Synthesis of Bridgehead Derivatives by Chromic Acid Oxidation

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The chromic acid oxidation of hydrocarbons is a rather selective process strongly influenced by strain factors. In competition with attack at the methylene groups, no significant oxidation occurs at the bridgehead positions of the smaller bicycloheptane and bicyclooctane bridged systems. With adamantane, bicyclo[3.3.1]nonane (I, X = H), bicyclo[3.2.2]nonane (II, X = H), and bicyclo[3.3.2]decane (III, X = H), attack at the bridgehead positions predominates, and chromic acid oxidation becomes a synthetically useful reaction for the preparation of the corresponding bridgehead alcohols. From these alcohols, other bridgehead derivatives can be prepared. As a substitution method for the larger bridged hydrocarbons, chromic acid oxidation has definite advantages as a general method. Free-radical chlorination is less selective, and ionic substitution processes may give rise to rearranged products.

Since it is often easy to prepare polycyclic hydrocarbons by rearrangement or by other means, substitution methods are needed to synthesize functional derivatives.[2] High selectivity is a desirable characteristic of such reactions.

The chromic acid oxidation of hydrocarbons has synthetic utility in special cases.[3–5] In ordinary structures, oxidation of tertiary C–H bonds predominates over CH_2 attack; methyl groups are essentially unaffected (the relative rates of oxidation of typical primary, secondary, and tertiary hydrogens are 1:110:7000).[3] One problem is that the oxidized products tend not to be stable to the reaction conditions; tertiary alcohols may be dehydrated to olefins which are further attacked, and ketones also are oxidizable. Bridgehead alcohols should be stable, since dehydration (to give bridgehead olefins) occurs poorly, if at all.[2] Such bridgehead alcohols were the objective of the present work.

Table I summarizes the results of an earlier investigation in this laboratory.[4a] With adamantane, reaction with CrO_3 in acetic acid–acetic anhydride solvent gave mainly 1-adamantanol, but some adamantanone also formed. More recent studies have confirmed this result.[4b,d] In addition, if excess oxidant is employed, good yields of 1,3-diols can be obtained in the adamantane series.[4d] However, norbornane, bicyclo[2.2.2]octane, and bicyclo[3.2.1]octane give no bridgehead products; only ketones (and some secondary acetates) result (Table I).[4a]

This inhibition of bridgehead oxidation of small bicyclic systems is consonant with the accepted mechanism of chromic acid–hydrocarbon oxidation.[3,6] The initial step is believed to be hydrogen atom abstraction to give a caged radical pair, collapse of which can occur to give retention of configuration[6] (in addition to literature cases,[3] see the results with *cis*- and *trans*-decalin in Table I). Electron transfer in the radical pair can also occur to give carbonium ions, from which certain products, *e.g.*, those involving skeletal rearrangement, occasionally result. This mechanism is preferred over a direct insertion process, which would also give retention of configuration. It is known that carbonium ion, free-radical, and insertion reactions are all inhibited to a decreasing degree at the bridgehead positions of the smaller bicyclanes (Table II).[7]

TABLE I[a]

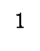
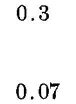
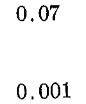
CHROMIC ACID OXIDATION OF POLYCYCLIC HYDROCARBONS

Triphenylmethane	98% triphenylcarbinol
Adamantane	71% 1-adamantanol, 9% 2-adamantanone
Norbornane	23% 2-norbornanone, 6% 2-*exo*-norbornyl acetate
Bicyclo[2.2.2]-octane	40% 2-bicyclo[2.2.2]octanone, 4% 2-bicyclo[2.2.2]octyl acetate
Bicyclo[3.2.1]-octane	15% 6-bicyclo[3.2.1]octanone, 7% 3-bicyclo[3.2.1]octanone, 3% 2-bicyclo-[3.2.1]octanone, 10% 2-bicyclo[2.2.2]-octanone, 4% acetate ester, mostly 2-bicyclo[2.2.2]octyl acetate
cis-Decalin	32% *cis* 9-decalol, 5% 9,10-*cis*-dihydroxydecalin, 4% decalones
trans-Decalin	7% *trans*-9-decalol, 3% 9,10-*trans*-dihydroxydecalin, 8% decalones

[a] Reproduced from ref 4a. Oxidations were carried out in AcOH–Ac_2O. The products were analyzed by a combination of column and gas chromatography, in most cases by comparison with authentic materials. 1-Bicyclo[2.2.1]heptanol, 7-bicyclo-[2.2.1]heptanol, 1-bicyclo[2.2.2]octanol, and 1-bicyclo[3.2.1]-octanol were specifically sought among the products but were not detected. For details see R. D. Nicholas, Ph.D. Thesis, Princeton University, 1960; R. E. Lehr, A.B. Thesis, Princeton University, 1964.

TABLE II

COMPARISON OF BRIDGEHEAD RELATIVE REACTIVITIES[a]

			
Nitrene insertion	1	0.3	0.07
Free radical (*tert*-butyl perester decomposition)[b]	1	0.07	0.001
Carbonium ion (bromide solvolyses)[c]	1	10^{-3}	10^{-10}

[a] Reference 7. [b] Reference 10. [c] Reference 2.

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[1] National Institutes of Health Predoctoral Fellow, 1968–1970; Ph.D. Thesis, Princeton University, 1970.

[2] A good example is afforded by adamantane. Reviews: R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); *Advan. Alicyclic Chem.*, **1**, 283 (1966); R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, in press.

[3] Review: K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 109–124.

[4] (a) P. v. R. Schleyer and R. D. Nicholas, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 75Q; (b) S. Landa, J. Vais, and J. Burkhard, *Z. Chem.*, **7**, 233 (1967); (c) P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, **91**, 5880 (1969); (d) R. E. Moore, private communication; *cf.* Sun Oil Co., Neth. Patent Appl., 6,516,807 [*Chem. Abstr.*, **65**, 15249e (1966)].

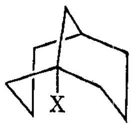
[5] L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Amer. Chem. Soc.*, **91**, 6779 (1969).

[6] J. Roček, *Tetrahedron Lett.*, 135 (1962).

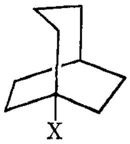
[7] D. S. Breslow, E. I. Edwards, R. Leone, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **90**, 7097 (1968).

However, the degree of bridgehead inhibition observed with norbornane and the bicyclooctanes would appear to be of a magnitude larger than would be expected of typical insertion processes.[7]

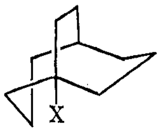
The solvolytic reactivity of 1-bicyclo[3.3.1]nonyl derivatives are known to be greater than adamantane compounds.[8,9] Since bridgehead radical reactivities seem to parallel carbonium ion reactivities,[7,10] it is reasonable to expect that chromic acid oxidation of bicyclo[3.3.1]nonane (I, X = H) would proceed well at the 1 position. This, in fact, is the case. In addition, bicyclo[3.2.2]nonane (II, X = H) and bicyclo[3.3.2]decane (III, X = H) give moderately good yields (40–50%) of the corresponding bridgehead alcohols. Side reactions interfere only with bicyclo[3.3.2]decane (III, X = H), where small amounts of 1,5-bicyclo[3.3.2]decanediol and unidentified ketones were found.



I



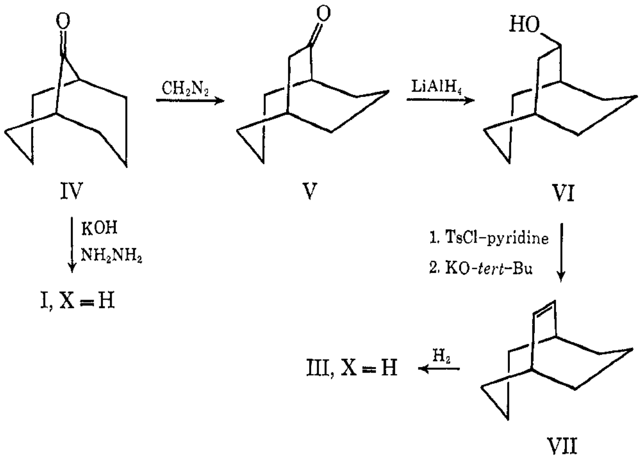
II



III

1-Bicyclo[3.3.1]nonanol (I, X = OH)[8,9] and 1-bicyclo[3.2.2]nonanol (II, X = OH)[11] have been obtained previously, generally *via* multistep reaction sequences. The physical properties observed, *e.g.*, mp 180–182° for I (X = OH) and 195–197° for II (X = OH), agree well with literature data.[8,9,11] However, a discrepancy exists for 1-bicyclo[3.3.2]decanol (III, X = OH). The literature reports mp 64–65°,[12] which seems much too low for such a bridgehead alcohol. Our value, mp 191–194°, and other evidence[13] support our structural assignment.

The starting hydrocarbons, I,[9] II,[14] and III (all X = H), are all readily available compounds. A new synthesis of III (X = H) was developed. 9-Bicyclo[3.3.1]nonanone (IV) may be prepared in one step by treatment of 1,5-cyclooctadiene with nickel carbonyl.[15] Wolff–Kishner reduction[16] gives I (X = H) in reasonable yield.[9] Homologation of IV with diazomethane[17] gives 9-bicyclo[3.3.2]decanone (V) which may be converted to III (X = H) as shown below.



Comparison with Other Substitution Methods.—Chromic acid oxidation may well be one of the best *general* substitution methods to gain access to various bridgehead derivatives of structures I–III. The alcohols, I (X = OH), II (X = OH), and III (X = OH), can readily be converted to other functional groups. On the other hand, ionic substitution reactions on the parent hydrocarbons, although working well with adamantane,[2] have drawbacks or give undesired products.

Although good yields of 1-bromobicyclo[3.3.1]nonane (I, X = Br) may be obtained by treatment of the hydrocarbon (I, X = H) with molecular bromine,[9] only rearrangement products (possibly 1-bicyclo[3.2.1]octyl carbinyl bromide and 1-bicyclo[2.2.2]octyl carbinyl bromide)[18] are obtained from II (X = H) under similar conditions. Such rearrangements have also been observed for the bromination of homoadamantane, which gives 1-adamantylcarbinyl bromide.[19] Apparently, the bromination reaction (conducted in liquid bromine, a Lewis acid) is a thermodynamically controlled process. Because of ring strain, the primary rearrangement products are more stable than the tertiary bromides obtained by direct substitution. For this reason, similar rearrangements are likely for III (X = H) and the bromination of this hydrocarbon was not attempted.

In contrast, the alcohols I (X = OH), II (X = OH), and III (X = OH) can readily be converted without rearrangement to the corresponding bridgehead halides under milder conditions. Thus, I (X = Cl),[8] II (X = Cl),[11a] and III (X = Cl) are obtained from the treatment of the alcohols with thionyl chloride. II (X = Br) can be prepared using thionyl bromide.

Similarly, the Koch–Haaf reaction[20] works well with I (X = OH) to give a 75% yield of 1-bicyclo[3.3.1]-

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(8) W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968).

(9) P. v. R. Schleyer, P. R. Isele, and R. C. Bingham, *ibid.*, **33**, 1239 (1968).

(10) (a) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, **90**, 5266 (1968); (b) R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968); (c) L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968); (d) C. Rüchardt, K. Herwig, and S. Eichler, *Tetrahedron Lett.*, 421 (1969); (e) A. Oberlinner and C. Rüchardt, *ibid.*, 4685 (1969); (f) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, in press; (g) C. Rüchardt, *Angew. Chem.*, **82**, 845 (1977); *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(11) (a) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958); (b) J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **91**, 7775 (1969).

(12) K. H. Baggerley, W. H. Evans, S. H. Graham, D. A. Jonas, and D. H. Jones, *Tetrahedron*, **24**, 3445 (1968). Dr. Graham (private communication) now concurs that the alcohol, mp 64–65°, is not III (X = H).

(13) Conversion of the alcohol to the corresponding chloride (III, X = Cl) followed by reduction of the chloride with triphenyltin hydride regenerates the original bicyclo[3.3.2]decane starting material. This, coupled with the absence of a carbinyl (CHOH) resonance in the nmr spectra, requires the assigned structure III (X = OH).

(14) M. Hartman, *Z. Chem.*, **7**, 101 (1967).

(15) B. Fell, W. Seide, and F. Asinger, *Tetrahedron Lett.*, 1003 (1968).

(16) A. C. Cope, D. L. Nealy, P. Scheiner, and G. Wood, *J. Amer. Chem. Soc.*, **87**, 3130 (1965), and references cited therein.

(17) *Cf.* T. J. deBoer and H. J. Backer, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 225.

(18) The treatment of 1-acetoxybicyclo[3.2.2]nonane with toluenesulfonic acid in acetic acid gives a mixture of 1-bicyclo[3.2.1]octyl- and 1-bicyclo[2.2.2]octylcarbinyl acetates. See J. A. Chong and J. R. Wiseman, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. ORGN 114.

(19) S. H. Liggero, unpublished observations; *cf.* J. E. Norlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966).

(20) H. Koch and W. Haaf, *Angew. Chem.*, **72**, 628 (1960), and references cited therein.

nonylcarboxylic acid (I, X = COOH).[21] While the same acid can be prepared directly from I (X = H) by use of *tert*-butyl alcohol–formic acid–sulfuric acid,[22] the yield is poorer (45%) and the separation of the pivalic acid by-product is difficult. The literature records the preparation of II (X = NHCHO)[11b] by the Ritter reaction[23] on II (X = OH) and the Koch–Haaf synthesis of III (X = COOH) starting with I (X = CH_2OH).[21b] Both Ritter and Koch–Haaf reactions are governed by kinetic attack on the most stable (tertiary) carbonium ions; monosubstituted acetic acid derivatives [*e.g.*, I (X = CH_2COOH)] are not formed.[23]

Free-radical chlorination is normally a rather unselective process (primary, secondary, and tertiary C–H substitution relative rates are 1:4:2:6.0),[24] and the bridged ring systems which have been studied give mixtures of products.[2,4c,25] Free-radical bromination is much more like chromic acid in selectivity[3] (primary, secondary, tertiary relative rates are given as 1:100:3000[3] or 1:220:19,400[24]), but the behavior of bridged ring systems (other than adamantane[25]) does not appear to have been studied. Such a selective free-radical substitution method might be a good choice as an alternative to chromic acid oxidation for the preparation of bridgehead derivatives I, II, and III.

Experimental Section

Bicyclo[3.3.1]nonane (I, X = H)[9] and **bicyclo[3.2.2]nonane (II, X = H)**[14] were prepared following literature procedures.

9-Bicyclo[3.3.2]decanone (V).—To a solution of 9-bicyclo-[3.3.1]nonanone (IV)[15] (20 g, 0.145 mol), potassium hydroxide (9 g), and water (30 ml) in 200 ml of methanol cooled in an ice bath was added *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, "Diazald" (60 g, 0.28 *M*), in 400 ml of methanol over a period of 1 hr.[17] After being stirred overnight the reaction mixture was diluted with 1500 ml of water and extracted with ether (three times). The ether was then removed *in vacuo* to give a viscous oil which was a mixture of 9-bicyclo[3.3.2]decanone (V) and methyl tosylate. This mixture was dissolved in 200 ml of 50% aqueous ethanol and refluxed for 15 hr. The reaction mixture was then diluted with water and extracted with pentane (three times). The pentane extracts were washed once with water and dried ($MgSO_4$). The pentane was removed by distillation and the product sublimed to give 15 g (68%) of V: mp 182–184°; nmr (CCl_4) δ 1.70 (13 H, b s), 2.35 (2 H, m), and 2.78 (1 H, m); ir (CCl_4) 1689.5 cm^{-1} (C=O). The corresponding tosylhydrazone had mp 184–187°.

Anal. Calcd for $C_{17}H_{24}N_2SO_2$: C, 63.75; H, 7.50; N, 8.75. Found: C, 63.46; H, 7.45; N, 8.87.

9-Bicyclo[3.3.2]decanol (VI).—To a suspension of lithium aluminum hydride (1.5 g, 0.04 mol) in anhydrous ether (50 ml) was added 9-bicyclo[3.3.2]decanone (18 g, 0.12 mol) dissolved in 100 ml of anhydrous ether. After addition was complete (1.5 hr) the reaction mixture was refluxed for 3 hr. The excess lithium aluminum hydride was then decomposed by the cautious addition of 10% Na_2CO_3 and water and dried (Na_2SO_4–$MgSO_4$). The product obtained after removal of solvent was recrystallized from hexane to give 14.5 g (78%) of VI: mp 213–215° (sealed tube); nmr ($CDCl_3$) δ 1.62 (14 H, b s), 2.00 (1 H, s, OH), 2.20 (2 H, m), and 4.10 (1 H, m); ir (CCl_4) 3600, 3300 cm^{-1} (OH).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.69. Found: C, 77.76; H, 11.78.

9-Bicyclo[3.3.2]decyl Tosylate (VI OTs).—The tosylate was prepared by the method described in Fieser and Fieser[26] in 60% yield: mp 66–68°; nmr (CCl_4) δ 1.55 (16 H, b m), 2.38 (3 H, s), 4.62 (1 H, b m), and 7.35 (4 H, q).

Anal. Calcd for $C_{17}H_{24}SO_3$: C, 66.23; H, 7.79. Found: C, 66.36; H, 8.00.

9-Bicyclo[3.3.2]dec-9-ene (VII).—To a solution of potassium *tert*-butoxide (12 g) in dimethyl sulfoxide (100 ml) was added a solution of 9-bicyclo[3.3.2]decyl tosylate (11 g, 0.036 mol) in dimethyl sulfoxide (100 ml). After addition was complete (1.5 hr), the reaction mixture was heated at 60° for 30 min. Water (500 ml) was then added and the product was extracted with pentane (two times). The extracts were dried ($MgSO_4$), the solvent was removed by distillation, and the product was sublimed and recrystallized from methanol to give 4 g of VII (83%): mp 128.4–130°; nmr (CCl_4) δ 1.53 (12 H, m) 2.43 (2 H, b s), and 5.77 (2 H, m).

Bicyclo[3.3.2]decane (III, X = H).—A solution of 9-bicyclo-[3.3.2]decene (4.6 g, 0.034 mol) and a catalytic amount of platinum oxide in ether was placed in a Parr apparatus under 50 psi of hydrogen. After 4 hr when the theoretical amount of hydrogen had been absorbed, the reaction mixture was filtered and the solvent removed by distillation. Sublimation of the product gave 5 g (86% yield) of III (X = H): mp 177–178° (lit. mp 162°[27] and 179–181°[28]); nmr (CCl_4) δ 1.52 (16 H, m) and 2.20 (2 H, m).

General Procedure for Chromic Acid Oxidations.—To a solution of the hydrocarbon (1 g, approximately 8 mmol), acetic acid (15 ml), and acetic anhydride (15 ml) was added chromium trioxide (1.6 g, 16 mmol) in small portions over a period of 1 hr. During addition the reaction mixture was kept below 35° by external cooling. After addition was complete the reaction was stirred at room temperature for 6 hr. (Reaction times on the order of 1 hr were required for the preparation of 1-bicyclo-[3.3.2]decanol; see below.) Dilution with ice water (50 ml) was followed by extraction with ether (five times). The ether extracts were then washed with 10% Na_2CO_3 (to remove all acetic acid) and with water. After drying ($MgSO_4$) solvent was removed *in vacuo* to give a product which was a mixture of the desired alcohol and the corresponding acetate. This mixture was added to a solution of lithium aluminum hydride in ether and stirred for 1 hr. The excess hydride was then destroyed by the addition of 10% H_2SO_4, the Li salts were separated by filtration, and the ether solution was dried ($MgSO_4$). After removal of the ether the desired alcohol was obtained in yields of 40–50%.

The alcohols prepared in this manner had the following physical properties. 1-Bicyclo[3.3.1]nonanol (I, X = OH): mp 180–182° (lit.[8] mp 182.5–184°); nmr (CCl_4) δ 1.63 (14 H, m), 2.17 (2 H, m), 2.27 (1 H, s, OH); ir (CCl_4) 3600, 3350 cm^{-1} (OH). 1-Bicyclo[3.2.2]nonanol (II, X = OH): mp 195–197° (lit.[11a] mp 199–201°); nmr (CCl_4) δ 1.65 with a shoulder at δ 1.85; ir (CCl_4) 3600, 3350 cm^{-1} (OH). 1-Bicyclo[3.3.2]decanol (III, X = OH): mp 191–194° (lit.[12,29] mp 64–65°); nmr (CCl_4) δ 1.55 (1 H, sh, OH), 1.75 (16 H, m), and 2.22 (1 H, m); ir (CCl_4) 3600, 3420 cm^{-1} (OH).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.69. Found: C, 77.58; H, 11.61.

If the oxidation of bicyclo[3.3.2]decane (III, X = H) was allowed to continue longer than 1 hr, significant amounts of 1,5-bicyclo[3.3.2]decanediol were formed in addition to the monoalcohol. These compounds may be readily separated by differential crystallization or column chromatography. The diol is only slightly soluble in ether and nearly insoluble in hexane. Recrystallization of the diol from ether gave mp 214–217°: nmr ($CDCl_3$) δ 1.42 (2 H, s, OH) and 1.80 (16 H, d); ir ($CDCl_3$) 3580, 3400 cm^{-1} (OH).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C, 70.24; H, 10.71.

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[21] For direct syntheses of this acid *via* ring closure reactions, see (a) J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967); (b) Smith Kline and French Laboratories, British Patent 1,104,058 [*Chem. Abstr.*, **69**, 51739e (1968)]; (c) S. H. Graham and D. A. Jonas, *J. Chem. Soc. C*, 188 (1969); (d) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 956 (1970); *J. Org. Chem.*, **35**, 3164 (1970).

[22] *Cf.* H. Koch and W. Haaf, *Org. Syn.*, **44**, 1 (1964).

[23] L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 213 (1969).

[24] G. A. Russell and C. DeBoer, *J. Amer. Chem. Soc.*, **85**, 3138 (1963).

[25] I. Tabushi, J. Hamuro, and R. Oda, *ibid.*, **89**, 7127 (1967); *J. Org. Chem.*, **33**, 2108 (1968); I. Tabushi, T. Okada, Y. Aoyama, and R. Oda, *Tetrahedron Lett.*, 4069 (1969); P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *J. Amer. Chem. Soc.*, **90**, 4122 (1968); G. J. Gleicher, J. L. Jackson, P. H. Owens, and J. D. Unruh, *Tetrahedron Lett.*, 833 (1969). However, *cf.* V. A. Nekrasova and N. I. Shiukin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 714 (1969).

[26] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1968, p 1180.

[27] K. Alder, S. Harting, and G. Hausmann, *Ber.*, **89**, 1972 (1956).

[28] G. Schröder, *ibid.*, **97**, 3140 (1964).

[29] See text and ref 13.

1-Chlorobicyclo[3.2.2]decane (III, X = Cl).—A procedure similar to that reported[11a] for the preparation of 1-chlorobicyclo-[3.2.2]nonane was employed. Thus, 1-bicyclo[3.3.2]decanol (187 mg, 1.2 mmol) was added to freshly purified thionyl chloride[30] (2 ml) and stirred for 12 hr. Chips of ice were then added to the reaction mixture until all excess thionyl chloride had decomposed. The product was extracted with ether and the ether extracts were washed with 10% Na_2CO_3, water, and brine and dried ($MgSO_4$). Removal of solvent by distillation and sublimation of the residue gave a white waxy solid (140 mg, 67%): mp 85–87°; nmr (CCl_4) δ 1.67 (11 H, m) and 2.28 (6 H, m); ir (CCl_4) 2900, 1450 cm^{-1}.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.56; H, 9.86; Cl, 20.58. Found: C, 69.54; H, 9.71; Cl, 20.25.

Reduction of 1-Chlorobicyclo[3.3.2]decane (III, X = Cl).—To a solution of 1-chlorobicyclo[3.3.2]decane (75 mg, 0.44 mmol), lithium aluminum hydride (5 mg, 0.13 mmol), and 2,2-azobisisobutyronitrile (catalytic amount) in 5 ml of anhydrous ether was added triphenyltin chloride (193 mg, 0.5 mmol) in ether (15 ml) at room temperature.[31] Care was taken to exclude moisture. A fine, light-colored precipitate developed during the course of the addition (30 min). The reaction mixture was then refluxed for 3 hr, filtered, washed with water (two times) and brine, and dried ($MgSO_4$). Removal of solvent and sublimation of the residue gave a product (67%) whose physical (mp 177–178°) and spectroscopic properties were identical in every respect with those of bicyclo[3.3.2]decane (III, X = H).

Bromination of Bicyclo[3.2.2]nonane (II, X = H).—To bromine (5 ml) cooled in an ice bath was added bicyclo[3.2.2]-nonane[14] (1 g). The reaction mixture was then gradually raised to room temperature and stirred for 20 hr. After addition of CCl_4 (35 ml), the excess bromine was destroyed with an aqueous solution of $NaHSO_3$. The organic layer was then separated, washed twice with water, and dried ($CaCl_2$). The solvent was removed *in vacuo* and the product distilled (1 g, 61%), bp 53–54° (0.3 mm). A sharp singlet attributable to $-CH_2Br$ appears at δ 3.33 in the nmr spectra indicating that rearrangement had occurred. The integration of this signal indicated that rearrangement was complete within experimental error. No conditions could be found for the separation of the two most likely products,[18] 1-bicyclo[3.2.1]octylcarbinyl bromide and 1-bicyclo-[2.2.2]octyl carbinyl bromide.

1-Bromobicyclo[3.2.2]nonane (II, X = Br).—To freshly distilled thionyl bromide (0.56 ml, 7 mmol) was added 1-bicyclo-[3.2.2]nonanol (0.5 g, 3.5 mmol) at room temperature. The reaction mixture was stirred at that temperature for 12 hr and heated at 85° for an additional 4 hr. Chips of ice were then added to decompose the excess thionyl bromide. The product was extracted with ether (two times) and the combined extracts were washed with 10% Na_2CO_3, water, and brine. After drying ($MgSO_4$) the solvent was removed *in vacuo* and the oily product was distilled (0.4 g, 55%): bp 123–125° (20 mm); nmr (CCl_4) δ 1.70 (9 H, m) and 2.40 (6 H, m); ir (CCl_4) 2925, 2860, 1460, 640 cm^{-1}.

Anal. Calcd for $C_9H_{15}Br$: C, 53.20; H, 7.39; Br, 39.41. Found: C, 53.27; H, 7.29; Br, 39.24.

1-Bicyclo[3.3.1]nonylcarboxylic Acid (I, X = COOH). A.—To a solution of 96% H_2SO_4 (125 ml), CCl_4 (50 ml), and 1-bicyclo-[3.3.1]nonanol (6.5 g, 0.046 mol) cooled in an ice–salt bath was added 28 g of HCOOH with vigorous stirring over a period of 1.5 hr. The reaction temperature was not allowed to rise above 15°. After stirring for an additional hour, the reaction mixture was poured over ice (350 g). The organic layer was separated and the acid layer was extracted with CCl_4 (three times). The combined CCl_4 extracts were washed with two 50-ml portions of 15 *N* NH_4OH. The alkaline washes were then acidified with 12 *N* HCl. The precipitated product was extracted with chloroform, the chloroform extracts were dried (Na_2SO_4), and the solvent was removed to give 5.8 g (75%) of crude product. Recrystallization from methanol–water (7:1) gave I (X = COOH): mp 96–97.5° (lit. mp 98–99°,[21a] 95.5–97°,[21b] 82–84° [21c]); nmr (CCl_4) δ 1.70 (15 H, m) and 11.95 (1 H, s); ir (CCl_4) 3100, 2925, 1695 cm^{-1}.

B.—Similar results in somewhat decreased yield were obtained when bicyclo[3.3.1]nonane was used instead of the 1-alcohol and *tert*-butyl alcohol (15 g) was added with the formic acid.[22] Separation of the 1-bicyclo[3.3.1]nonylcarboxylic and pivalic acids obtained in this manner was accomplished by distillation. A fraction boiling at 113–118° (0.1 mm) gave a 47% yield of 1-bicyclo[3.3.1]nonylcarboxylic acid (I, X = COOH).

Registry No.—I (X = OH), 15158-56-2; I (X = CO_2H), 17530-63-1; II (X = OH), 28054-86-6; II (X = Br), 28054-87-7; III (X = OH), 18216-08-5; III (X = Cl), 28054-89-9; III 1,5-diol, 28054-90-2; V, 28054-91-3; V tosylhydrazone, 28054-94-6; VI, 19388-80-8; VI OTs, 28054-92-4; VII, 6571-74-0; chromic acid, 7738-94-5.

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Correlation Constants in the Chemistry of Organophosphorus Compounds

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Two correlation methods of ionization constants of the organophosphorus acids are discussed. The first involves application of σ^Φ constants characteristic of the substituents bonded to phosphorus. In the second approach the σ_I and σ_R constants found for the substituents bonded to carbon are used. The best correlations are obtained for σ^Φ constants. Correlation of σ^Φ constants with σ_I and σ_R values employing the Taft equation gives only a fairly good correlation coefficients. Electronic effects of the substituents at phosphorus are of the same nature as those at carbon atom, but some specific difference in the resonance effects is observed probably owing to the difference between p–π or π–π and p–d or π–d overlaps. Thus the use of σ^Φ constants for correlation of the organophosphorus reactions is preferable.

Jaffé, Freedman, and Doak were the first to employ the Hammett equation in the chemistry of organophosphorus compounds in 1953.[1] They found that the ionization constants of aromatic phosphonic acids show linear correlation with σ_m and σ_p values reported by Jaffé.[2] In 1956 one of us found[3,4] that, besides for aromatic acids, the Hammett equation

$$pK = pK^0 - \rho\Sigma\sigma^\Phi \qquad (1)$$

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