heights gave the relative specific radioactivities of 1-chloro-2-methyl-1-propene-*t* and isobutyl chloride-*t*.

Photochlorination of 2-Methylpropane-2-*t*.—A known volume of gaseous 2-methylpropane-2-*t* (approximately 0.45 g) measured at a known temperature and pressure was condensed on the vacuum line into 3 ml of previously degassed carbon tetrachloride. A portion (0.25 ml) of the reaction mixture was removed in order to measure the initial specific radioactivity of the isobutane. Enough chlorine in 0.5 ml of carbon tetrachloride was added to the reaction mixture to react with 1.5% of the isobutane and all of the isobutylene and the mixture was again degassed on the vacuum line.

The unopened reaction tube was irradiated at 24° with a 200-w incandescent bulb until the color of chlorine had disappeared (30 min). The reaction tube was returned to the vacuum line where most of the unreacted isobutane and all of the hydrogen chloride were removed. The remaining solution, containing some 2-methylpropane-2-*t* and most of the isobutyl and *t*-butyl chlorides, was used for determination of the specific radioactivity of the isobutyl chloride. The results of three runs are shown in Table I.

Registry No.—2-Methylpropane-2-*t*, 7101-09-9.

Acknowledgment.—We wish to thank Dr. Stuart Scheppele for his interest in this investigation.

A Highly Selective Allylic Bromination in a Bicyclic System

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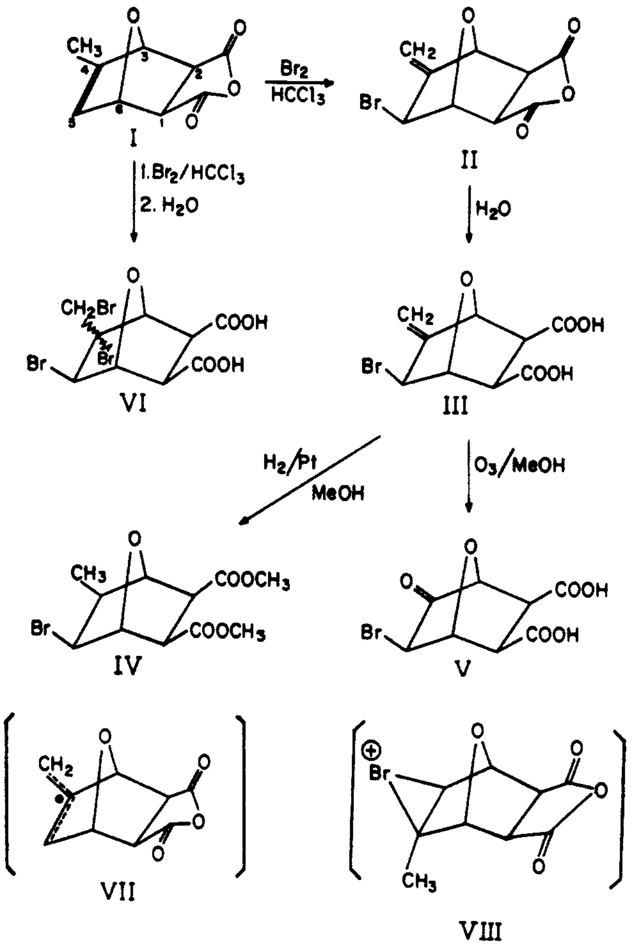
The study of bromination reactions in oxobicyclic analogs of norbornene has attracted our attention lately. The system of our choice has been the *exo-cis*-3,6-endoxo-Δ^4-tetrahydrophthalic anhydride and its methyl derivatives.[2] Bromination of these compounds in inert solvents (CCl_4, $HCCl_3$, H_2CCl_2), under sunlight, leads to *cis*- and *trans*-dibromo compounds when the unmethylated, the 3-methylated, and the 3,6-dimethylated substrates are used. The results of that study will be published elsewhere.

We now wish to report the bromination of the *exo-cis*-3,6-endoxo-4-methyl-Δ^4-tetrahydrophthalic anhydride (I). When I is treated with an equimolecular amount of bromine in $HCCl_3$ solution, only one product is isolated, in very high yield. The main features of this compound are the following: it contains only one bromine atom; its nmr spectrum shows the absence of methyl groups and the disappearance of the 4,5-unsaturation; nmr spectroscopy also indicates that one hydrogen atom has been lost during the reaction. This information allowed the tentative assignment of structure II to the bromination product. Scheme I shows the path selected in order to prove the validity of the assignment made.

The stereochemistry around C-4 was established on the basis of the nmr spectra of compounds IV and V which show the absence of coupling between hydrogens at C-5 and C-6, implying that hydrogen at C-5 is at the *endo* side of the system.[2,3] The same criterion was used in ascertaining the stereochemical course of the reduction III → IV.

SCHEME I



The nmr data for all compounds studied are collected in Table I. Compounds II and III present a complicated spectrum where assignment of bands is difficult due to the great number of couplings between the vinylic hydrogens, which are nonequivalent, and hydrogens at C-3 and C-5. Nevertheless, the main features previously mentioned are clear-cut and unambiguous.

There are two additional relevant points. First, the reaction is catalyzed by addition of a very small amount of water and, second, when it is carried out in the presence of 2 equiv of bromine further bromination occurs and compound VI is formed. If one takes the dimethyl ester of III in $HCCl_3$ solution and treats it with an equivalent amount of bromine, the dimethyl ester of VI is obtained. Unfortunately, the stereochemistry at C-4 in compound VI is not known.

Two possible pathways may be postulated to explain the course of this reaction, namely, a free radical and an ionic-type mechanism. The free radical mechanism, through an allylic intermediate (VII) originated by hydrogen abstraction from the methyl group, is strongly supported by two important facts. First, all efforts to isolate the bromo compound II failed when the reaction was carried out in the dark; in contrast to bromination reactions of similar Diels–

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[2] E. Payo, L. Cortés, J. Mantecón, and C. Piemonti, *J. Org. Chem.*, **31**, 1888 (1966).

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TABLE I

NMR SPECTRAL DATA FOR COMPOUNDS III, IV, V, AND VI

Compound	Protons	Chemical shift, ppm	Integral protons	Multiplicity[a]	Coupling constants, cps
III[b]	C-1,2	2.90	2	bs	
	$=CH_2$	4.86	2	bd	
	C-5	5.08	1	bs	
	C-3,6	5.42	2	bs	
IV[c]	C-1,2	3.05	2	s	
	4-CH_3	1.22	3	d	$J_{CH_3,4} = 7.2$
	C-4	2.18	1	m	$J_{4,5} = 7.2$ $J_{4,6} = 0.6$
	C-5	4.28	1	d	$J_{4,5} = 7.2$
	C-3	4.52	1	d	$J_{3,6} = 1.5$
	C-6	5.00	1	q	$J_{6,4} = 0.6$ $J_{3,6} = 1.5$
V[d]	C-1,2	3.35	2	m(AB)	$J_{1,2} = 11.8$
	C-3,6	4.90	2	m(AB)	$J_{3,6} = 1.4$
	C-5	4.47	1	s	
VI[b]	C-1,2	3.36	2	m(AB)	$J_{1,2} = 9.8$
	$-CH_2Br$	4.32	2	s	
	C-3,6	5.20	2	m(AB)	$J_{3,6} = 1.6$
	C-5	4.48	1	s	

[a] bs, broad singlet; bd, broad doublet; s, singlet; d, doublet; q, quartet; m, multiplet. [b] In D_2O–K_2CO_3 solution and TMS as external standard. [c] In $DCCl_3$ solution and TMS as internal standard. [d] In DMSO-d_6 solution and TMS as internal standard.

Alder adducts that follow an ionic pathway[4] and, second, when the reaction was carried out in the presence of a small amount of hydroquinone, it was not possible to detect even traces of the bromination product by the use of nmr spectroscopy.

Once the allylic intermediate VII has been formed, the results indicate that the reaction is completed by attack at the 5 position of the intermediate in a highly selective manner. This selectivity could be rationalized considering the nature of the two products of possible formation from intermediate VII. Attack of bromine at the 5 position gives the product actually isolated experimentally (II) which has only one sp^2 carbon atom in the bicyclic system, whereas attack at the other end of the allylic system would retain the unsaturation between carbon atoms 4 and 5 and, therefore, the product formed would have had two sp^2 carbon atoms in the bicyclic system. Apparently the latter situation is a more energetic one and the course leading to II is preferred. The increase in energy content of the endocyclicly unsaturated structure must be due to internal strain in the bicyclic skeleton. If the preceding considerations are correct, the transition state for this reaction should resemble very closely the final products where the energy differences created by the internal strain factor should be more decisive.

However, the fact that the reaction is water-catalyzed strongly suggests an ionic mechanism which may occur through a bromonium ion intermediate (VIII). The latter, instead of being attacked by a bromide ion in the usual way, simply loses a proton to yield product II. The relief of strain due to the methyl group when going from an sp^3—in the bromonium ion—to an sp^2 hybridization of the product might be the driving force for this reaction. It should be mentioned, however, that in the bromination of the Diels–Alder adduct from maleic anhydride and 2,4-dimethylfurane the formation of the expected dibromo derivatives has been observed[5] in spite of the fact that the above-mentioned compound also has a methyl group in position 4. The observed water catalysis may be visualized, in the case of a free radical mechanism, as a simple mechanical action that facilitates the separation of the product.

Referees of this article have suggested that the ionic pathway is the more feasible, since that mechanism is in agreement with the observed water catalysis. We consider that, with the available information, it is very difficult to dismiss in a definite manner either of the two possible mechanisms proposed.

Experimental Section

***exo-cis*-3,6-Endoxo-4-methyl-Δ⁴-tetrahydrophthalic anhydride** (I) was prepared from 3-methylfuran[6] and maleic anhydride following the procedure described by Rinkes.[7]

***exo-cis*-3,6-Endoxo-4-methylene-5-*exo*-bromotetrahydrophthalic Acid (III).**—To a solution of I (5.7 g, 0.031 mole) in $HCCl_3$ (150 ml) bromine (1.8 ml, 0.035 mole) was added with vigorous stirring in an ice bath. Small pieces of ice were added to the reaction mixture. After a few minutes the solution became clear and a white solid precipitated. Recrystallization from water afforded 8 g (91%) of III, mp 182–186°.[8]

Anal. Calcd for $C_9H_9O_5Br$: C, 39.01; H, 3.27; Br, 28.87. Found: C, 38.75; H, 3.35; Br, 28.65.

Dimethyl *exo-cis*-3,6-Endoxo-4-*exo*-methyl-5-*exo*-bromotetrahydrophthalate (IV).—A solution of III (3 g, 0.011 mole) in methanol (70 ml) to which 5% Pt/C catalyst (0.15 g) had been added was left overnight under a hydrogen pressure of 45 psi. Filtration of the reaction mixture and evaporation of the solvent afforded 0.9 g (27%) of IV, mp 151–154° (water–acetone).

Anal. Calcd for $C_{11}H_{15}O_5Br$: C, 43.01; H, 4.92; Br, 26.02. Found: C, 43.23; H, 5.08; Br, 26.12.

***exo-cis*-3,6-Endoxo-4-one-5-*exo*-bromotetrahydrophthalic Acid (V).**—Ozonolysis of 2.5 g (0.009 mole) of III dissolved in 200 ml of methanol afforded 0.6 g (24%) of V, mp 173–175° (acetone). The 2,4-dinitrophenylhydrazone of the dimethyl ester of V was prepared, mp 253–256° dec.

***exo-cis*-3,6-Endoxo-4-bromo-4-bromoethyl-5-*exo*-bromotetrahydrophthalic Acid (VI).**—To a solution of I (5.7 g, 0.031 mole) in $HCCl_3$ (70 ml) placed in an ice bath, bromine (3.5 ml, 0.070 mole) was added with vigorous stirring. The white precipitate formed was crystallized from water to yield 12 g (88%) of VI, mp 241° dec.

Anal. Calcd for $C_9H_9Br_3O_5$: C, 24.74; H, 2.07; Br, 54.87. Found: C, 24.38; H, 2.05; Br, 55.01.

Dimethyl *exo-cis*-3,6-Endoxo-4-methylene-5-*exo*-bromotetrahydrophthalate (IX).—A suspension of 8.6 g (0.031 mole) of II in 150 ml of ether was sterified with an excess of diazomethane in ether. The white needles formed were crystallized from 1:1 water–acetone mixture to yield 8.6 g (90%) of IX, mp 113–114°.

Anal. Calcd for $C_{11}H_{13}BrO_5$: C, 43.30; H, 4.29; Br, 26.19. Found: C, 43.51; H, 4.47; Br, 26.31.

Dimethyl *exo-cis*-3,6-Endoxo-4-bromo-4-bromomethyl-5-*exo*-bromotetrahydrophthalate (X).—To a solution of IX (1.5 g, 0.0049 mole) in chloroform (20 ml) placed in an ice bath, bromine (0.5 ml, 0.01 mole) was added. After completion of the reaction and removal of the solvent, the remaining solid was crystallized from a 1:1 water–acetone mixture to yield 2.1 g (93%) of X, mp 151–154°.

Anal. Calcd for $C_{11}H_{13}Br_3O_5$: C, 28.41; H, 2.82; Br, 51.56. Found: C, 28.49; H, 2.98; Br, 51.71.

Nmr spectra were run at approximately 34° on a Varian A-60 spectrometer unless otherwise stated. The information obtained is collected in Table I.

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Registry No.—III, 15292-78-1; IV, 15292-79-2; V, 15292-80-5; 2,4-DNPH of Me ester of V, 15292-81-6; VI, 15292-84-9; IX, 15292-82-7; X, 15292-83-8.

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The Solvolysis of 1-Chlorobicyclo[3.3.1]nonane[1]

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Ever since the pioneering work on reactions of bridgehead substituted bicyclic systems by Bartlett and Knox in 1939,[3] many studies of a wide variety of bicyclic compounds have provided valuable information about mechanisms and transition-state geometries of nucleophilic substitution reactions.[4] Recently, Gleicher and Schleyer[5] reported a correlation of experimental rate constants with the calculated energy difference between the hydrocarbon and the respective carbonium ion for five compounds. In addition, they used the correlation to predict the solvolytic rate constants of three bridgehead substituted compounds for which rate data had not been reported. One of these compounds was 1-bromobicyclo[3.3.1]nonane, whose predicted rate was approximately half the rate predicted for *t*-butyl bromide; the predicted rate of the latter compound was one-fifth the known experimental rate. We should like to report our results on the related 1-chlorobicyclo[3.3.1]nonane.

Recent work in this laboratory, related to the solvolysis of bicyclo[3.3.0]octane-1-carbinyl tosylate,[6] provided a convenient synthesis of bicyclo[3.3.1]nonan-1-ol. The methyl ester of 1-carboxybicyclo[3.3.0]octane[7] was converted into 1-hydroxymethylbicyclo[3.3.0]octane,[6] mp 41–42°, with lithium aluminum hydride. The toluenesulfonate ester,[6] mp 22–23°, was prepared in 91% yield from the bicyclic carbinol and tosyl chloride in pyridine at 0°. Hydrolysis of bicyclo[3.3.0]octane-1-carbinyl *p*-toluenesulfonate in 60% aqueous acetone gave bicyclo[3.3.1]nonan-1-ol[6] (88%), mp 182.5–184°. The alcohol was easily converted in 84% yield into 1-chlorobicyclo[3.3.1]nonane, mp 87–88.5°, with thionyl chloride. Solvolytic studies were carried out in 60% aqueous ethanol, following a procedure similar to that of Winstein and Fainberg.[8] Rate constants were calculated by the method of nonlinear least squares[9] and are presented in Table I. Activation parameters were determined by a least-square analysis:[9] $\Delta H^{\ddagger}_{25°} = 22.8 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger}_{25°} = -8.2 \pm 1.0$ eu. Preparative scale solvolysis at 55° in 60% aqueous ethanol gave bicyclo[3.3.1]nonan-1-ol (90%) and 1-ethoxybicyclo[3.3.1]nonane (10%). The infrared spectrum of the alcohol was identical with that of an authentic sample and the ether was prepared from bicyclo[3.3.1]nonan-1-ol by a modified Williamson synthesis.

TABLE I

FIRST-ORDER RATE CONSTANTS[a] IN 60% AQUEOUS ETHANOL

Substrate[b]	Temp,[c] °C	$k_1 \times 10^5$,[d] sec^{-1}
t-Butyl chloride	25.0	12.1[e]
1-Chlorobicyclo[3.3.1]nonane	25.0	0.202 (calcd)
	44.9	2.34
	55.0	7.67
	65.0	21.2

[a] Determined from two runs at each temperature. [b] $0.0008\ M \leq$ [substrate] $\leq 0.0011\ M$. [c] ±0.1. [d] ±3%. [e] Previously reported as $12.3 \pm 0.10 \times 10^{-5}$ sec^{-1}.[8]

The experimental solvolytic rate of 1-chlorobicyclo[3.3.1]nonane is $\frac{1}{60}$ that of *t*-butyl chloride. The relative rates of a large number of tertiary alicyclic and bridged substrates with different halide leaving groups have been studied[10,11] and no large variations in the halide rate ratios were reported. Also, a large body of evidence exists which suggests that solvent variations have little effect on the relative reactivities of alicyclic tertiary halides to bridgehead halides.[4c] Thus, the difference in rates between *t*-butyl chloride and 1-chlorobicyclo[3.3.1]nonane should be a good approximation for the corresponding bromides. Consequently, the estimated rate of 1-bromobicyclo[3.3.1]nonane at 25° in 80% aqueous ethanol is 5.6×10^{-6} sec^{-1},[12] a rate which is seven times slower than predicted by Gleicher and Schleyer.[5]

A comparison of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the solvolysis of the 1-chlorobicyclo[3.3.1]nonane with the values reported for *t*-butyl chloride[13] indicates that in the former compound both terms make significant contributions to the decreased rate at 25°. The small difference in the free energies of activation (2.4 kcal/mol, 25°) of these two compounds may be anticipated in view of the conformation of the bicyclic system. The infrared spectrum of 1-chlorobicyclo[3.3.1]nonane had four sharp bands at 1484, 1464, 1449, and 1441 cm^{-1}, which were characteristic of the substituted bicyclo[3.3.1]nonanes encountered in this study. The band at 1490 cm^{-1} in the infrared spectrum of bicyclo[3.3.1]nonane has been assigned[14] as a scissoring methylene vibration ($\delta(CH_2)$) which

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(1) (a) This work was supported in part by Grant GP-3890, National Science Foundation. (b) After completion of this work, Professor P. von R. Schleyer kindly informed us of his study using the 1-bromo derivative; these two studies are being published simultaneously.

(2) National Institutes of Health Predoctoral Fellow, 1966–1967.

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(9) We are indebted to Professor A. Streitwieser for providing copies of LSKIN1 and ACTENG computer programs, both of which were developed by Professor D. F. DeTar, Florida State University.

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(12) A value of 3.38×10^{-4} sec^{-1} was used for the rate of *t*-butyl bromide in 80% aqueous ethanol at 25°.[10]

(13) For *t*-butyl chloride in 60% aqueous ethanol, $\Delta H^{\ddagger} = 21.7$ kcal/mol and $\Delta S^{\ddagger} = -3.7$ eu [S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957)].

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