A sample of **11**, prepared for analysis by recrystallization from ethanol, had mp 117.5–118°; ultraviolet, λ_{max} 330 mμ (log ε 4.33), 314 (4.43), sh 299 (4.36); infrared, 3300 (N–H), 1800 (cyclopropene), 1690 cm^{-1} (C=O); nmr, δ 7.4 (m, 16, phenyl hydrogens and N–H), 4.3 (d, 2, J = 5 cps, methylene attached to ring), 4.0 (q, 2, J = 7 cps, methylene of ethyl), 1.1 (t, 3, J = 7 cps, methyl of ethyl).

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.30; H, 6.28; N, 3.79. Found: C, 81.12; H, 6.32; N, 3.75.

A sample of **12** prepared for analysis by recrystallization from acetone had mp 323.5–325°; ultraviolet, λ_{max} 326 mμ (log ε 3.92), 255 (4.33); infrared, 2450 (N–H), 1630 cm^{-1} (C=O).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30. Found: C, 85.39; H, 5.38.

Photolysis of Azide 8b.—An anhydrous ether solution (200 ml) of **8b** (from 0.35 g of acid chloride) was irradiated in a quartz cell under positive nitrogen pressure. A Srinivasan–Griffin reactor with 2537-Å lamps was used as a light source. The disappearance of the azide bands in the infrared spectrum was complete after 6 hr. After allowing some solvent to evaporate, there was obtained 0.025 g of colorless fluffy crystals, mp 272–275°; a second crop gave 0.013 g, mp 268–271°; a third crop gave 0.008 g, mp 267–271°. The total yield of 4,5,6-triphenyl-2-pyridone (**13**) was 0.046 g (14%). A mixture melting point with **13**, mp 276–277°, prepared by a different route (see below), was 275–276°. The infrared spectra of the two samples were also identical.

A sample prepared for analysis by recrystallization from acetone had mp 276–277°; ultraviolet, λ_{max} 326 mμ (log ε 3.91), 259 (4.25); infrared, 2450 (N–H), 1635 cm^{-1} (C=O).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.31; H, 5.30; N, 4.14.

The remainder of the reaction mixture was evaporated to a yellow oil, whose infrared showed a band at 2270 cm^{-1} (isocyanate). Absolute ethanol was added to the oil and after 4 days was removed under reduced pressure. The resulting gum was chromatographed on Fisher adsorption alumina giving 0.005 g (2%) of **11**, mp 115–117°. The rest of the material was an intractable red gum.

Photolysis of 1,2,3-Triphenylcycloprop-3-enylcarbinyl Isocyanate (9).—An anhydrous ether solution of **8b** (from 0.385 g of acid chloride) was added dropwise to 20 ml of refluxing dry benzene over the course of 5 min. It was then refluxed an additional 1 hr. The solvents were evaporated under reduced pressure to give a brown oil whose infrared spectrum showed a band at 2270 cm^{-1}. The oil was dissolved in 200 ml of anhydrous ether and photolyzed for 6 hr. The solvent was evaporated leaving an oil which showed a peak at 2270 cm^{-1} (isocyanate). Absolute ethanol was added to the oil and the solution allowed to stand at room temperature for 4 days. By filtering, 0.032 g (9%) of **12**, mp 315–318°, was obtained. Chromatography of the remaining material on Fisher adsorption alumina gave 5% (0.020 g) of **11**, mp 116–118°. The rest of the material was an intractable red gum.

No pyridone could be obtained before treating the reaction mixture with ethanol.

Preparation of 4,5,6-Triphenyl-2-pyridone (13).[11]—To 75 g of stirred polyphosphoric acid was added 3.6 g (0.025 mol) of 3-phenyl-3-oxopropanenitrile and 5.0 g (0.025 mol) of deoxybenzoin. The mixture was stirred for 5 min and then heated and stirred on a steam bath for 30 min during which time the reaction mixture turned red. Another 5 g of deoxybenzoin was added and the mixture heated at 135–145° in an oil bath for 35 min. The mixture was poured onto 300 g of ice. To this was added 200 ml of ether, and the mixture was stirred for 0.5 hr. The mixture was filtered to give a solid which on recrystallization from acetone gave 0.037 g (0.48%) of **13**, mp 276–277°.

Registry No.—**1b**, 15707-48-9; **2**, 15983-99-0; **6a**, 15983-93-4; **6b**, 15983-94-5; **7**, 15983-95-6; **8b**, 15983-96-7; **10**, 15983-97-8; **11**, 15983-98-9; **12**, 15984-00-6; **13**, 15984-01-7.

Acknowledgments.—The authors wish to thank the National Science Foundation and the Institute of Scientific Research, New Mexico Highlands University, for their support in 1963–1964. We wish to thank Professor Ernest Wenkert for some of the nmr spectra. This research was also partially supported by grants from the Research Corporation, University of Connecticut Research Foundation, and the Petroleum Research Fund. Grateful acknowledgment is made to the donors of these funds.

Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. IV.[1] The Free-Radical Chlorination and Chloroformylation of Bicyclo[3.1.0]hexane

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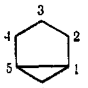
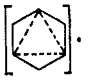
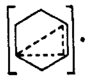
Free-radical chlorination of bicyclo[3.1.0]hexane (I) using *t*-butyl hypochlorite results in substitution at C-2 (78%) and C-3 (22%). Radical chloroformlyation of I using oxalyl chloride generates, after esterification, 2-carbomethoxy- (16%) and 3-carbomethoxybicyclo[3.1.0]hexane (12%) derivatives, as well as rearrangement products methyl Δ^2-cyclopentenylacetate (36%) and 4-carbomethoxycyclohexene (33%).



I



II



III

Our interest in bicyclo[3.1.0]hexyl carbonium ions[1,3] and bicyclo[3.1.0]hexylidene bivalent carbon intermediates[4] led us quite naturally to a consideration of bicyclo[3.1.0]hexyl free-radical intermediates. Hydrogen abstraction from bicyclo[3.1.0]hexane (I) appeared to be a straightforward method of generation of bicyclo[3.1.0]hexyl free radicals. Abstraction of a hydrogen atom from C-3 might produce free radical II, analogous to the trishomocyclopropenyl carbonium ion,[5] while abstraction at C-2 might generate radical III, analogous to a bicyclobutonium ion intermediate.[6] We chose to consider free-radical halogenation using

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[1] Part III: P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **32**, 24 (1967).

[2] Undergraduate research participants, supported by National Science Foundation Grants NSF G-21900 and NSF G-16215.

[3] P. K. Freeman, M. F. Grostic, and F. A. Raymond, *ibid.*, **30**, 771 (1965).

[4] P. K. Freeman and D. G. Kuper, *ibid.*, **30**, 1047 (1965).

[5] (a) S. Winstein, E. C. Friedrich, R. Baker, and Y.-I Lin, *Tetrahedron*, 621 (1966). (b) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235 (1961); **83**, 3244 (1961). S. Winstein, *ibid.*, **81**, 6524 (1959). S. Winstein, J. Sonnenberg, and L. de Vries, *ibid.*, **81**, 6523 (1959).

[6] M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961).

t-butyl hypochlorite, which proceeds utilizing the *t*-butoxy radical as the chain carrier,[7] and the lesser known

$$\mathrm{RH} + t\text{-}\mathrm{BuO}\cdot \longrightarrow \mathrm{R}\cdot + t\text{-}\mathrm{BuOH}$$

$$\mathrm{R}\cdot + t\text{-}\mathrm{BuOCl} \longrightarrow \mathrm{RCl} + t\text{-}\mathrm{BuO}\cdot$$

chloroformylation reaction,[8-12] for which the radical sequence in Scheme I has been proposed.[8]

SCHEME I

$$\begin{array}{ll}
\mathrm{I} & (\mathrm{COCl})_2 \xrightarrow{h\nu} 2\cdot\mathrm{COCl} \\
 & \text{and/or } (\mathrm{COCl})_2 \xrightarrow{h\nu} \mathrm{Cl}\cdot + \cdot\mathrm{COCOCl} \\
\mathrm{II} & \cdot\mathrm{COCl} \longrightarrow \mathrm{Cl}\cdot + \mathrm{CO} \\
 & \cdot\mathrm{COCOCl} \longrightarrow \mathrm{Cl}\cdot + 2\mathrm{CO} \\
 & \mathrm{RH} + \mathrm{Cl}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{HCl} \\
 & \mathrm{R}\cdot + (\mathrm{COCl})_2 \longrightarrow \mathrm{RCOCl} + \cdot\mathrm{COCl}
\end{array}$$

A different view of the transfer step is favored by Runge[9] and by Treibs and Orttmann (for oxalyl bromide),[11] who support a two-step process, in spite of evidence presented against this alternative.[8] Additional research on this point would appear to be worthwhile.

$$\mathrm{R}\cdot + (\mathrm{COX})_2 \longrightarrow \mathrm{RCOCOX} + \mathrm{X}\cdot$$

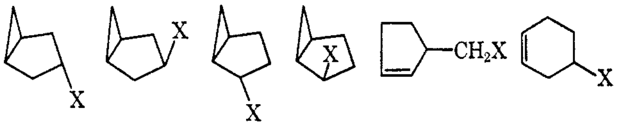
$$\mathrm{RCOCOX} \longrightarrow \mathrm{RCOX} + \mathrm{CO}$$

Results

The photochlorination of bicyclo[3.1.0]hexane was accomplished by irradiation of mixtures of bicyclo[3.1.0]hexane (10% mole excess) and *t*-butyl hypochlorite. The yields of monochlorides varied from 24 to 42%. The reaction mixtures were analyzed by vapor phase chromatography, using an 8-ft column of tris(cyanoethoxy)propane, and showed peaks with retention times corresponding to substitution at C-2 and C-3 on the bicyclo[3.1.0]hexane ring skeleton: *trans*-3-chlorobicyclo[3.1.0]hexane (IVa)/*cis*-3-chlorobicyclo[3.1.0]hexane (Va) and/or *trans*-2-chlorobicyclo[3.1.0]hexane (VIa)/*cis*-2-chlorobicyclo[3.1.0]hexane (VIIa) in an average ratio of 7:71:22 (Table I). The *trans*-3 and *cis*-2 chlorides were identified by comparison of their infrared and nmr spectra with those of authentic samples.[1] Comparison of the infrared spectra of the major component (71%) with the spectra of *trans*-2- and *cis*-3-chlorobicyclo[3.1.0]hexane previously recorded[1] demonstrated that the major component was principally the *trans*-2 chloride accompanied by a smaller amount of *cis*-3 chloride in a ratio of 57:14 (base-line calculation using the 747 cm^{-1} *cis*-3 chloride band). Δ^2-Cyclopentenylcarbinyl chloride (VIIIa) and 4-chlorocyclohexene (IXa) have retention times on the tris(cyanoethoxy)propane column corresponding to those for *trans*-3 and *trans*-2 chloride, respectively, but were found not to be present by infrared analyses of the individual component peaks.

TABLE I
PHOTOCHLORINATION OF BICYCLO[3.1.0]HEXANE WITH *t*-BUTYL HYPOCHLORITE

Run	Yield, %	Composition of the monochloride fraction *trans*-3	*cis*-3	*trans*-2	*cis*-2
1	24	7%	15%	55%	23%
2	35	7	14	57	22
3	40	7	14	57	22
4	34	7	14	56	23
5	30	6	14	57	23
6	35	6	14	57	23
7	42.5	8	13	56	23



IV V VI VII VIII IX

a, X = Cl
b, X = COCl
c, X = CO_2CH_3
d, X = CN

Chloroformylation of bicyclo[3.1.0]hexane was carried out by irradiation of an equimolar solution of oxalyl chloride and bicyclo[3.1.0]hexane. The 15–18% yield of acid chlorides, which was obtained, was converted into a methyl ester fraction by treatment with methanol and pyridine. It was possible to separate two unsaturated components in sufficient purity from the complex mixture of methyl esters by vapor phase chromatography for identification. Infrared and nmr spectral comparison with authentic samples demonstrated that these two components were 4-carbomethoxycyclohexene (IXc) and methyl Δ^2-cyclopentenylacetate (VIIIc). Although the methyl ester fraction resisted all attempts to achieve satisfactory resolution of all components on a variety of vpc columns, adequate resolution of 4-carbomethoxycyclohexene, methyl Δ^2-cyclopentenylacetate, and the remaining carbomethoxybicyclo[3.1.0]hexanes was accomplished by a combination of hydrogenation of the methyl ester fraction over palladium on carbon, a reaction which leaves the bicyclo[3.1.0]hexane skeleton intact, and use of a 25-ft Carbowax 1500 column. Vapor phase chromatographic analysis of this reduced methyl ester fraction and nmr and infrared spectral comparison with standards revealed that the original ester fraction had the composition 36% methyl Δ^2-cyclopentenylacetate (VIIIc), 33% 4-carbomethoxycyclohexene (IXc), and 10% *trans*-3-carbomethoxy-, 2% *cis*-3-carbomethoxy-, 6% *trans*-2-carbomethoxy-, and 10% *cis*-2-carbomethoxybicyclo[3.1.0]hexane (IVc–VIIc).

Discussion

In comparing the *t*-butyl hypochlorite chlorination with the chloroformylation, one is first struck with the large degree of rearrangement products (VIIIb, IXb) formed in the latter reaction. The rearrangement pathways leading to these products would appear to be analogous to previously reported examples of β fission

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(7) C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6108 (1960).

(8) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, **64**, 1621 (1942); **64**, 333 (1942). M. S. Kharasch and H. C. Brown, *ibid.*, **64**, 329 (1942); **62**, 454 (1940).

(9) F. Runge, *Z. Elektrochem.*, **60**, 956 (1956); **56**, 779 (1952).

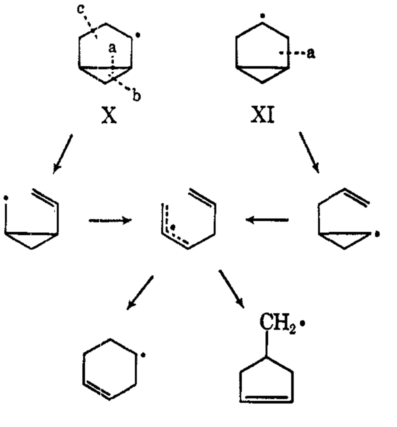
(10) M. T. Ahmed and A. J. Swallow, *J. Chem. Soc.*, 3918 (1963).

(11) W. Treibs and H. Orttmann, *Naturwissenschaften*, **45**, 85 (1958).

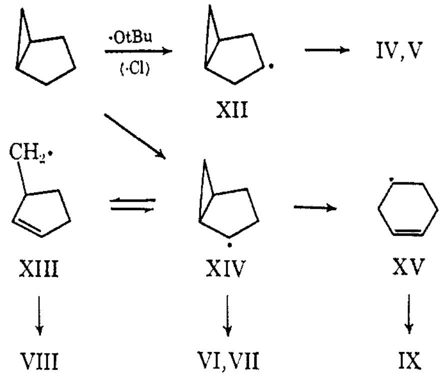
(12) A. I. Gershenovich and A. K. Mikhailova, *Sintez i Svoistva Monomerov, Akad. Nauk SSSR, Inst. Neftekhim. Sinteza, Sb. Rabot 12-oi [Dvenadtsatoi] Konf. po Vysokolomolekul. Soedin.*, 216 (1962); *cf. Chem. Abstr.*, **62**, 6404*d* (1965).

in cyclopropylcarbinyl free-radical systems.[13,14] However, in addition to fission of bonds a and b in cyclopropylcarbinyl radical X, β fission at bond c in X or a in 3-bicyclo[3.1.0]hexyl radical XI might produce cyclopentenylmethyl and 4-cyclohexenyl derivatives (Scheme II). There are, however, no products in either the chlorination or chloroformylation reactions, which correspond to the acyclic or monocyclic, cyclopropyl free-radical intermediates of Scheme II. In addition the double bond in the cyclopentenylmethyl radical formed in this manner is in the Δ^3 and not the Δ^2 position. It is possible that a small amount of Δ^3 isomer may have gone undetected in the Δ^2-cyclopentenyl product, however. Walling, Cooley, and coworkers[15] have recently demonstrated the preference of 5-hexenyl and analogous free radicals for cyclization to five-membered ring systems. Although this raises the question as to whether the 4-cyclohexenyl radical might be formed in the above manner, it seems unlikely that the resonance stabilized hexadienyl free radical of Scheme II would undergo ring closure to either of the cyclohexenyl or cyclopentenylmethyl radicals pictured, since the analogous resonance-stabilized intermediate formed by treatment of allyl chloroacetate with tri-*n*-butyltin hydride does not cyclize.[15] Thus the simplest rationalization of product formation in both the chlorination and chloroformylation reactions involves hydrogen abstraction at C-2 and C-3, followed by β fission of the cyclopropane ring, in the case of chloroformylation, as pictured in Scheme III. Slaugh has found that the generation of Δ^2-cyclopentenylmethyl free radical (XIII) by thermal decomposition of *t*-butyl Δ^2-cyclopentenylperacetate in the presence of *p*-cymene or benzotrichloride resulted in a 1,2-vinyl rearrangement producing the 4-cyclohexenyl radical (XV), whereas similar reactions utilizing *t*-butyl 4-cyclohexenylpercarboxylate gave no evidence of rearrangement products.[16] In agreement with the latter finding, Wilt and Levin[17] found no evidence for rearrangement of the 4-cyclohexenyl free radical produced by decarbonylation of 4-cyclohexenylcarboxaldehyde. It appears, then, that some equilibration of Δ^2-cyclopentenylmethyl and 2-bicyclo[3.1.0]hexyl free radicals may be established during the chloroformylation reaction, but equilibration of the 4-cyclohexenyl and 2-bicyclo[3.1.0]hexyl radical intermediates seems unlikely. Furthermore, our results lend support to the mechanistic alternative suggested by Slaugh for rearrangement of the cyclopentenyl radical XIII to cyclohexenyl radical XV *via* bicyclohexyl intermediate XIV.

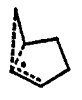
Scheme II



Scheme III



Since the chlorination and chloroformylation reactions have been carried out at reaction temperature ranges which were not too divergent (*ca.* 70–85° and 70–100°, respectively), the greater degree of rearrangement in the case of chloroformylation appears to be most simply explained on the basis of a smaller transfer constant relative to that for the reaction of radical XIV with *t*-butyl hypochlorite. This necessarily leads to the presentation of the fate of the radical intermediate formed by hydrogen abstraction at C-2 in terms of classical radicals XIII, XIV, and XV (Scheme III), rather than in terms of a single nonclassical radical such as XVI.[18]



XVI

Basing our analysis of product formation on Scheme III, we find no evidence for C-1 or C-6 abstraction. This is not surprising in view of the relative reactivities of cyclopentane and cyclopropane to hydrogen abstraction by ·OtBu and ·Cl as reported by Walling.[14] The total lack of free-radical bridgehead substitution in these reactions of bicyclo[3.1.0]hexane provides a substitution pattern similar to that found for norbornane[19] and bicyclo[2.1.1]hexane,[20] rather than bicyclo[2.2.0]hexane[21] and bicyclo[1.1.1]pentane[22] (Table II). An interesting facet of the chlorination and chloroformylation of bicyclo[3.1.0]hexane is the preference

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(13) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 3051 (1967); L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 3050, 934 (1967); L. K. Montgomery, J. W. Matt, and J. R. Webster, *ibid.*, **89**, 923 (1967); D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); D. E. Applequist and J. A. Landgrebe, *ibid.*, **86**, 1543 (1964); E. E. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963); E. Renk, P. D. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 1987 (1961).

(14) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962); C. Walling and M. F. Mayahi, *ibid.*, **81**, 1458 (1959).

(15) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5361 (1966).

(16) L. H. Slaugh, *ibid.*, **87**, 1522 (1965).

(17) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

(18) This picture is consistent with the results of a study of radical intermediates generated by free-radical addition of methyl mercaptan to bicyclo[3.1.0]hexene-2: P. K. Freeman, M. F. Grostic, and F. A. Raymond, unpublished results, University of Idaho.

(19) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

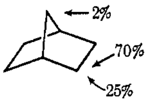
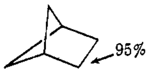
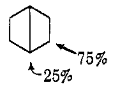
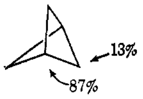
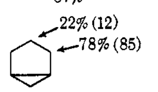
(20) R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **89**, 407 (1967).

(21) R. Srinivasan and F. I. Sonntag, *Tetrahedron Lett.*, 603 (1967).

(22) K. B. Wiberg and D. S. Connor, *J. Amer. Chem. Soc.*, **88**, 4437 (1966).

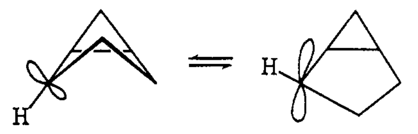
TABLE II

FREE-RADICAL SUBSTITUTION PATTERNS IN SOME BICYCLOALKANES

Substrate	Reacn conditions	Ref
	Cl_2, *hν*, CH_2Cl_2, 42°	*a*
	Cl_2, *hν*, CCl_4, 77°	*b*
	Cl_2, *hν*	*c*
	*t*-BuOCl, *hv*, 0°	*d*
	*t*-BuOCl, *hν*, 70–85° (ClOCCOCl, *hν*, 70–100°)	This work

[a] See ref 19. [b] See ref 20. [c] See ref 21. [d] See ref 22.

for C-2 over C-3 hydrogen abstraction. Correcting for the fact that substitution at C-2 is favored statistically over C-3, the ratio of C-2/C-3 hydrogen abstraction (per hydrogen) for ·OtBu is 1.8:1, while chloroformylation gives a C-2/C-3 abstraction ratio (per hydrogen) of 3.6:1. The preference for C-2 over C-3 abstraction occurs in spite of the electron-withdrawing polar effect of cyclopropane,[23] which should promote C-3, rather than C-2 abstraction[24] for electrophilic radicals such as ·OtBu[25] and ·Cl.[24,26] The resonance effect of the cyclopropane ring must, therefore, be responsible for the preference for hydrogen abstraction at C-2. Since electrophilic radicals are involved in both reactions, the transition state for abstraction would be expected to be polarized conferring some carbonium ion character upon the developing hydrocarbon fragment, which should contribute to a preference for C-2 abstraction.[1,3] In this regard, it is interesting that inspection of a Dreiding model reveals that the 2-bicyclohexyl free radical can achieve the bisected conformation (XVII) preferred for cyclopropylcarbinyl free radicals with excess charge $q_i \geq 0$[27] by puckering C-3 toward the cyclopropane ring to form a boat-shaped conformation. In fact, little conformational adjustment would be required for production of XVII, since the most stable conformation for the starting hydrocarbon, bicyclo[3.1.0]hexane, appears to be a boat-shaped structure.[28] On balance, a boat conformation for free radical XVII also appears to relieve nonbonded interactions more effectively, relative to a planar cyclopentane configuration, than the conformation obtained by puckering C-3 in the opposite direction (XVIII).[29]



XVII XVIII

In addition to a consideration of the preference for C-2 over C-3 hydrogen abstraction in both chlorination and chloroformylation, a comparison of the difference in the apparent selectivities for C-2/C-3 hydrogen abstraction for ·OtBu (1.8:1.0) and ·Cl (3.6:1.0) is of interest. Since the reaction temperature ranges for chlorination and chloroformylation are not too widely different, and since the selectivity of the *t*-butoxy radical appears to be insensitive to temperature changes between 40 and 135°,[30] the differences in selectivity for the abstracting radicals are due to their inherent characteristics. The fact that ·OtBu appears to be less selective than Cl·, in contrast to the usual order observed,[31,32] suggests that Cl· may not be the only H-transfer agent involved in chloroformylation or that ·Cl may be complexed with oxalyl chloride.[32]

One final feature of Table I is particularly intriguing. The 2:1 ratio of *cis*-3/*trans*-3 substitution found, in spite of the steric blocking of *cis* approach by the cyclopropane methylene, provides a hint that anchimeric assistance to *cis*-C-3 hydrogen abstraction, analogous to that observed in the solvolysis of the *cis*-3-tosylate,[5] may play a role. Further experimentation along this line is in progress.

Experimental Section[33]

Preparation of Bicyclo[3.1.0]hexane.—Bicyclo[3.1.0]hexane was prepared by the method of Simmons and Smith.[34] The infrared spectra exhibit the typical bicyclo[3.1.0]hexyl high energy C–H stretching frequencies at 3055, 3025, and 2995 cm^{-1} and a cyclopropyl absorption band at 1022 cm^{-1}. The nmr spectrum shows high field cyclopropyl methylene protons in the region τ 9.60–10.00 and a complex absorption for the other eight protons in the region τ 8.00–9.23.

Chlorination of Bicyclo[3.1.0]hexane with *t*-Butyl Hypochlorite.—A mixture of bicyclo[3.1.0]hexane (2.50 g, 30.5 mmol) and *t*-butyl hypochlorite[35] (3.00 g, 27.6 mmol) was irradiated with a General Electric sun lamp until a gentle reflux was obtained. Upon completion of the spontaneous reaction the mixture was irradiated for an additional period of 2–3 min to ensure completion of the reaction (reaction temperature *ca.* 70–85°). The reaction mixture (5.31 g) was analyzed by vpc using a 30-ft copper column of 30% Carbowax 1500 on Chromosorb P at 135°. The over-all yield of monochlorides was calculated to be 34% on the basis of vpc data. The area of the chromatogram representing the monochlorides in a known amount of reaction mixture was

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[23] T. L. Brown, *J. Amer. Chem. Soc.*, **80**, 6489 (1958).

[24] G. A. Russell and A. Ito, *ibid.*, **85**, 2983 (1963); G. A. Russell, A. Ito, and R. Konaka, *ibid.*, **85**, 2988 (1963).

[25] H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967).

[26] G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

[27] G. A. Russell and H. Malkus, *ibid.*, **89**, 160 (1967); N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967).

[28] Winstein and coworkers[5a] have presented nmr spectral evidence for a preferred boat conformation for both *cis*- and *trans*-3-bicyclo[3.1.0]hexyl derivatives. We have come to a similar conclusion as a result of consideration of nmr data of *trans*-2-bicyclo[3.1.0]hexyl substrates.[1,3] It thus seems entirely likely that the most stable conformation for the parent hydrocarbon, bicyclo[3.1.0]hexane, is also the boat form.

[29] Conformation XVII relieves the nonbonded interactions between the hydrogens at *cis*-C-4 and *syn*-C-6 and *trans*-C-4 and C-5, and increases interaction between hydrogens at C-1 and C-2, while conformation XVIII achieves the converse.

[30] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N. Y., 1966, p 167.

[31] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961); G. A. Russell, *ibid.*, **80**, 4997 (1958).

[32] G. A. Russell, *ibid.*, **80**, 4987 (1958).

[33] Infrared spectra were determined as pure liquids using Perkin-Elmer Models 137 and 237 spectrophotometers. Nmr spectra were run in carbon tetrachloride with tetramethylsilane as the internal reference using a Varian Associates A-60 nmr spectrometer. Gas chromatographic analyses were performed using either an Aerograph Model A-700 or Model A-90-P chromatograph, and helium was used as the carrier gas. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Max Bernhardt, Mikroanalytisches Laboratorium, Max-Planck Institute, Mülheim, Germany.

[34] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[35] H. M. Teeter and E. W. Bell, *Org. Syn.*, **32**, 20 (1952).

compared with the peak areas of known amounts of 4-chlorocyclohexene. Numerous vpc columns were tested and the one which was found to be most satisifactory for analysis of this mixture of chlorides was an 8-ft aluminum column of 13% tris(cyanoethoxy)-propane (TCEP) on HMDS-treated Chromosorb W. Vpc analysis using this column, coupled with spectral comparison with authentic samples,[1] gave the following reaction composition in one typical run (see Table I): 7% *trans*-3-chlorobicyclo[3.1.0]hexane, 14% *cis*-3-chlorobicyclo[3.1.0]hexane, 57% *trans*-2-chlorobicyclo[3.1.0]hexane, and 22% *cis*-2-chlorobicyclo[3.1.0]hexane. The compounds had the following retention times on the TCEP column at a column temperature of 70° and a flow rate of *ca.* 60 ml/min: *trans*-3-chlorobicyclo[3.1.0]hexane, 10.0 min; *cis*-3- and *trans*-2-chlorobicyclo[3.1.0]hexane, 12.1 min; *cis*-2-chlorobicyclo[3.1.0]hexane, 16.0 min. Δ^2-Cyclopentenylcarbinyl chloride and 4-chlorocyclohexene had retention times corresponding to those for *trans*-3 and *trans*-2 chloride, respectively, but were found not to be present by infrared analysis of the individual peaks. The percentage of *cis*-3-chlorobicyclo[3.1.0]hexane in *trans*-2-chlorobicyclo[3.1.0]hexane was determined by infrared analysis (base-line calculation at 747 cm^{-1}).

Chloroformylation of Bicyclo[3.1.0]hexane.—A mixture of 19.2 g (0.151 mol) of oxalyl chloride and 12.4 g (0.151 mol) of bicyclo[3.1.0]hexane was irradiated, under nitrogen, with a General Electric sun lamp, held approximately 1 in. from the reaction flask, for 46 hr. The reaction mixture was stirred during this period with a magnetic stirring bar; the heat from the sun lamp caused the reaction mixture to reflux gently (reaction temperature was *ca.* 70–100°). After the irradiation period was complete, the reaction mixture was distilled and 3.40 g (15.6% yield), bp 75–120° (30 mm), of acid chlorides was obtained. The acid chlorides were converted into methyl esters by treatment with methanol and pyridine.

The use of a 25-ft Carbowax 1500 vapor phase chromatographic column allowed the partial resolution of two of the seven components ultimately determined to be present. Infrared comparison with authentic samples demonstrated that these two components, the two most abundant products, were methyl Δ^2-cyclopentenylacetate and 4-carbomethoxycyclohexene. It was discovered that hydrogenation of the methyl ester product fraction over palladium-on-carbon catalyst reduced the cyclopentene and cyclohexene esters and that the corresponding saturated products had somewhat shorter retention times on a 25-ft Carbowax 1500 column. The combination of reduction and use of the Carbowax column allowed a separation of the cyclopentane and cyclohexane esters from the bicyclo[3.1.0]hexane esters and determination of product composition: 36% methyl Δ^2-cyclopentylacetate, 33% 4-carbomethoxycyclohexane, 10% *cis*-2-carbomethoxybicyclo[3.1.0]hexane, 6% *trans*-2-carbomethoxybicyclo[3.1.0]hexane, 2% *cis*-3-carbomethoxybicyclo[3.1.0]hexane, 10% *trans*-3-carbomethoxybicyclo[3.1.0]hexane, and 3% unidentified component. In two additional experiments, subjection of bicyclo[3.1.0]hexane and a mixture of methyl Δ^2-cyclopentenylacetate and 4-carbomethoxycyclohexene to the reduction conditions demonstrated that conditions sufficient for complete reduction of the unsaturated esters left the bicyclo[3.1.0]hexane skeleton intact.

***cis*- and *trans*-2-Cyanobicyclo[3.1.0]hexane.**—To a stirred mixture of potassium cyanide (1.6 g, 25 mmol) in 2.6 ml of aqueous acetone (54% water by volume) was added 1.0 g of *cis* and *trans*-2-chlorobicyclo[3.1.0]hexane (60:40). After 30 hr of stirring, the reaction mixture was diluted with about 10 ml of water and the nitriles were extracted with several 15-ml portions of ether. After drying over anhydrous magnesium sulfate, the ether was removed at reduced pressure, using a rotary evaporator, to yield 1.03 g of crude product. Vpc analysis using a 10-ft aluminum column of 25% Carbowax 1500 on Chromosorb P (flow rate *ca.* 60 ml/min. and a column temperture of 150°) showed the crude product to be 52% nitriles, 27% alcohols, and 21% residual chlorides. The nitriles were shown to be *trans*-2-cyanobicyclo[3.1.0]hexane, 4-cyanocyclohexene and *cis*-2-cyanbicyclo[3.1.0]hexane in the ratio of 48:7:45. The retention times were 16.3, 18.7, and 20.9 min, respectively, on the 10-ft Carbowax 1500 column, using the flow and temperature listed above.

Anal. Calcd for C_7H_9N: C, 78.48; H, 8.46. Found for *cis*-2 nitrile: C, 78.35; H, 8.49. Found for *trans*-2 nitrile: C, 78.43; H, 8.60.

The nmr spectrum of the *trans*-2-cyanobicyclo[3.1.0]hexane shows typical high field absorption for cyclopropane methylene (τ 9.30–10.00) for *trans* isomers, a complex splitting pattern for six protons in the region τ 7.60–8.90 and a doublet centered at 7.13 (J = 7.1 cps). The infrared spectra show typical bicyclo[3.1.0]hexane[1,3] C–H stretching frequencies at 3070, 3030, and 3000, a cyclopropyl absorption band at 1025, and a nitrile absorption band at 2250 cm^{-1}.

The nmr spectrum of *cis*-2-cyanobicyclo[3.1.0]hexane shows typical high field absorption for cyclopropane methylene (τ 9.23–9.63) for *cis* isomers, a complex splitting pattern for six protons in the region 7.69–8.82 and a sextet for the proton α to the cyano group in the region 6.78–7.30. The infrared spectra show typical bicyclo[3.1.0]hexane C–H stretching frequencies at 3000, 3030, and 3070, a cyclopropyl absorption band at 1025, and a nitrile band at 2250 cm^{-1}. The 3030-cm^{-1} band is enhanced in the *cis* isomer relative to that for the *trans* isomer. The infrared spectra of 4-cyanocyclohexene show high energy C—H stretching frequency at 3030, a C=C band at 1650, and a nitrile band at 2250 cm^{-1}.

The alcohols were identified as *trans*-2-bicyclo[3.1.0]hexanol, *cis*-2-bicyclo[3.1.0]hexanol, and 4-hydroxycyclohexene in the ratio of 55:9:36. The alcohol fraction exhibited two peaks on a 10-ft Carbowax 1500 column (flow rate *ca.* 60 ml/min, column temperature 150°). The retention times for the two peaks were 10.6 and 11.4 min corresponding to those for *trans*- and *cis*-2 alcohols in a ratio of 55:45. The infrared spectrum of the 55% peak showed it to be *trans*-2-bicyclo[3.1.0]hexanol when compared with the spectrum of an authentic sample. The infrared spectrum of the 45% peak showed it to be predominantly 4-cyclohexenol. Since the 45% peak could not be collected pure, the amount of 4-cyclohexenol was determined from the mixture of all three alcohols collected from an XF-1150 column as one peak. Using the C=C band at 1650 cm^{-1} and the 735-cm^{-1} bands, the amount of 4-cyclohexenol in the mixture was determined to be 36%.

Preparation of *cis*-3-Cyanobicyclo[3.1.0]hexane. A. In Acetone.—To a stirred mixture of 2.3 g (35 mmol) of potassium cyanide in 35 ml of acetone was added 3.5 g (30 mmol) of *cis*- and *trans*-3-chlorobicyclo[3.1.0]hexane (76:24). The reaction was stirred at room temperature for 8 hr and vpc analysis on a 10-ft copper column of 25% nitrile silicone fluid XF-1150 on Chromosorb P (flow rate *ca.* 50 ml/min, column temperature 150°) showed no sign of reaction. The reaction was refluxed for 8 hr, after which the salts were filtered off and the acetone was removed by evaporation at reduced pressure to yield 4.45 g of crude material containing some acetone. Vpc analysis of the recovered material on the 10-ft XF-1150 column showed it to be *cis*- and *trans*-3-chlorobicyclo[3.1.0]hexane having the same ratio (76:24) as in the starting material.

The recovered material was added to 45 ml of aqueous acetone (80% water by volume) containing 3.0 g (46 mmol) of potassium cyanide. After 35 hr of heating at reflux, the reaction mixture was extracted with ether and the ether layer was dried over anhydrous magnesium sulfate. Evaporation of the solvents at reduced pressure yielded 1.65 g of crude product. This product showed residual chloride (33%) (in the ratio of 41:39 for *cis,trans*), *cis*-3-bicyclo[3.1.0]hexanol (27%), and *cis*-3-cyanobicyclo[3.1.0]hexane (40%). The *cis*-3-bicyclo[3.1.0]hexanol was identified by retention time on an XF-1150 column and the identification of the *cis*-3-cyanobicyclo[3.1.0]hexane is described below.

B. In Aqueous Acetone.—To a stirred mixture of 9.00 g (0.14 mol) of potassium cyanide in 13.5 ml of 60% aqueous acetone was added 6.00 g of *cis*- and *trans*-3-chlorobicyclo[3.1.0]hexane (74:26). After heating at reflux for 3 days, the reaction mixture was diluted with 25 ml of water and extracted several times with 20–30-ml portions of ether. The ether extracts were dried over anhydrous magnesium sulfate and the ether was removed under reduced pressure yielding 4.80 g of crude material. Vpc analysis of the crude material on the 10-ft XF-1150 column (flow rate *ca.* 60 ml/min, column temperature 150°) showed it to be 21% unreacted 3 chlorides (97:3 for *trans,cis*), 7% *cis*-3-bicyclo[3.1.0]hexanol, and 72% *cis*-3-cyanobicyclo[3.1.0]hexane. The crude material was distilled on an 18-in. semimicro spinning-band distillation column to yield 2.52 g of a mixture containing *cis*- and *trans*-3 chlorides, *cis*-3 alcohol, and *cis*-3 nitrile, bp 80–105° (50 mm), and 1.05 g of *cis*-3 nitrile forced over by reducing the pressure. The *cis*-3-cyanobicyclo[3.1.0]hexane was further purified by collecting it from a 10-ft XF-1150 column, for infrared, nmr, and carbon–hydrogen analysis.

Anal. Calcd for C_7H_9N: C, 78.48; H, 8.46. Found: C, 78.36; H, 8.42.

The structure of the one 3-cyanobicyclo[3.1.0]hexane isomer obtained was determined by nmr and infrared analyses. The nmr spectrum exhibits typical high field absorption (τ 9.20–9.60) for a bicyclo[3.1.0]hexane derivative substituted with an electronegative *cis*-3 substituent, a complex band for two tertiary protons on a cyclopropane ring in the region τ 8.38–8.75, a complex splitting pattern for four methylene protons in the region 7.50–8.05, and a complex splitting pattern for the proton α to the nitrile group in the region 6.86–7.30. The splitting pattern for the two methylene protons (τ 9.20–9.60) of the cyclopropane ring, as well as being shifted downfield relative to the parent hydrocarbon, falls into the same splitting pattern as those for the analogous protons of the *cis*-3 alcohol, *cis*-3 methyl ether, and the *cis*-3 thioether. The splitting pattern for the four methylene protons (τ 7.50–8.05) is similar to the pattern found for the same protons in the *cis*-3 alcohol and *cis*-3 methyl ether. These splitting patterns mentioned for the *cis*-3 isomers are quite different from those found in the corresponding *trans* isomers.

The infrared spectra show typical bicyclo[3.1.0]hexyl C–H stretching frequencies at 3005, 3040, and 3070, a cyclopropyl absorption band at 1030, and a nitrile band at 2230 cm^{-1}. The 3040-cm^{-1} band is the strongest band of the three C–H stretching frequencies and this reinforces the *cis*-3 assignment based on nmr spectral analysis.[1,3]

Preparation of *cis*- and *trans*-2-Carbomethoxybicyclo[3.1.0]-hexane.—To 771 mg (7.2 mmol) of nitriles (*cis*- and *trans*-2 nitrile and 4-cyanocyclohexene, 27:63:10) and 230 mg of methyl alcohol was added 260 mg of dry hydrogen chloride without cooling. Upon placing in an ice bath, the reaction mixture solidified. After several hours the imino ether hyrochlorides were hydrolyzed to the methyl esters by adding an excess of water and stirring for several hours. The esters were extracted with ether and the ether extracts were washed with 0.1 *N* NaOH to extract any acid formed during isolation of the products. After washing with distilled water, the ether extracts were dried over magnesium sulfate. Removal of the ether yielded 0.63 g of methyl esters. Analysis of the esters using a 30-ft aluminum column of 25% Carbowax 1500 (flow rate *ca.* 60 ml/min, column temperature 130°) showed three peaks in the ratio of 73:20:7 with retention times of 34.4, 36.8, and 38.7 min. The peaks were identified as *trans*-2-carbomethoxybicyclo[3.1.0]hexane, *cis*-2-carbomethoxybicyclo[3.1.0]hexane, and 4-carbomethoxycyclohexene, respectively.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.56; H, 8.63. Found for *cis*-2 ester: C, 68.44; H, 8.62. Found for *trans*-2 ester: C, 68.45; H, 8.61.

The nmr spectrum of *cis*-2-carbomethoxybicyclo[3.1.0]hexane shows high field absorption (τ 9.40–9.90) for cyclopropane methylene, a complex splitting pattern for six protons in the region 7.80–9.00, a complex splitting pattern for the *trans*-2 proton (α to the carbomethoxy group) in the region 6.92–7.35, and a O-methyl singlet at 6.37. The infrared spectra show typical bicyclo[3.1.0]hexyl C—H at 3070, 3035, and 3005, a cyclopropyl band at 1020, an ester C=O band at 1730, and a C—O band in the region 1140–1200 cm^{-1}. The 3035-cm^{-1} band is enhanced relative to the analogous band in the *trans* epimer.

The nmr spectrum of *trans*-2-carbomethoxybicyclo[3.1.0]-hexane shows typical high field absorption (τ 9.37–10.00) for cyclopropane methylene of *trans*-2-bicyclo[3.1.0]hexyl derivatives, a complex splitting pattern for six protons in the region 7.74–8.92, a doublet centered at 7.23 (J = 7.8 cps), and a O-methyl singlet at 6.37. The doublet at τ 7.23 is characteristic of *trans*-2-bicyclo[3.1.0]hexyl derivatives. The infrared spectra show typical bicyclohexyl C—H stretching frequencies at 3000, 3030, and 3070, a cyclopropyl band at 1020, an ester C=O band at 1730, and the C—O band in the region 1140–1200 cm^{-1}.

Preparation of *cis*- and *trans*-3-Carbomethoxybicyclo[3.1.0]-hexane.—The imino ether hydrochloride was prepared by adding 160 mg of dry hydrogen chloride to a mixture of 494 mg of *cis*-3-cyanobicyclo[3.1.0]hexane and 150 mg of methanol in an ice bath. After the imino ether hydrochloride had solidified, about 6 hr, it was hydrolyzed to the methyl esters by adding an excess of water. The esters were extracted with ether and the ether layer was washed with several milliliters of 0.1 *N* NaOH and a few milliliters of distilled water and then dried over anhydrous magnesium sulfate. Evaporation of the ether yielded 400 mg of the bicyclic esters. Analysis using a 30-ft aluminum column of 25% Carbowax 1500 on Chromosorb P (flow rate *ca.* 60 ml/min, column temperature 155°) showed two peaks at 25.0 and 28.0 min in the ratio of 73:27 for *cis*- and *trans*-3-carbomethoxybicyclo-[3.1.0]hexane.

The nmr spectrum of the *trans*-3-carbomethoxybicyclo[3.1.0]-hexane shows high field absorption (τ 9.48–10.08) for cyclopropane methylene, a complex splitting pattern for two tertiary protons on a cyclopropane ring in the region 8.50–8.87, a complex splitting pattern for five protons in the region 7.35–8.40, and an O-methyl singlet at 6.42. The *cis*-3 proton undoubtedly contributes to the lower part of the τ 7.35–8.40 region. The infrared spectra show typical bicyclo[3.1.0]hexyl C—H stretching frequences (for *trans* isomers) at 3000, 3030, and 3070, an ester C=O at 1740, C—O band at 1100–1210, and a cyclopropyl absorption band at 1020 cm^{-1}.

The nmr spectrum of the *cis*-3-carbomethoxybicyclo[3.1.0]-hexane shows a high field absorption (τ 9.40–10.15) for cyclopropane methylene, a complex splitting pattern for the two tertiary protons on a cyclopropane ring in the region 8.57–8.95, an absorption band for the four C-2 and C-4 protons at 7.6–8.3, a complex splitting pattern for the *trans*-3 proton α to the carbomethoxy group in the region 6.88–7.40, and an O-methyl singlet at 6.41. The infrared spectral show typical bicyclo[3.1.0]hexyl C—H stretching frequencies (for *cis* isomers) at 3000, 3035, and 3070, an ester C=O band at 1745, a C—O band at 1160–1220, and a cyclopropyl band at 1030 cm^{-1}.

It is surprising that the methylene protons on the cyclopropyl ring have such unusually high absorption in the case of the *cis* isomer. The structural assignment was based on the enhancement of the 3030-cm^{-1} band in the infrared spectra for the *cis* isomer and the fact that the absorption for the C-3 proton (α to carbomethoxy) occurs at higher field in the *trans*-3 epimer. This is ascribed to the anisotropic shielding effect of the cyclopropane ring[36] which would be expected to shield the *cis*-C-3 proton. Shielding of the *cis*-C-3 proton has been noted for all 3-bicyclo[3.1.0]hexyl epimeric pairs studied so far.[37] Finally the nmr spectrum of the isomer assigned as *cis* is identical with the nmr spectrum published by Gassman and Zalar for *cis*-3 methyl ester, and, in addition, the infrared spectra of *cis*-3 and *trans*-3 methyl esters prepared by this procedure match those obtained in Professor Gassman's laboratory.[38]

Registry No.—I, 285-58-5; IVc, 5861-26-7; Vc, 1777-47-5; Vd, 15733-78-5; VIc, 15733-77-4; VId, 15733-75-2; VIIc, 15733-76-3; VIId, 15815-98-2.

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