acetone, *l* 4). The infrared spectra (chloroform solutions) of the active and racemic methyl ethyl esters were precisely superimposable.

Anal. Calcd. for $C_{12}H_{16}O_4Br_2$: C, 37.52; H, 4.20. Found: C, 37.74; H, 4.26.

Pyrolysis of the Active Monomethyl Ester to the *meso*-Anhydride.—A sample (0.225 g.) of (+)-VIIIb, $[\alpha]_D$ +1.5°, was heated at 185–190° for five minutes. The pyrolysis residue was cooled, made up accurately to a volume of 10 cc. in acetone, treated with a pinch of Norit A and finally freed of charcoal by centrifugation. The solution was optically inactive, α +0.006 ± 0.016°. (The precision of the readings was lower than usual in this case because the solution was faintly colored.) From 7.3 cc. of the polarimetry solution there was obtained 0.140 g. (94%) of the anhydride (VIb), m.p. 252–255°, alone or mixed with an authentic specimen.

LOS ANGELES 7, CALIFORNIA

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

Isomerism in the Diels–Alder Reaction. III. The Bromination of the Diels–Alder Adduct, Norbornylene[1]

BY HAROLD KWART AND LLOYD KAPLAN

RECEIVED NOVEMBER 13, 1953

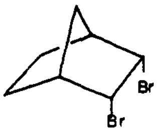
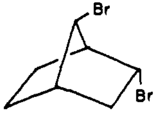
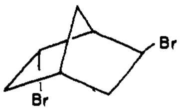
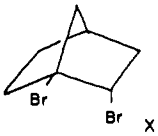
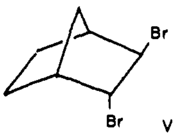
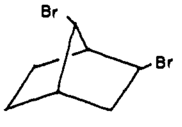
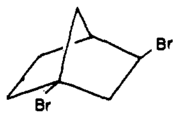
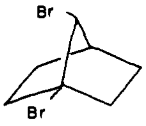
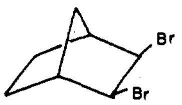
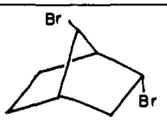
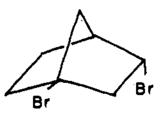
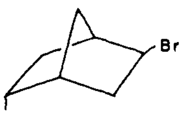
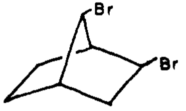
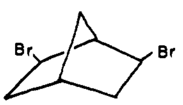
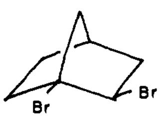
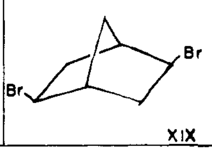
The bromination of norbornylene yields two distinct dibromides, whose structures have been elucidated by dipole moment measurement and characterization of their dehydrobromination products. Some consideration is given to the path of reaction by which these structures are formed. The dehydrobromination reaction and the isomerization under the influence of electrophilic reagents also are discussed.

Introduction.—Previous studies[2] on the bromination of norbornylene, I (bicyclo[2.2.1]heptene-2), have shown that a complex mixture of products is obtainable, among which *exo*-norbornyl bromide II and 3-bromonortricyclene III could be identified. The constitution of the dibromide products was not determined. We undertook to separate the components of the dibromide fraction and determine their structures in order to further our studies[3] of the stereochemical course of addition reactions of the double bond of bicyclic Diels–Alder adducts. We are reporting here the isolation of two pure dibromide products of this reaction and the structural assignments we have made thereto based on dipole moment measurements and chemical reactivity studies.

Discussion of Results

Designating the two dibromides as compounds A and B, respectively, Table I contains a summary of the dipole moment results as well as the calculated moments of all possible structures for comparison. On this basis a preliminary screening of the possible structures that could be assigned to A and B was obtained.

TABLE I. DIPOLE MOMENTS OF DIBROMONORCAMPHANES

Structure	μ calc'd.	Structure	μ calc'd.	Structure	μ calc'd.	Structure	μ calc'd.
 IV	3.7 D	 VIII	2.1 D	 XII	2.3 D	 XVI	3.3 D
 V	2.0 D	 IX	2.0 D	 XIII	2.3 D	 XVII	2.8 D
 VI	3.8 D	 X	2.1 D	 XIV	2.2 D	 XVIII	1.9 D
 VII	3.9 D	 XI	2.3 D	 XV	3.3 D	 XIX	1.9 D

Compound	*Observed*	*Alternative configurations consistent with these moments*
A	2.3*D*	V, VIII, IX, X, XI, XII, XIII, XIV, XVIII, XIX
B	3.5*D*	IV, VI, VII, XV, XVI

A C–Br bond moment of 2.0 *D* was used in calculating the above dipole moments (see reference 1b).

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[1] The research work being reported here has been supported by the Office of Naval Research under contract N-onr-567(00).

[2] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

[3] For the previous paper in this series see *ibid.*, **75**, 3356 (1953).

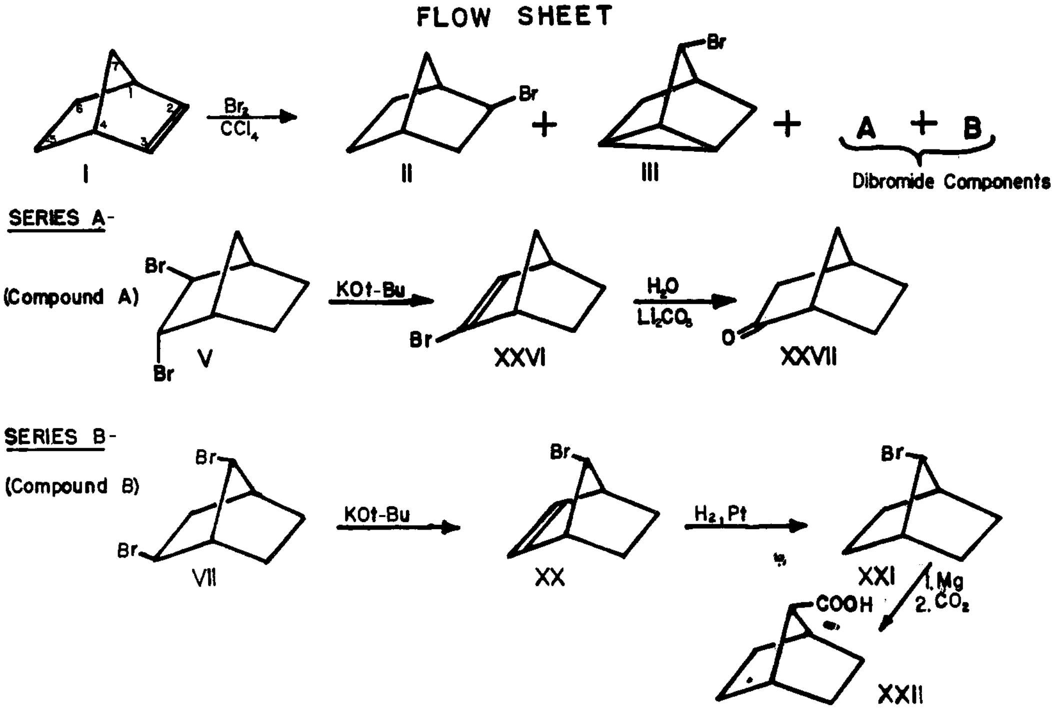
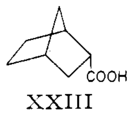


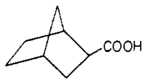
Fig. 1.

The evidence, on which final structural assignment was based, is outlined in the accompanying flow sheet (Fig. 1). Treating compound B with one equivalent of potassium *t*-butylate produced an olefin bromide XX which on subsequent catalytic hydrogenation afforded in good yield compound XXI. This end-product was a saturated bromide whose infrared spectrum and refractive index was different from those of both *exo*- and *endo*-norbornyl bromide[2,4] (see Experimental section).

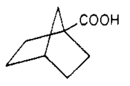
Further characterization of XXI was obtainable by conversion to the Grignard reagent and carbonation of the Grignard reagent to the acid XXII (m.p. 77–78°). Of the four possible norcamphanemonocarboxylic acids three have been previously prepared and identified; *endo*-2,5-endomethylenehexahydrobenzoic acid (XXIII),[5] m.p. 65–66°; *exo* - 2,5 - endomethylenehexahydrobenzoic acid (XXIV)[6a] m.p. 48°; and 1-carboxynorcamphane (XXV),[6b] m.p. 113°. We concluded, therefore, that XXII corresponds to the fourth possibility, 7-carboxynorcamphane. The isomeric acid 3-carboxynortricyclene XXX,[7] m.p. 49–51°, strongly depressed the melting point of XXII and exhibited an entirely different infrared absorption spectrum (see Experimental).



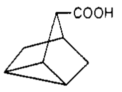
XXIII



XXIV



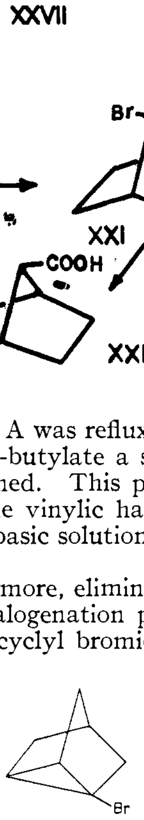
XXV



XXX

When compound A was refluxed with an equivalent of potassium *t*-butylate a second unsaturated bromide was obtained. This product was readily characterized as the vinylic halide XXVI by hydrolysis in weakly basic solution to the known norcamphor XXVII.

We have, furthermore, eliminated the possibility that the dehydrohalogenation products of both A and B were nortricyclyl bromides, *viz*., either III or XXXI.



XXXI

Thus, the dehydrobromination product obtained from A was strongly unsaturated to permanganate in acetone solution but a pure sample of III gave a negative test.[8] In addition, this product was hydrolyzable in good yield to norcamphor under exactly the same conditions that III affords only 3-hydroxynortricyclene. Comparison of the infrared spectra convincingly disproved the possibility of any considerable contamination of the vinyl bromide with 3-bromonortricyclene. The dehydrobromination product obtained from B also showed a positive permanganate test. Furthermore, it readily took up slightly more than 100% of the theoretical amount of hydrogen when reduced (at room temperature and atmospheric pressure) with Adams

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(4) J. D. Roberts, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).

(5) K. Alder and G. Stein, *Ann.*, **514**, 197 (1934).

(6) (a) K. Alder and G. Stein, *ibid.*, **514**, 197 (1934). (b) W. von E. Doering, THIS JOURNAL, **75**, 1008 (1953), and private communication.

(7) Sample provided by Dr. J. D. Roberts.

(8) Roberts[3] reports that nortricyclene is not oxidized by potassium permanganate and employs this as a method of separating it from unsaturated impurities. A similar report is to be found in the literature on tricyclene and its derivatives; see, for example, J. Simonsen, "The Terpenes," Cambridge Univ. Press, New York, N. Y., Vol. II, p. 333 (1949). We have inferred that a negative permanganate test should also be expected of XXXI.

catalyst. Roberts[4] has reported that III cannot be reduced under these conditions and has used this hydrogenation procedure for estimating the olefinic impurities in samples of III. The infrared spectra of XX and XXI provided a further basis for distinction from III.

We have concluded on these grounds that only the *trans*-dibromide structure V may be assigned to compound A and the 2,7 rearranged structure VII to compound B.

The identification of two dibromide products in addition to 3-bromonortricyclene on brominating norbornylene in carbon tetrachloride suggested the possibility that one of the products was formed by the action of hydrogen bromide (evolved during the reaction) on the 3-bromonortricyclene.[9] On investigating the addition of dry hydrogen bromide in carbon tetrachloride solution to III at ice-bath temperatures we obtained the two dibromide products in good yield in the approximate ratio of two parts of V to one part of VII. This ratio is precisely the inverse of that obtained by direct bromination of norbornylene in carbon tetrachloride and indicated that all of V may have been formed in this manner. An experiment was therefore undertaken in which one equivalent of pyridine was added to the brominating medium with the purpose of preventing the formation of the *trans*-dibromide arising from the reaction of III with hydrogen bromide.

While the pyridine had the expected effect of eliminating the reaction leading to *exo*-norbornyl bromide, the same dibromide products observed in the pure carbon tetrachloride bromination were again obtained. The only observable effect of the pyridine was to increase the ratio of VII to V by approximately a factor of two, indicating that V was not formed *exclusively* from a side reaction of hydrogen bromide and 3-bromonortricyclene during bromination in either case. Furthermore, the fact that the proportion of VII was increased in the presence of pyridine indicated that it was the predominant product of the direct bromination in the absence of pyridine.

There remained the possibility that one of the products was readily isomerizable to the other in the presence of acidic catalysts, and consequently was a secondary reaction product of the other. The ease of isomerization of VII was therefore examined in the presence of hydrogen bromide and stannic bromide, with the identical result of almost complete conversion to V. These experiments confirmed the greater stability of V and indicated that under conditions of bromination which might also tend to establish the equilibrium of the isomers VII may be partially transformed to V. (This inference could be drawn from the increased proportion of VII observed when the acidity of the reaction mixture was lowered from that of hydrogen bromide to pyridine hydrobromide.) When repeated attempts to isomerize VII to V in the presence of pyridine hydrobromide at room temperature produced no reaction, we concluded that both VII and V are primary dibromination products, with VII being formed predominantly in the direct bromination reaction of norbornylene. However, we have not ruled out the possibility that VII and V were formed by mechanisms involving different intermediates; the former by a polar process (favored by the presence of pyridine), the latter by a radical chain reaction unaffected by the medium nature. This possibility is being explored further.

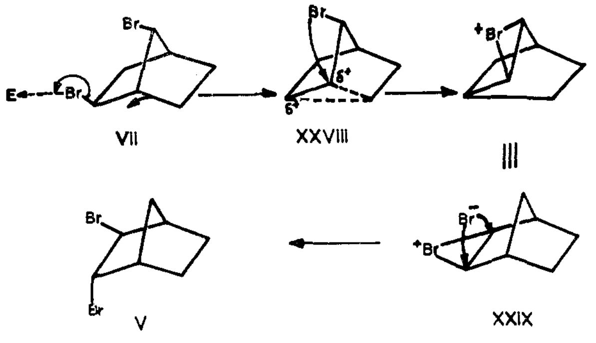

Fig. 2.—The Nametkin isomerization of VII to V.

Our work with perhydroxylation reactions has shown that a symmetrical reagent, X_2, that commonly exhibits *trans* addition to olefins, yields entirely a rearranged product with norbornylene under purely ionic conditions of reaction. In a forthcoming publication, we will comment on the significance that these results hold for the mechanism of the bromination reaction of norbornylene leading to VII.

The transformation of VII to V under the influence of electrophilic catalysts, as demonstrated above, is viewed as an interesting example of the Nametkin[10] change. This reaction mechanism is illustrated in Fig. 2. Maintenance of configuration in each of the intermediates and Walden inversion at each displacement is required to account for the complete stereospecificity of the reaction.

The relative reactivity of the dibromides toward elimination was somewhat unexpected. Thus, it was readily observed that the *trans* vicinal dibromide V was very much more rapidly dehydrobrominated with potassium tertiary butoxide than the dibromide VII where the halogen relationship is 1,3. Since the requirement of *trans* coplanar relationship[11] of the elements to be eliminated is not fulfilled in V, here again is another instance of *cis* elimination.[12] The striking feature of this reaction is its rate, for *exo*-norbornyl bromide eliminates very much more slowly under these conditions. Judging from the disparity in ease of dehydrobromination between VII and V it is clear that a proton is removed by base much more readily from a carbon which carried a bromine than from one where there is no bromine closer than one carbon away. Though the bromine atom on C_7 is very close in space to the seat of proton abstraction in VII, its influence is determined less by actual distance than by its separation along the carbon chain.[13]

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(9) The reaction of hydrogen chloride on tricyclene (in the camphane family) is known to yield isobornyl chloride; H. Meerwein and K. von Emster, *Ber.*, **53**, 1815 (1920); **55**, 2500 (1922).

(10) See, for example, J. Houben and E. Pfankuch, *Ann.*, **489**, 204 (1931).

(11) D. H. R. Barton, *J. Chem. Soc.*, 1030 (1953).

(12) S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).

(13) For a discussion of the influence of substituents remotely separated from a reaction center in bicyclic systems see J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953).

Experimental

Preparation of Bicyclo[2.2.1]heptene-2 (I).—This compound was prepared by condensing ethylene with cyclopentadiene according to the procedure of Joshel and Butz.[14] The fraction boiling from 95–97° was used in the following experiments.

Bromination of I.—One and six-hundredths moles (100 g.) of norbornylene in 220 cc. of dry carbon tetrachloride were brominated with a solution of 0.92 mole (148 g.) of bromine in 100 cc. of carbon tetrachloride, at −5°, according to the procedure in reference 2. After pumping off the solvent with a water aspirator, the residue was fractionated through an 8-inch Widmer column. The following fractions were obtained:

Temp., °C.	Pressure, mm.	Weight, g.
74–75.5	19–20	82.6[a]
55	2	8.6
57–60	0.30–0.32	23.3[b]
59–66	.28– .32	8.0
69–72.5	.28– .34	42.9[c]

[a] n^{25}_D 1.5205; Roberts[2] reports this fraction to be composed of 60% 3-bromonortricyclene and 40% *exo*-norbornyl bromide (n^{25}_D 1.5222). [b] This fraction was redistilled through a 12.5 cm. Vigreux column directly into glass ampoules which were sealed off in a nitrogen vacuum; b.p. 62–63° (0.4 mm.), n^{20}_D 1.5618 (see ref. *d*). *Anal.* Calcd. for $C_7H_{10}Br_2$: Br, 62.93. Found: Br, 62.93, 63.18. [c] This fraction was redistilled as above; b.p. 74–75° (0.4 mm.), n^{20}_D 1.5710 (see ref. *d*). *Anal.* Calcd. for $C_7H_{10}Br_2$: Br, 62.93. Found: Br, 63.60, 63.39.

$$\text{Ratio: } \frac{\text{g. 2,7-dibromide}}{\text{g. 2,3-dibromide}} = \frac{42.9}{23.3} = 1.8$$ [15]

[d] The refractive index of each dibromide fraction varied within ±0.0005 unit from the values obtained on repeated refractionation of the respective cuts. Infrared spectra of all fractions of the same dibromide did not show any differences. Repetition of these preparative procedures always produced almost identical results.

SPECTRAL DATA

λ max in microns; S-sharp, B-broad

Strong	Intermediate	Weak
	trans-2,3-Dibromobicyclo[2.2.1]heptane (V)	
7.7B, 8.1B, 8.2S, 8.4S, 8.5S, 8.8S, 9.6S, 10.6B, 11.1S, 11.8S, 12.6B, 13.0S, 13.2B, 13.4S, 13.6S	9.7S, 10.4S, 10.9S, 11.6S, 12.3S, 15.7B	5.7S, 7.9S, 9.4S, 10.0S, 12.5B, 14.0B
	2-*exo*-7-*cis*-Dibromobicyclo[2.2.1]heptane (VII)	
6.8S, 7.6S, 8.0B, 8.8S, 10.1S, 10.6S, 11.1S, 11.4S, 12.3B, 12.8S, 13.0B, 13.4S	7.8S, 8.2S, 8.3S, 9.8S, 11.8S	8.5S, 8.6S, 9.4S, 9.9S, 10.9S, 11.6S, 13.6S, 15.5B
	Norcamphor 2,4-dinitrophenylhydrazone	
	6.1S, 6.3S, 6.7S, 7.3S, 7.5S, 7.7S, 7.9S, 8.2S, 8.8B, 9.4S, 10.9B, 11.9S, 13.5S	4.2B, 7.1S, 14.2S
	7-Bromobicyclo[2.2.1]heptane (XX)	
3.3S, 7.4S, 8.1S, 12.4S, 14.0B	3.2S, 3.4S, 6.8S, 6.9S, 7.6S, 7.7S, 8.3S, 8.8S, 10.7S, 11.5S, 11.7S, 13.1S	6.1B, 6.3S, 6.7S, 7.9S, 8.5S, 8.7S, 9.0S 9.1S, 10.3S, 10.9S, 12.6S, 12.7S, 14.6S
	7-Bromobicyclo[2.2.1]heptane (XXI)	
3.4S, 7.6S, 8.1S, 12.4S, 12.9S, 13.7S	3.5S, 6.8S, 6.9S, 8.3S, 8.5S, 8.8S, 10.1S, 10.7S, 11.4S	6.7S, 9.0S, 9.3S, 9.7S, 11.2S, 12.0S, 14.0B
	2-Bromobicyclo[2.2.1]heptane-2 (XXVI)	
3.3B, 6.3S, 6.9S, 7.6S, 7.8S, 8.3B, 8.6S, 8.8S, 9.0B, 9.6B, 10.9B, 11.4B, 12.2B, 12.6B, 13.0B, 13.4B, 13.8B, 14.1B, 14.4B	3.2S, 5.7S, 7.2S, 7.3S, 7.35S, 7.4S, 7.5S, 10.4S, 10.5S, 10.6B, 12.0S	3.4S, 6.1S, 8.0S, 9.8S, 10.0S, 10.1S, 15.9S
	exo-2-Bromobicyclo[2.2.1]heptane (II)	
3.4S, 3.5S, 6.9S, 7.6S, 7.7S, 8.1S, 8.4S, 10.6S, 11.2S 13.0S	7.9S, 8.0S, 8.8S, 9.6S, 10.9B, 11.4S, 12.0S, 12.4S, 15.5S	6.8S, 7.0S, 7.8S, 8.5S, 8.9S, 9.9S, 10.0S, 10.4S, 11.6S, 12.1S, 12.5S, 13.1S
	3-Bromotricyclo[2.2.1.0^{2,6}]heptane (III)	
3.3S, 3.4B, 6.8S, 6.9S, 7.4S (doublet), 7.6S, 7.7S, 7.9S, 8.1–8.3B, 8.5S, 9.4S, 10.5S, 10.8S, 10.9S, 11.0B, 11.3S, 12.2–12.6B, 13.4–13.8B	8.8S, 11.8S, 14.8S, 15.6S	5.2S, 5.4S, 6.2S, 9.6S, 9.8S, 9.9S, 10.2B, 13.0B, 15.1B
	3-Carboxytricyclo[2.2.1.0^{2,6}]heptane (XXX) (Nujol mull)	
3.2–3.6B, 5.9S	7.1S, 7.7S, 12.2B, 12.4S	2.3S, 7.3S, 7.5S, 8.1S, 8.3S, 8.5S, 8.8S, 9.4S, 13.5B
	7-Carboxybicyclo[2.2.1]heptane (XXII) (Nujol mull)	
3.5S, 5.9S, 6.9S, 7.1S, 7.7S, 8.1B, 10.5–10.8B	7.3S, 7.4S, 8.7S, 9.6S, 13.7B	2.3–2.7B, 8.3S, 8.4S, 9.3S, 11.3S, 11.4S, 11.9S, 12.5S, 12.8S

In Carbon Tetrachloride with One Equivalent of Pyridine.—To a solution of 0.63 mole (60 g.) of I and 0.63 mole (51 g.) of dry (Karl Fischer) pyridine in 300 cc. of carbon tetrachloride (carbon disulfide-free and distilled from phosphorus pentoxide) in a flask fitted with a condenser, dropping funnel and a mercury sealed stirrer, was added 0.63 mole (102 g.) of bromine over a period of two hours. During the addition the mixture was cooled in an ice–salt-bath and the internal temperature did not rise above 0°. When the addition was complete, the mixture was filtered with suction to remove the pyridinium hydrobromide, washed with 200 cc.

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[14] L. M. Joshel and L. W. Butz, THIS JOURNAL, **63**, 3350 (1941).

[15] This ratio was identical in duplicate runs.

of 6 *N* hydrochloric acid and dried over calcium chloride. The carbon tetrachloride was removed with a water pump and the residue fractionated under reduced pressure through a 6-inch Widmer column. The following fractions were obtained:

Temp., °C.	Pressure, mm.	Weight, g.
68–74	12–13	14.24[a]
53–59	0.25–0.30	17.51[b]
60–72	.40– .45	5.82
70–74	.25– .30	62.25[c]

[a] Roberts[2] has shown this fraction to be pure 3-bromonortricyclene and not a mixture of 3-bromonortricyclene and *exo*-norbornyl bromide. [b] $n^{20}\text{D}$ 1.5612. [c] $n^{20}\text{D}$ 1.5714.

$$\text{Ratio:}\quad \frac{\text{g. 2,7-dibromide}}{\text{g. 2,3-dibromide}} = \frac{62.25}{17.51} = 3.6$$

2-Bromobicyclo[2.2.1]heptene-2 (XXVI).—Twelve-hundredth mole (31 g.) of compound B (V) was added to a hot solution of 0.13 mole (5.07 g.) of potassium in 110 cc. of *t*-butyl alcohol (distilled from calcium hydride). Potassium bromide was observed to precipitate immediately. The mixture was then refluxed for an additional 12 hours and poured into its own volume of water to dissolve the potassium bromide. Twenty-five cc. of ether was added and the layers separated. The aqueous layer was extracted with four 50-cc. portions of ether and the combined ether extracts dried over magnesium sulfate. The ether and *t*-butyl alcohol were distilled off at atmospheric pressure and the residue fractionated under reduced pressure into glass ampoules which were sealed under a nitrogen vacuum. Nine and two-tenths grams (44%) of the olefin bromide, b.p. 61–63° (16 mm.), $n^{20}\text{D}$ 1.5058, was recovered. Additional yield could be obtained by redistillation of the remaining fractions.

Anal. Calcd. for C_7H_9Br: Br, 46.18. Found: Br, 45.81, 46.60.

7-Bromobicyclo[2.2.1]heptene-2 (XX).—Twenty-three hundredths mole (58.4 g.) of the dibromide VII was added to a hot solution of 0.24 mole (9.0 g.) of potassium in 200 cc. of dried *t*-butyl alcohol. Potassium bromide was precipitated only very slowly in this instance. After refluxing for 12 hours, the reaction mixture was worked up as above and upon distillation 18.46 g. (46%) of the olefin bromide, b.p. 68–70° (13 mm.) ($n^{20}\text{D}$ 1.5260), was recovered.

Anal. Calcd. for C_7H_9Br: Br, 46.18. Found: Br, 46.71, 46.30.

Material balances in the dehydrohalogenation of both V and VII were accounted for by tarry pot residue. The pure olefin bromides XXVI and XX slowly darkened when stored at room temperature. Stability was considerably greater on storage at Dry Ice temperature in ampoules sealed at 16 mm. under dry nitrogen. The loss of yield as tarry residue in the dehydrohalogenation reaction was apparently attributable to a thermally induced side reaction.

7-Bromobicyclo[2.2.1]heptane (XXI).—To 200 cc. of ethyl acetate in a Parr low pressure hydrogenator was added 0.13 mole (22.49 g.) of the olefin bromide XV and 0.11 g. of platinum oxide. The system was evacuated with a water aspirator and the hydrogen pressure adjusted to 380 mm. (gage). The mixture absorbed hydrogen rather rapidly at first, but after one hour the gage reading was essentially constant. At this point the hydrogen uptake was 110% of the theoretical amount. The solution was filtered from the catalyst and as much ethyl acetate as possible was distilled off at atmospheric pressure on a water-bath. On fractionating the residue under reduced pressure 20.9 g. (92%) of the saturated bromide, b.p. 70–72.5° (15–16 mm.), $n^{20}\text{D}$ 1.5169, was obtained.

Anal. Calcd. for $C_7H_{11}Br$: Br, 45.65. Found: Br, 44.75, 44.99.

7-Carboxynorcamphane (XXII).—To 0.10 mole (2.43 g.) of magnesium turnings and 100 cc. of anhydrous ether in a 200 cc. two-necked flask fitted with a dropping funnel, reflux condenser and magnetic stirrer was added 0.02 ml. of methyl iodide. After the methyl Grignard had formed, 0.1 mole (17.5 g.) of the saturated bromide XXI in 20 cc. of anhydrous ether was added over a period of 15 minutes, with continuous stirring. After the addition was complete, the mixture was stirred for 12 hours. Thoroughly dried carbon dioxide was then passed into the reaction mixture until most of the ether had been swept out by the gas stream. The residue was taken up in 100 cc. of water and acidified with 6 *N* hydrochloric acid. The solution was extracted with two 100-cc. portions of ether and the combined ether extracts were then extracted with saturated sodium carbonate solution until the aqueous layer was basic. Acidification of the aqueous extract with 6 *N* hydrochloric acid precipitated the carboxylic acid. The product was then extracted into ether. Two and eight-tenths grams of white crystals melting at 77.5–78.5° was recovered on evaporation of the dried ether solution. Repeated recrystallization did not alter the melting point.

The material balance was partly accounted for by 3 g. of crystalline, non-acidic material (m.p. 107–109° sealed tube). This compound did not contain a hydroxyl group (infrared spectrum) and did not correspond in other respects either to norcamphane (m.p. 86–87°) or nortricyclene[2] (m.p. 56–57°). It is entirely possible that this compound was 7,7′-binorcamphane formed by the Grignard coupling reaction. On this assumption the side reaction product constituted a 50% loss of starting material.

The *p*-phenylphenacyl ester of the acid was prepared[16] and recrystallized from ethanol–water; m.p. 118–119.2°. Analysis was performed on this derivative.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63. Found: C, 79.15, 78.93; H, 6.20, 6.32.

While the *p*-phenylphenacyl esters of XXII and 3-carboxynortricyclene[2] have similar melting points, the melting point difference between the respective pure acids is of sufficient magnitude to assume non-identity of the *p*-phenylphenacyl esters. If the higher melting XXII were an impure mixture, a much lower and longer range melting derivative should have been expected. Furthermore, comparison of infrared spectra leaves little doubt that XXII was not contaminated with 3-carboxynortricyclene.

Addition of Hydrogen Bromide to 3-Bromonortricyclene.—Twenty-seven hundredths mole (46.5 g.) of 3-bromonortricyclene was added to 50 cc. of dry, carbon disulfide-free carbon tetrachloride in a 200 cc. 3-necked, flask fitted with a gas inlet tube, mercury sealed stirrer, and condenser protected with a calcium chloride drying tube. Dry hydrogen bromide was passed through the mixture for 12 hours with continuous stirring, while the flask was immersed in an ice-water-bath at 0°. The carbon tetrachloride was removed on a water-pump and the residue fractionated under reduced pressure through a 9-cm. Widmer column directly into glass ampoules and sealed off under a nitrogen vacuum. The following fractions were obtained:

Temp., °C.	Pressure, mm.	$n^{20}\text{D}$	Wt., g.	V, g.	VII, g.
50	0.2 –0.3	1.5223		...	...
51–54	.20– .25	1.5612	2.03	2.03	...
50–53	.20– .25	1.5630	7.38	6.61	0.77
55–57	0.35	1.5635	3.70	3.11	.59
60–62	.45– .5	1.5638	3.56	3.22	.34
51–55	.2 – .3	1.5640	6.14	4.82	1.32
51–54	.18– .25	1.5647	12.77	9.07	3.70
53–59	.18– .25	1.5662	7.01	3.86	3.15
61.5–70	.35	1.5686	3.92	1.16	2.76
69–74	.35	1.5708	4.45	0.29	4.16
			Total	34.17	16.79

The components of the fractions in the above table were estimated from a graph of refractive index *vs.* % composition of mixtures of V and VII. This relation is entirely linear.

Isomerization of VII. A. With 47% Hydrobromic Acid.—Eighty-seven hundredths mole (22 g.) of the 2,7-dibromide was refluxed with 25 cc. of 47% hydrobromic acid for two hours with vigorous stirring. After dilution with an equal volume of water the mixture was extracted with two 50-cc. portions of ether. The combined ether extracts were dried over magnesium sulfate and the ether distilled off at atmospheric pressure. Fractionation of the residue through a 9-cm. Vigreux column yielded 14.5 g. of material (b.p. 60–63° (0.3 mm.)). The refractive index, $n^{20}\text{D}$ 1.5620, and infrared spectrum were identical with that of an authentic

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(16) N. L. Drake and J. Bronitsky, THIS JOURNAL, **52**, 3715 (1930)

sample of V. The poor material balance was partially accounted for by 4 g. of tarry pot residue.

B. **With Stannic** Bromide.—Five-hundredths mole (12.7 g.) of the 2,7-dibromide was refluxed with 0.01 mole (4.39 g.) of stannic bromide in 50 cc. of dry toluene for 48 hours. When cool, the reaction mixture was shaken with 50 cc. of cold 25% sulfuric acid, washed once with water and dried over magnesium sulfate. The toluene was distilled off at atmospheric pressure and the residue was fractionated through a 9-cm. Widmer column directly into glass ampoules sealed off in a vacuum. The following fractions were obtained:

Temp., °C.	Pressure, mm.	$n^{20}D$	Wt., g.	V, g.	VII, g.
25–48	0.1–0.15	....	*ca.* 0.05	..	..
46–48	.1–0.15	1.5621	3.54	3.50	0.04
43	.1	1.5631	2.40	2.11	0.29
			Total	5.61	0.33

The composition of the fractions was determined as described above. The pot residue was approximately 4 g.

This amounts to a 94% conversion of VII to V based on recovered dibromides. When the identical mixture was refluxed for two hours, only a 5% conversion of the 2,7-dibromide to the 2,3-dibromide was obtained.

Bicyclo[2.2.1]heptanone-2 (Norcamphor) XXVII.—*endo*-Dehydronorbornyl acetate was prepared in 49% yield by the reaction of vinyl acetate (3.9 moles) and cyclopentadiene (4.3 moles) as previously described.[17]

Hydrogenation of 1 mole (154 g.) of *endo*-dehydronorbornyl acetate in an equal volume of glacial acetic acid with platinum oxide in the Parr low pressure hydrogenator gave an 88% yield of *endo*-norbornyl acetate, b.p. 73–74°.

Saponification of the ester with methanolic potassium hydroxide gave a mixture of *exo*- and *endo*-norborneols[2] in 81% yield. Oxidation of the mixed norborneols with chromic anhydride in acetic acid[2] gave norcamphor in 80% yield, m.p. 93–95°. The 2,4-dinitrophenylhydrazone was prepared by treating the ketone with a hot solution of 2,4-dinitrophenylhydrazine hydrochloride in aqueous methanol. On cooling, the 2,4-dinitrophenylhydrazone crystallized out. One recrystallization from absolute ethanol gave orange plates, m.p. 129.5–130.5°.

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: N, 19.30. Found: N, 18.95.

Hydrolysis of XXVI.—Twenty-eight thousandths mole (4.8 g.) of the vinyl bromide was refluxed with a suspension of 0.05 mole (3.35 g.) of lithium carbonate in 150 cc. of water for seven days. The mixture was then steam distilled and the distillate extracted with two 50-cc. portions of low boiling petroleum ether (30–60°) and one 50-cc. portion of ethyl ether. The combined extracts were dried over anhydrous magnesium sulfate and the solvent removed by slow distillation through a 6-inch Widmer column. The residue, about 1 g., possessed the strong, characteristic odor of norcamphor. Rather than chance loss in distillation it was converted directly to the 2,4-dinitrophenylhydrazone as above. The crude 2,4-dinitrophenylhydrazone was chromatographed on a column of silicic acid and Celite.[18] The purified material (orange band) was obtained by eluting the column with a 4% (by volume) solution of ethyl ether in *n*-pentane. A dark red band remained near the top of the column. This was presumably 2,4-dinitrophenylhydrazine as it is absorbed more strongly than 2,4-dinitrophenylhydrazones.[18] After evaporating the solvent from the eluent and recrystallizing the residue three times from chloroform–*n*-pentane, the 2,4-dinitrophenylhydrazone melted at 123–126.5°. While the melting point of a known sample of norcamphor 2,4-dinitrophenylhydrazone was depressed one degree by this derivative, the infrared spectra of the two samples were identical.

TABLE II

DATA FROM DIPOLE MOMENT CALCULATIONS

Concn. (moles/cc. × 10^5)	ϵ	n^2	Concn. (moles/cc. × 10^5)	ϵ	n^2
		Compound B (structure VII)			
0.00	2.2252	2.0167	0.00	2.2101	2.0167
1.74	2.2499	2.0181	0.99	2.2237	2.0181
3.32	2.2746	2.0187	1.61	2.2359	2.0184
6.50	2.3191	2.0207	3.13	2.2587	2.0195
9.58	2.3658	2.0224	6.38	2.3047	2.0212
$S^0 = 0.0143, \mu = 3.5\ D$			$S^0 = 0.0140, \mu = 3.4\ D$		
		Compound **A** (structure V)			
0.00	2.2252	2.0167	0.00	2.2101	2.0167
1.50	2.2352	2.0178	0.71	2.2131	2.0178
3.12	2.2469	2.0190	1.39	2.2181	2.0181
6.30	2.2696	2.0204	3.12	2.2298	2.0192
10.75	2.3228	2.0229	6.22	2.2525	2.0207
$S^0 = 0.0061, \mu = 2.3\ D$			$S^0 = 0.0055, \mu = 2.2\ D$		

Dipole Moment Measurements.—The dipole moments of the dibromides (fractions 3 and 5) were calculated from the dielectric constants and refractive indices by the Guggenheim method of initial slopes.[19] Values of the dielectric constant for the various solutions were obtained using the heterodyne beat apparatus similar to that of Smyth and Lewis.[20] See reference 1b for a fuller discussion of these practices. The solvent used was 1,4-dioxane which had been refluxed over sodium for two days, distilled, and used immediately.

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[17] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

[18] The dimensions of the column were 50 × 2.2 cm. The column was packed with a slurry of the absorbent in *n*-pentan and the procedure of Roberts and Green (*Anal. Chem.*, **18**, 335 (1946)) was followed in absorbing and developing the column.

[19] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

[20] C. P. Smyth and G. L. Lewis, *J. Chem. Phys.*, **7**, 1085 (1939).