] Bain, THIS JOURNAL, **68**, 638 (1946).