Reactions of the Dibromocarbene Adducts of Bicyclo[2.2.1]heptene and Bicyclo[2.2.1]heptadiene

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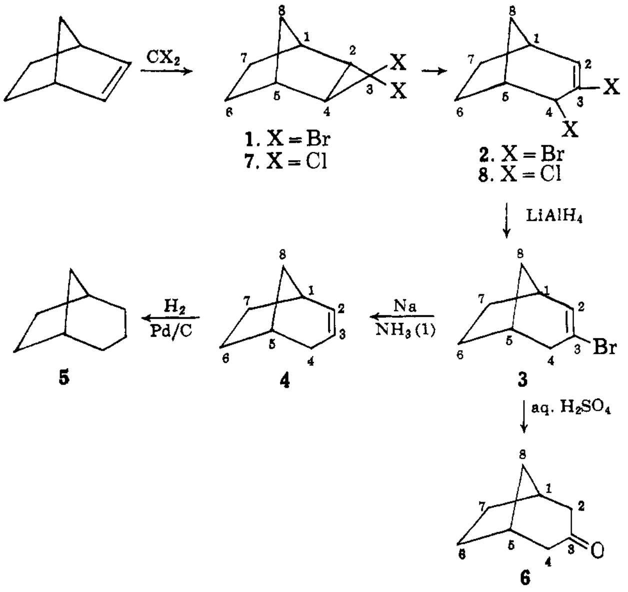
Received March 5, 1963

The addition of dichlorocarbene to bicyclo[2.2.1]heptene gives the expected *exo* dichlorocyclopropane adduct which readily rearranges to *exo*-3,4-dichlorobicyclo[3.2.1]octene-2. The dibromocyclopropane formed upon addition of dibromocarbene to bicyclo[2.2.1]heptene must rearrange directly, since the product isolated was shown to be *exo*-3,4-dibromobicyclo[3.2.1]octene-2. The latter has been converted to several derivatives of bicyclo[3.2.1]octane. Addition of dibromocarbene to bicycloheptadiene gives mainly *exo*-3,4-dibromobicyclo[3.2.1]octadiene along with smaller amounts of the *endo* epimer and *exo*-3,6-dibromotricyclo[3.2.1.0^{2,7}]octene-3. The former two compounds rearrange to the latter on standing. All three compounds are reduced by lithium aluminum hydride to 3-bromobicyclo[3.2.1]octadiene. This vinyl bromide, which can be further reduced to bicyclo[3.2.1]octadiene, upon treatment with aqueous sulfuric acid gave tricyclo[3.2.1.0^{2,7}]octanone-3 and 3-bromotricyclo[3.2.1.0^{2,7}]octene-3. Mechanistic interpretations of several of these transformations are presented.

The addition of dihalocarbenes to olefins, a reaction discovered by Doering and Hoffmann[2] in 1954, has provided an exceptionally useful synthesis of *gem*-dihalocyclopropanes. When acyclic olefins are employed the dihalides are relatively stable, but certain cyclic olefins have been found to undergo rearrangement to ring expanded products.[3] A particularly pertinent case is the facile rearrangement of 6,6-dibromobicyclo[3.1.0]hexane to 2,3-dibromocyclohexene.[3c] In the course of studies of the reaction of *gem*-dihalocyclopropanes with alkyllithium reagents,[4,5] we have prepared, or attempted to prepare, a variety of *gem*-dihalocyclopropanes with the intent of extending the self-insertion reactions[5] we have found in certain systems. In one phase of this work, dihalocarbenes were added to bicyclo[2.2.1]heptene and bicyclo[2.2.1]heptadiene and in both systems it was found that the *gem*-dihalocyclopropanes are either not isolable or are particularly prone to undergo rearrangement with ring expansion.[6] In this paper we discuss some of the chemistry of these products of ring expansion.

Bicyclo[2.2.1]heptene Adducts.—The reaction of bromoform with potassium *t*-butoxide in the presence of bicyclo[2.2.1]heptene in pentane at −15° gave a dibromide $C_8H_{10}Br_2$ which infrared and nuclear magnetic resonance (n.m.r.) spectra clearly showed was not the dibromocyclopropane **1** (or the *endo* isomer of **1**) but rather was the dibromoolefin **2**.[7] This assignment was confirmed by the reaction sequence summarized in Chart I. Reduction of dibromide **2** with lithium aluminum hydride gave a vinyl bromide **3** which was further reduced with sodium in ammonia to bicyclo[3.2.1]octene-2 (**4**). The identity of the latter was confirmed by hydrogenation to bicyclo[3.2.1]octane (**5**), a high-melting solid. The hydrolysis of vinyl bromide **3** with aqueous sulfuric acid has given moderate yields of bicyclo[3.2.1]octanone-3 (**6**). Since bicyclo[2.2.1]heptene is readily available and it should be possible to telescope the reactions leading to **6**, the route indicated in Chart I appears to be a potentially useful method for synthesizing this ketone.

CHART I



Inasmuch as it was found that, upon addition of dichlorocarbene to bicyclo[2.2.1]heptene, the initially formed *gem*-dichlorocyclopropane **7** could be isolated, although on heating it readily underwent rearrangement to the dichloroolefin **8**, the possibility arose that the corresponding dibromocyclopropane **1** had rearranged to **2** in the course of purification procedures. However, infrared analysis of the dibromocarbene adduct of norbornene isolated without allowing the temperature to

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(1) National Institutes of Health Predoctoral Fellow, 1960–1963.

(2) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(3)(a) W. E. Parham and H. E. Reiff, *ibid.*, **77**, 1177 (1955), and later papers by Parham; (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (c) S. J. Winstein and J. Sonnenberg, *J. Org. Chem.*, **27**, 748 (1962); (d) A. J. Birch and J. M. H. Groves, *Proc. Chem. Soc.*, 282 (1962).

(4) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); **27**, 4179 (1962).

(5) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

(6) (a) In the latter stages of this work we discovered (May, 1962) that R. C. DeSelms was engaged in a study of the dichlorocarbene adducts of these systems. Since this work will be discussed elsewhere, for the most part we will restrict our attention here to the dibromocarbene adducts. (b) After completion of the present studies, E. Bergman, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–12, 1962, p. 79Q, reported that addition of dichlorocarbene to bicyclo[2.2.1]heptene gave **8** (the stereochemistry was not indicated; apparently **7** was not isolated). (c) NOTE ADDED IN PROOF.—C. W. Jefford, *Proc. Chem. Soc.*, 64 (1963), in a brief communication has reported some of the reactions we have outlined in Chart I. L. Ghosez and P. Laroche, *ibid.*, 90 (1963), have reported the isolation of **8**.

(7) Complete spectral data obtained for the compounds encountered in this work are summarized in the experimental section. The n.m.r. assignments can be utilized most readily by referring to the numbered structural formulas appearing in the charts in the text. All n.m.r. chemical shifts, δ, are in parts per million at lower field from internal tetramethylsilane.

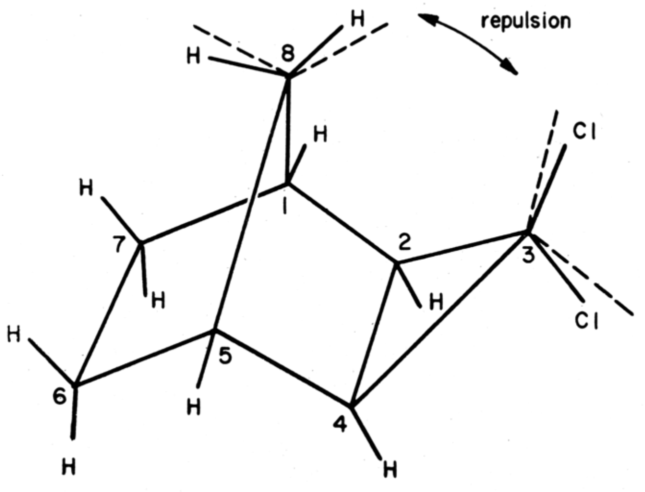

Fig. 1.—*exo*-3,3-Dichlorotricyclo[3.2.1.$0^{2,4}$] octane. Dashed lines represent "normal" bond angles; the deviations from normal bond angles indicate the possible effect of strain.

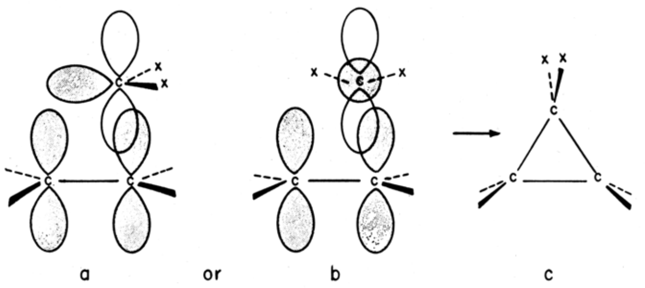

Fig. 2.—Possible transition states for the addition of a carbene to an olefin. Shaded areas represent filled orbitals.

exceed 25° at any time indicated that this material was essentially pure **2**.

The addition of dihalocarbenes to bicyclo[2.2.1]-heptene could give either *exo* or *endo* adducts. Since this hydrocarbon undergoes *exo* addition (presumably the least hindered approach) with other reagents,[8] the same course of addition appears to be reasonable here. Furthermore, the n.m.r. spectrum of **7** definitely supports the indicated *exo* structure. Molecular models (warped Dreiding models) indicate that in **7** there must be very strong repulsion between the *syn*-C-8 proton (*syn* to the CCl_2 group) and the *cis*-C-3 chlorine; these atoms occupy the "flagpole" positions of what amounts to a rigidly fused boat-form cyclohexane (Fig. 1). This repulsion must cause some bond angle deformation, in particular rocking the C-8 CH_2 group away from the chlorine atom. The proximity of the *cis*-C-3 chlorine to the *syn*-C-8 hydrogen is reflected in the n.m.r. spectrum: the *syn*-C-8 proton appears at 2.15 δ, deshielded by the *cis*-C-3 chlorine, whereas the *anti*-C-8 proton appears at 0.78 δ, shielded presumably by being somewhat shoved into the molecule.[9] Unquestionably, then, **7** must experience pronounced steric strain (which would be further amplified in the bromo compound **1**). Thus a valid question arises: why should *exo* addition of a dihalocarbene occur if such a strained product results?

Since the addition of a carbene to an olefin assuredly must be a highly exothermic process, the transition state must resemble the reactants fairly closely. If one assumes that a singlet carbene has essentially the structure proposed by Skell,[10] it seems probable that the bonding in the transition state stems from overlap of the vacant p-orbital of the carbene with the π-orbital of the olefin. Such overlap should be maximized if the carbene, CX_2 of Fig. 2, lies over the olefin in a plane essentially *parallel* to the plane of the double bond and probably closer to one than to the other of the olefinic carbon atoms. It is likely that the groups X of the carbene would be disposed fairly symmetrically over the olefin (Fig. 2a) unless the combined steric requirements of the carbene and the olefin necessitate that an energetically less favorable[11] twisted orientation be assumed (in the limit this becomes Fig. 2b). As the transition state passes on to the cyclopropane, the group CX_2 must rotate into a plane perpendicular to the plane originally defined by the double bond (Fig. 2c). In the case of addition to bicyclo[2.2.1]heptene, this motion would produce the large nonbonded interaction that is noted in Fig. 1, but the resultant repulsion (absent in the transition state) must be more than compensated by the tightening of the bonding.[12]

Both **2** and **8** appear to be isomer-free. Since these compounds have identical C-4,C-5 coupling (>CH—CHX—), $J = 2.8$ c.p.s., it seems fairly certain that both have the same stereochemistry at C-4. Molecular models indicate that the dihedral angle between the C-5 proton and an *exo*-C-4 proton (*endo* halogen) would be *ca.* 44° and that between the C-5 proton and an *endo*-C-4 proton (*exo* halogen) would be *ca.* 78°. A coupling constant of 2.8 c.p.s is compatible with the latter but not with the former, suggesting that in both **2** and **8** the C-4 halogen is *exo*.[13,14]

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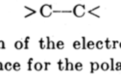
[8] (a) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954); (b) H. Kwart and W. B. Vosburgh, *ibid.*, **76**, 5400 (1954); (c) S. B. Soloway and H. Kwart, *J. Org. Chem.*, **25**, 327 (1960).

[9] (a) The 2.15- and 0.78-δ signals appear as doublets ($J = 11.2$ c.p.s., geminal coupling) of, apparently, pentuplets. This fine splitting must arise from vicinal coupling with the C-1 and C-5 protons and long range (1,3) coupling: *anti*-C-8 . . . C-2, C-4, and *syn*-C-8 . . . *endo*-C-6, -C-7, (*cf.* ref. 9b). Any distortion of bond angles in the sense indicated in Fig. 1 should increase both vicinal- and 1,3-coupling of the *syn*-C-8 proton relative to that for the *anti*-C-8 proton. In fact, the fine splitting is greater for the 2.15-δ (*syn*-C-8) than for the 0.78-δ signal. (b) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962). (c) In benzene solution all of the n.m.r. signals of **7** undergo pronounced shifts (0.3–0.4 p.p.m.) to higher field *except* that assigned to the *syn*-C-8 proton (0.07 p.p.m.), a finding we believe to be consistent with the assignment of the 2.15-δ signal to this proton.

[10] (a) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956) and other papers in this series; (b) also, see W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1960), and related papers.

[11] The twisted orientation precludes any overlap (not shown in Fig. 2) of the sp^2-orbital of the carbene with the p-orbital of the second olefinic carbon and would certainly increase the distance between, and thus the potential generated by, any developing charges of the following type.

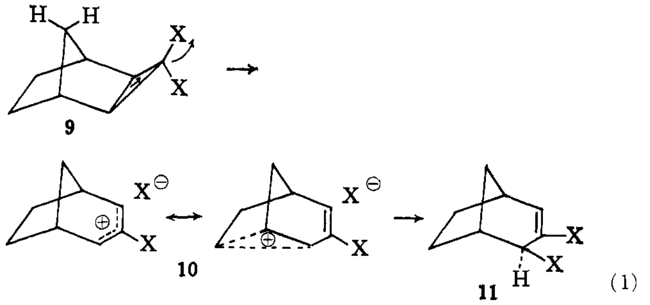


$$\begin{array}{c} {}^{\ominus}C< \\ {}^{\oplus}\quad | \\ >C—C< \end{array}$$

[12] (a) The demonstration of the electrophilic nature of carbenes (ref. 10) has provided ample evidence for the polar contribution to the transition state of the carbene–olefin reaction, but we interpret the previous representations of the transition state as implying that the geometry is essentially that of the resultant cyclopropane. (b) The recent report by G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962), that arylcarbenes and chlorocarbene react with certain unsymmetrical olefins to produce significantly higher amounts of *cis* than *trans* adducts does not argue for or against the transition state depicted in Fig. 2a. Unless the substituents on the olefin and/or the carbene are fairly bulky, little or no steric repulsion originating from the substituents would be expected if, as we believe, the carbene–olefin bonding has not proceeded far at the transition state.

[13] This argument is substantiated by the coupling constants obtained for the related *exo* and *endo* bromides obtained from bicyclo[2.2.1]heptadiene (discussed later).

The rearrangement of a dihalocyclopropane **9** (eq. 1, X = Cl, Br) to a dihaloolefin **11** must proceed through a transition state that resembles a tight ion pair **10** (that may actually be an intermediate). Due to severe crowding of the *syn*-C-8 hydrogen of **9** with the *cis*-C-3 halogen, migration of the latter may be sterically accelerated. Thus, the great tendency to rearrange shown by the dihalocyclopropanes **9** probably reflects relief of steric strain accompanied by some anchimeric assistance.[15] Whether the cation of **10** is regarded as a "nonclassical" ion, as shown, or as equilibrating "classical" ions, *exo* addition of X^- would be expected.[16,17]

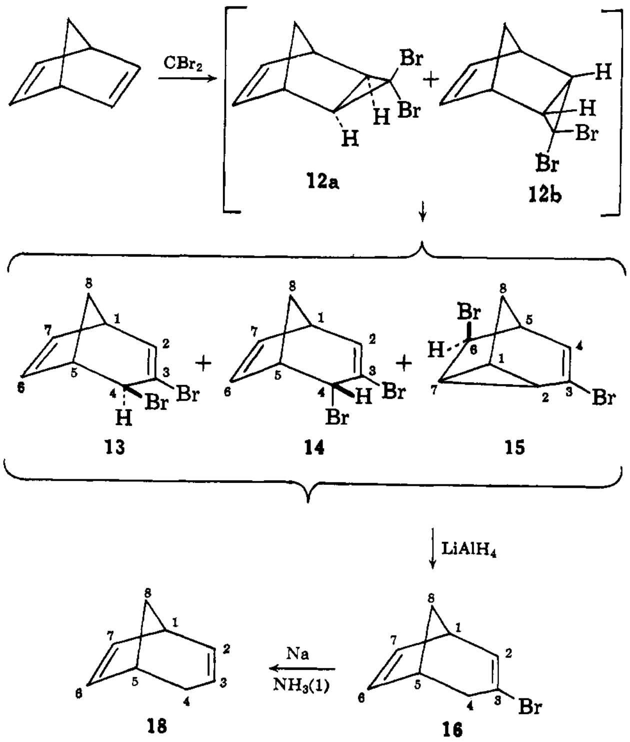


(1)

Bicyclo[2.2.1]heptadiene Adducts.—Addition of dibromocarbene to norbornadiene gave a dibromide fraction with a molecular composition of $C_8H_8Br_2$. Examination of this material by infrared and n.m.r. spectroscopy prior to distillation (the product was not heated above room temperature) indicated that it was not a dibromocyclopropane **12**, but consisted only of rearranged material.

The n.m.r. spectrum of the product clearly established that it consisted of a mixture of predominantly three compounds, **13**, **14**, and **15** in relative amounts 83:11:6. Analysis of the spectrum (aided by that subsequently obtained for **15**) showed that two of these compounds, **13** and **14**, had to be essentially identical and were the epimeric 3,4-dibromobicyclo[3.2.1]octa-2,6-dienes; the most significant spectral difference being due to the signal arising from the proton of the –CHBr– group. In **13**, this proton (C-4) appears as a doublet at 4.44 δ with J = 2.0 c.p.s. while in **14** it appears as a doublet at 4.89 δ with J = 5.0 c.p.s. Molecular models show that in the bicyclo[3.2.1]octadiene system the C-5, *endo*-C-4 dihedral angle must be *ca.* 76° whereas the C-5, *exo*-C-4 angle is *ca.* 45°. On the basis of the dependence of the coupling constant for vicinal protons on the dihedral angle,[14] then, the C-4 bromine must be *exo* in **13** (*endo* proton) and *endo* in **14** (*exo* proton). Furthermore the chemical shifts support this assignment. An *endo* proton at C-4 should experience some long range shielding by the C-6,C-7 double bond, an effect nonexistent for an *exo* proton. In fact, the *endo*-C-4 proton of **13** falls over 0.4 p.p.m. upfield from the corresponding *exo* proton of **14**.

CHART II



Heating or prolonged storage of the mixture of **13**, **14**, and **15** resulted in extensive rearrangement to **15**. Taken together, the n.m.r. and infrared spectra of **15** establish that it is a tricyclic vinyl bromide. The bromine at C-6 potentially could be either *exo*, as shown in Chart II, or *endo*. Subsequently, we have obtained the vinyl bromide **17** (Chart V) corresponding to **15** minus the bromine at C-6. In **17**, C-6 and C-8 are equivalent. However the geminal protons at these positions must experience quite different magnetic environments. The protons *syn* to the C-3,C-4 double bond should be shifted upfield due to long range shielding by the double bond. The spectrum of **17** shows two protons at 0.92 δ as a doublet with J = 11.8 c.p.s. (geminal coupling) which must be the *syn* protons (*syn* to the double bond). The *anti* protons cannot be uniquely distinguished, but must fall in the region of 1.4–1.8 δ. In the spectrum of **15**, the *syn*-C-8 proton appears essentially unchanged as a doublet at 1.04 δ (J = 12 c.p.s.) whereas the *anti*-C-8 proton has been shifted downfield by at least 0.5 p.p.m., appearing at 2.29 δ as an octet with apparent J values of 12, 4.6, and 2 c.p.s.,[18] a deshielding that could only arise with the C-6 bromine *exo* oriented (*anti* to the double bond). Finally, the fact that the proton of the –CHBr– group of **15** appears at 3.65 δ (*i.e.*, at relatively high field, compared to **13** and **14**) is also consistent with a *syn* orientation of the C-6 proton.

We assume that in the reaction of dibromocarbene with bicyclo[2.2.1]heptadiene the dibromocyclopropanes **12a**, **12b** were actually formed but underwent es-

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(14) For the dependence of vicinal coupling constants on dihedral angle, see (a) H. Conroy in R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., "Advances in Organic Chemistry: Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 311, and also (b) J. N. Shoolery, "NMR and EPR Spectroscopy," Pergamon Press, Oxford, 1960, p. 115.

(15) In addition to the strain mentioned before, rearrangement relieves the strain inherent in the bicyclo[2.2.1]heptane system and that in the cyclopropane ring.

(16) See H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961), and H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961), who have discussed the evidence for a nonclassical ion related to **10** in the solvolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl tosylate.

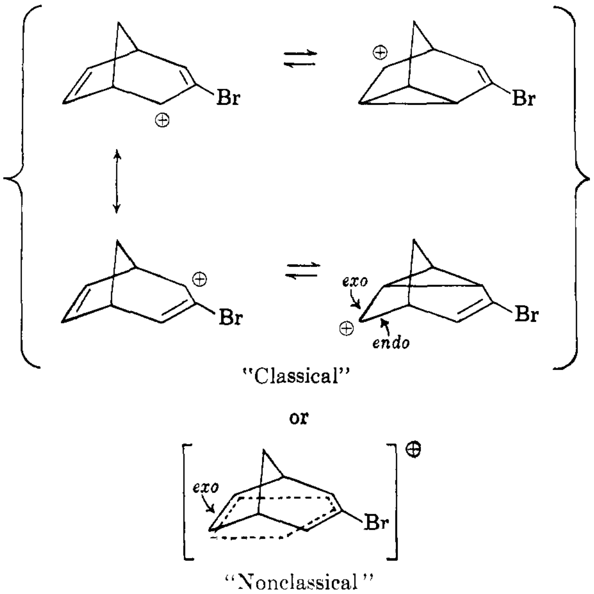
(17) R. C. DeSelms has informed us that he has obtained evidence which indicates that **8** has the *exo*-configuration.

(18) From models it appears that vicinal coupling to the C-1 and C-5 protons should be greater for the *anti*- than for the *syn*-C-6 and -C-8 protons of **15** and **17**, a prediction in agreement with the spectra.

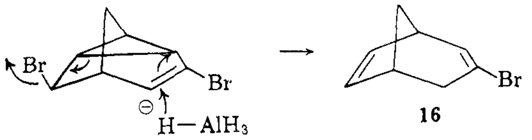
sentially immediate rearrangement to the mixture of **13**, **14**, and **15** initially obtained. This view gains some support from the observation that **13** isomerizes to **15** with little or no isomerization to **14**. The apparent stereospecificity of the similar rearrangement of the bicyclo[2.2.1]heptene adducts suggests that **13** may stem from the *exo* dibromocyclopropane **12a** and **14** from the *endo* isomer **12b**. If this postulate is correct it means that *exo* addition of dibromocarbene to bicyclo[2.2.1]-heptadiene is favored over *endo* addition by a factor of about eight.[19]

The isomerization of **13** to **15** presumably involves tight ion pairs. Depending upon one's viewpoint the cation could be considered to be either a "nonclassical" ion or equilibrating "classical" ions (Chart III). The present results offer no definitive choice but the observed stereospecificity of the rearrangement (no evidence has been found for the formation of the epimer of **15** although, admittedly, a small amount may have escaped detection) might logically be construed as evidence supporting a nonclassical ion hypothesis. Thus it is not apparent to us that there should be any striking preference for *exo* attack on the classical ions. On the other hand *exo* attack by bromide ion would seem to be required in the nonclassical picture. In any event, the bicyclo[3.2.1]octadienyl system looks like a fruitful area for investigations of potential bridged ions.

CHART III



Reduction of any of the mixtures of **13**, **14**, and **15** with lithium aluminum hydride gave good yields of an apparently isomer-free bicyclic vinyl bromide **16** along with varying amounts of recovered dibromides. With increasing reaction times the latter consisted of nearly pure **15**. The formation of **16** from **13** and **14** is to be expected and presumably involves either SN2 or SN2′ displacement of bromide by hydride. The failure of **15** to give the tricyclic bromide **17** might stem from a slow ionization to the ion(s) indicated in Chart III followed by hydride attack at C-2 or C-4, probably the most positive and least hindered centers. Alternatively, a direct hydride attack might occur as depicted in eq. 2.

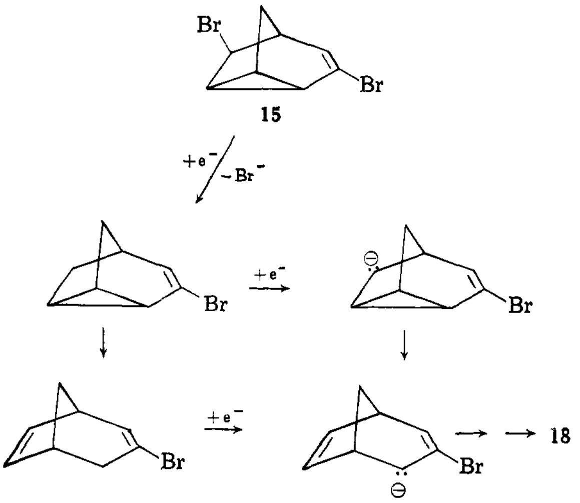


(2)

The structure of **16** was confirmed by reduction with sodium in liquid ammonia to bicyclo[3.2.1]octa-2,6-diene, (**18**), Chart II, which was characterized spectroscopically and by hydrogenation to bicyclo[3.2.1]octane (**5**). Over-all, conversion of bicyclo[2.2.1]heptadiene to **18** appears to be a sensibly useful route to the latter.

Reduction of the tricyclic bromide **15** with sodium in liquid ammonia also gave diene **18** as the only hydrocarbon detected. Several different pathways for this reduction can be envisioned, but it appears highly probable that the bromine attached to the saturated carbon (C-6) would be removed first. Rupture of the C-2,C-7 bond must then occur at either a one-electron (free radical) or two-electron (carbanion) stage of reduction (Chart IV). A strong indication that the former would occur comes from the nearly quantitative reduction of **15** to **16** with tributyltin hydride, a reagent that Kuivila[20] has recently shown appears to reduce halides by a free radical chain mechanism.

CHART IV



Hydrolysis of monobromide **16** with 80% aqueous sulfuric acid gave, in addition to recovered **16**, the isomeric tricyclic bromide **17**, a tricyclic ketone **19**, and small amounts of an unidentified carbonyl compound (about half of the **16** taken was converted to tars). The formation of **17** and **19** can be rationalized as shown in Chart V. Whether bicyclic ketone **20** was not formed or was destroyed under the reaction conditions is not known.[21]

The tricyclic structure assigned to **19** is required by the molecular formula (confirmed by mass spectrometry), the absence of olefinic protons (n.m.r.), the infrared absorption in the 3-μ region reminiscent of that of nortricyclene, and the far-ultraviolet absorption maxi-

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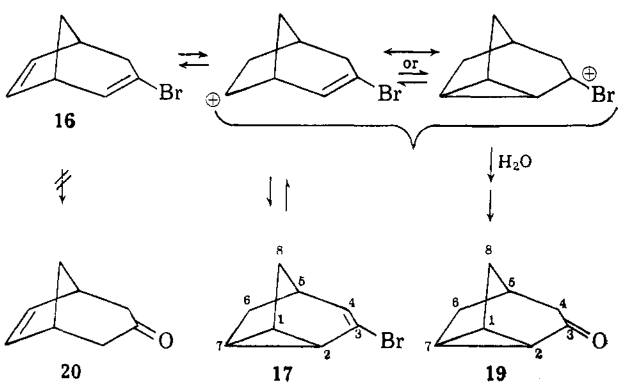
[19] (a) Elwood P. Blanchard, Jr., has informed us that application of the Simmons-Smith reaction (ref. 19b) to bicyclo[2.2.1]heptadiene gives both *exo* and *endo* adducts; (b) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

[20] H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3586 (1962).

[21] In view of the C=O stretching frequency (*ca.* 1745 cm.$^{-1}$) of the unidentified carbonyl compound it seems unlikely that it was **20**.

CHART V



mum in heptane at 192 mμ which is consistent with a "twisted" cyclopropyl ketone chromophore.

Experimental

General.—Infrared spectra were determined in carbon tetrachloride solution or as pure liquids employing Perkin-Elmer Model 21, 137, and 237 spectrophotometers. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. Mass spectra were determined with a Consolidated Electrodynamics Model 21-130 mass spectrometer with an inlet temperature of about 130° and an ionizing potential of 70 volts. N.m.r. spectra were recorded on about 25% solutions in carbon tetrachloride with tetramethylsilane as an internal standard employing a Varian A-60 spectrometer. Elemental analyses were performed by Dr. S. M. Nagy and associates at this institute. The gas chromatographs generally employed 0.5 × 200 cm. columns with thermal conductivity detectors (homemade) and 0.2 × 300 cm. columns with a flame ionization detector (Wilkens A-600) employing 80–100-mesh acid and base-washed Chromosorb. The following liquid phases (per cent by weight) were employed: Carbowax 20M, C20M (20%); SE-30 silicone rubber, SE30 (2%); silicone 710, S710 (20%). Internal standards were employed utilizing response factors where appropriate and determining areas by planimetering. Melting points are corrected and boiling points are not. All reactions employing organometallic reagents, active metals, alkoxides, or hydrides were conducted under a nitrogen atmosphere.

exo-**3,4-Dibromobicyclo[3.2.1]octene-2** (**2**).—A solution of 64.4 g. of freshly distilled bromoform in an equal volume of pentane was added dropwise with stirring to a mixture of 31.1 g. of potassium *t*-butoxide[2] and 19.1 g. of bicyclo[2.2.1]heptene in 15 ml. of pentane maintained at −15°. Stirring was continued for 30 min. after the addition was completed. Then, after the mixture had warmed to room temperature, water was added. The hydrocarbon layer was washed with water, dried, and short-path distilled at 80–90° (0.2–0.3 mm.) giving 13.4 g. of **2** (25% based on bicyclo[2.2.1]heptene) which was freed of minor impurities indicated by gas chromatography (S710, 170°) by low temperature recrystallization five times from pentane and redistillation; b.p. 80° (0.2 mm.); n^{25}D 1.5875. Infrared: 3030, 1616 cm.$^{-1}$ with many strong peaks in the fingerprint region. N.m.r.: 1.3–2.4 δ (6H) complex; 2.75 δ (2H) broad band (C-1, C-5); 4.46 δ (1H) doublet, J = 2.8 c.p.s. with ~1 c.p.s. fine splitting (C-4); 6.31 δ (1H) doublet, J = 7.0 c.p.s. with ~1 c.p.s. fine splitting (C-2).

Anal. Calcd. for $C_8H_{10}Br_2$: C, 36.1; H, 3.8; Br, 60.1. Found: C, 36.0, H, 3.6; Br 59.9.

The reaction was repeated employing the same work-up, but the volatile materials were removed from the product at low pressure without applied heat (rotary evaporator). The infrared spectrum of the residue was virtually identical to that of pure **2**.

exo-**3,3-Dichlorotricyclo[3.2.1.0^{2,4}]octane** (**7**).—The reaction of 407 g. of chloroform, 1.53 moles of potassium *t*-butoxide, and 100 g. of bicyclo[2.2.1]heptadiene was carried out as described for **2**. Distillation gave a recovery of 63 g. of bicyclo[2.2.1]-heptene and 11.2 g. of **7** (30% based on recovered bicyclo[2.2.1]-heptene) which infrared and n.m.r. analysis showed contained only a trace of **8**; b. p. 41° (0.1 mm.); n^{25}D 1.5223. Infrared: 3030 (doublet), 1305, 1200, 1135, 995, 905 cm.$^{-1}$. N.m.r.: 0.78 δ (1H) doublet, J = 11.2 c.p.s. of (apparently) pentuplets with ~1 c.p.s. separation (*anti*-C-8); 1.62 δ (2H) sharp band (C-2, C-4) superimposed on 1.0–1.7 δ (4H) complex; 2.15 (1H) doublet, J = 11.2 c.p.s. of (apparently) pentuplets with ~2 c.p.s. separation (*syn*-C-8); 2.63 δ (2H) sharp band (C-1 C-5). The mass spectrum established the molecular formula $C_8H_{10}Cl_2$ based on the isotopic molecular ions, mass numbers 176, 178, 180 in ratios 9:6:1.

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69. Found C, 54.74; H, 5.66.

exo-**3,4-Dichlorobicyclo[3.2.1]octene-2** (**8**).—A sample of was distilled slowly twice, causing rearrangement to **8** which gas chromatography indicated contained only trace impurities b.p. 79° (1.6 mm.); n^{31}D 1.5310. Infrared: 3040, 1632 cm.$^{-}$ with many strong bands in the fingerprint region. N.m.r. 1.15–2.3 δ (6H) complex; 2.68 δ (2H) broad band (C-1, C-5) 4.16 δ (1H) doublet, J = 2.8 c.p.s. with ~1 c.p.s. fine splitting (C-4); 6.10 δ (1H) doublet, J = 7.0 c.p.s. with ~1 c.p.s. fine splitting (C-2).

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05 Found: C, 54.30; H, 5.66; Cl, 40.32.

3-Bromobicyclo[3.2.1]octene-2 (**3**).—Dibromide **2** (2.35 g. was added dropwise to a stirred mixture of 1.10 g. of lithium aluminum hydride in 300 ml. of ether. After the addition wa completed the mixture was refluxed for 24 hr. The excess hydride was destroyed and the mixture was worked up in the usua way. Short-path distillation gave 1.03 g. (63%) of **3**; n^{25}D 1.5336. Infrared: 3020, 1633, and 665 cm.$^{-1}$. N.m.r.: 1.1–3.0 (10 H) complex; 6.12 δ (1H) broad doublet, J ~ 7 c.p.s. (C-2).

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93. Found: C 51.09; H, 6.08.

Reduction of **3** with excess sodium in liquid ammonia followed by the usual work-up gave bicyclo[3.2.1]octene-2-(**4**)[22] in *ca* 90% yield. Infrared: 3015, 2940, 1640 cm.$^{-1}$. N.m.r.: 1.1–2. δ (7H) complex; 2.25 δ (3H) broad band (C-1, C-4); ~5.24 (1H) broad doublet, J ~ 9 c.p.s. of unresolved multiplets (C-3) ~5.77 δ (1H) broad quartet, J_1 ~ 9 c.p.s., J_2 ~ 7 c.p.s. (C-2).

Anal. Calcd. for C_8H_{12}: C, 88.88; H, 11.12. Found: C 88.50; H, 11.42.

Microhydrogenation of **4** over palladium on charcoal in ethano proceeded with the uptake of 0.99 mole of hydrogen. Isolation of the product by gas chromatography gave a very volatile white solid, m.p. 133–135° (sealed capillary), with an infrared spectrum identical to that of bicyclo[3.2.1]octane[23] (**5**); lit. m.p. 133°[24] m.p. 139.5–141°.[25]

Bicyclo[3.2.1]octanone-3 (**6**).—Vinyl bromide **3** (0.72 g.) wa stirred for 6 hr. with 100 ml. of 80% aqueous sulfuric acid Then ice was added and the mixture was extracted with ethe (leaving some insoluble tar). The ether extract was concentrated and gas chromatographed (C20M, 200°) giving a 4% recovery of the starting material and a 38% yield of ketone **6**[26] m.p. 137–139°; infrared: 1708 cm.$^{-1}$; there are no clear maxima in the far-ultraviolet, but in heptane it appears that there may be a maximum just below the accessible range of the instrument λ_{end} mμ 186 (ε 715). N.m.r.: ~1.65 δ (6H) broad complex band 2.25 δ (4H) sharp band (C-2, C-4); 2.50 δ (2H) band (C-1, C-5)

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C 77.83; H, 10.07.

The 2,4-dinitrophenylhydrazone prepared in the usual way and repeatedly recrystallized from ethanol had m.p. 165–166.2°

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30. Found C, 55.54; H, 5.44.

When 13.7 mg. of **3** was shaken with 2 ml. of concentrated sulfuric acid at 0° for 15 min. followed by hydrolysis with ice and extraction with ether, gas chromatographic analysis (C20M 200°, naphthalene internal standard) indicated a 64% yield of and a 2% recovery of **3**.

Addition of Dibromocarbene to Bicyclo[2.2.1]heptadiene.—Bromoform (118 g.) was added dropwise to a stirred pentan slurry of 42.5 g. of bicyclo[2.2.1]heptadiene and 0.385 mole o potassium *t*-butoxide at −15°. The mixture was then warme to room temperature, hydrolyzed, and extracted with pentane

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[22] A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegte *Tetrahedron*, **9**, 230 (1960).

[23] American Petroleum Institute Infrared Spectrum no. 2037.

[24] J. W. Barrett and R. P. Linstead, *J. Am. Chem. Soc.*, **58**, 611 (1936

[25] W. von E. Doering and M. Tarber, *ibid.*, **71**, 1514 (1949).

[26] K. Alder and R. Reubke, *Ber.*, **91**, 1525 (1958), reported isolation o a mixture of **6** and bicyclo[2.2.2]octanone.

Volatile materials were removed at reduced pressures (ultimately 0.05 mm.) without heating. Infrared and n.m.r. spectra of the residue established that the subsequent distillation did not materially change the ratios of **13**, **14**, and **15**. Rapid distillation gave 35.6 g. (35% based on potassium *t*-butoxide) of a colorless liquid, b.p. 77° (0.05 mm.), $n^{25}\text{D}$ 1.5964, which gave an immediate precipitate with silver nitrate in aqueous alcohol. This material underwent extensive decomposition on the gas chromatography columns at hand. Infrared: 3040, 1608, 738, 690 cm.$^{-1}$. N.m.r.: 1.04 δ weak doublet, $J = 12$ c.p.s. (**15**, *syn*-C-8); 1.6–2.6 δ complex; ~2.9 δ multiplet (**13** and **14**, probably C-5); 3.30 δ multiplet (**13** and **14**, probably C-1); 3.65 δ weak singlet (**15**, C-6); 4.44 δ doublet, $J = 2.0$ c.p.s. (**13**, C-4); 4.89 δ weak doublet, $J = 5.0$ c.p.s. (**14**, C-4); 5.86 δ quartet, $J_1 = 5.5$ c.p.s., $J_2 = 3$ c.p.s. (**13**, C-6) superimposed on weaker signals (the 5.97 δ quartet of **15** and, by differences, a signal due to **14**); 6.37 δ weak quartet, $J_1 = 5.5$ c.p.s., $J_2 = 3$ c.p.s. (**14**, C-7); 6.5–6.7 δ a complex pattern which appears to arise from overlapping of a perturbed doublet at ~6.57 δ (**13**, C-2) with a quartet at 6.62 δ, $J_1 = 5.5$ c.p.s., $J_2 = 3$ c.p.s. (**13**, C-7), and, by differences, a signal due to **14**. The integrals from the 3.65-δ, 4.44-δ, and 4.89-δ signals give the ratios **13**:**14**:**15** = 83:11:6. The area obtained from the signals in the 1.5–3.0-δ region appeared to be a little too high for a mixture of only **13**, **14**, and **15** indicating that one or more isomers with no -CHBr- groups and no olefinic protons might be present in small amounts.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.59; H, 3.21.

In a second preparation employing 1.1 moles of bromoform, 1.2 moles of potassium *t*-butoxide, and 1.46 moles of bicyclo[2.2.1]heptadiene, after two slow distillations, a total of 96 g. (33% based on bromoform) of a dibromide fraction was obtained b.p. 90° (0.1 mm.). The n.m.r. spectrum was similar to that above and indicated ratios of **13**, **14**, and **15** to be 62:14:24. Again the integral of the signals in the 1.5–3-δ region was somewhat higher than would be expected for these three compounds alone.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.42; H, 3.21.

Upon standing for six weeks at *ca.* −10°, the composition changed to **13**:**14**:**15** = 20:10:70.

Reduction of $C_8H_8Br_2$ Mixtures with Lithium Aluminum Hydride.—A mixture (32.9 g.) of **13**, **14**, and **15** (62:14:24) was added dropwise to a stirred mixture of 4.7 g. of lithium aluminum hydride in 1.5 l. of refluxing ether. After the addition was completed, refluxing was continued for 8 hr. then the mixture was worked up in the usual way. Distillation gave 17.6 g. (76%) of 3-bromobicyclo[3.2.1]octadiene (**16**); b.p. 63° (5 mm.); $n^{25}\text{D}$ 1.5453; no reaction with alcoholic silver nitrate. Infrared: 3040, 1625, 725, 675 cm.$^{-1}$. N.m.r.: 1.5–2.9 δ (6H) complex; 5.64 δ (1H) quartet, $J_1 \sim 5.6$ c.p.s., $J_2 \sim 2.8$ c.p.s. (C-6); 6.10 δ (1H) quartet, $J_1 \sim 5.6$ c.p.s., $J_2 \sim 2.6$ c.p.s. (C-7) superimposed on ~6.17 δ broad doublet, $J \sim 7$ c.p.s (C-2). The mass spectrum established the molecular formula C_8H_9Br based on equally intense peaks due to isotopic molecular ions at mass numbers 184 and 186.

Anal. Calcd. for C_8H_9Br: C, 51.92; H, 4.90. Found: C, 51.46; H, 4.94.

From the distillation above 1.4 g. (4%) of a higher boiling fraction, b.p. 74–75° (0.3 mm.), was obtained which n.m.r. analysis showed was mainly **14** and **15**.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.67; H, 3.28.

Reduction of 15.6 g. of **13**, **14**, and **15** (20:10:70) with 2.6 g. lithium aluminum hydride in 300 ml. of ether for 37 hr. gave 6.6 g. (61%) of **16** and 4.2 g. (27%) of a higher boiling fraction, b.p. 65° (0.1 mm.) which n.m.r. analysis showed was nearly pure **15**. Infrared: 3060, 1620, 1190, 1165, 1020, 970 cm.$^{-1}$. N.m.r.: 1.04 δ (1H) doublet, $J = 12$ c.p.s. (*syn*-C-8); 2.29 δ (1H) octet, $J_1 = 12$ c.p.s., $J_2 = 4.6$ c.p.s., $J_3 = 2$ c.p.s. (*anti*-C-8) included in a complex pattern from 1.6–2.5 δ; ~2.73 (1H) broad quartet, $J_1 \sim 7.7$ c.p.s., $J_2 \sim 4.6$ c.p.s. (C-5); 3.65 δ (1H) singlet (C-6); 5.97 δ (1H) sharp quartet, $J_1 = 7.7$ c.p.s., $J_2 = 2.5$ c.p.s. (C-4). Weak signals at 2.97 δ triplet, 4.13 δ quartet, and 5.67 δ singlet indicated the presence of minor amounts of presumably isomeric impurities.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.80; H, 3.27.

Addition of 0.56 g. of this sample of (predominantly) **15** to 1 g. of sodium in liquid ammonia gave a 43% yield (isolated by gas chromatography) of **18** (below), identified by comparison of retention times and infrared spectra. Reversal of this procedure, *i.e.*, addition of sodium to a solution of **15** in liquid ammonia, afforded only traces of hydrocarbons.

A solution of 15 mg. of **15** (above) in 68 mg. of *n*-tributyl tin hydride was heated at *ca.* 100° under nitrogen in a sealed glass tube for 20 hr. Ammonia was then passed through the solution until no further precipitate formed.

Then the mixture was extracted with pentane, naphthalene was added as an internal standard and the solution was analyzed by gas chromatography (C20M, 213°), indicating a 98% yield of a compound shown to be **16** and 0.5% of **18**.

Bicyclo[3.2.1]octadiene (**18**).—Reduction of **16** with excess sodium in liquid ammonia gave **18** in about 85% yield; b.p. 50° (120 mm.); $n^{24}\text{D}$ 1.4918. Infrared: 3040, 3020, 1625, 1587, 725, 675 cm.$^{1-}$. N.m.r.: 1.5–2.7 δ (6H) complex; 5.03 δ (1H) very broad perturbed doublet (C-3); 5.53 δ (1H) sharp quartet, $J_1 \sim 5.3$ c.p.s., $J_2 \sim 2.8$ c.p.s. (C-6); 5.86 δ (1H) very broad perturbed doublet (C-2); 6.07 δ (1H) sharp quartet, $J_1 \sim 5.3$ c.p.s., $J_2 \sim 2.8$ c.p.s. (C-7).

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.71; H, 9.43.

Microhydrogenation of **18** over 30% palladium on charcoal in ethanol resulted in the absorption of 99% of two equivalents of hydrogen giving bicyclo[3.2.1]octane, m.p. 133.5–135° (sealed capillary), lit. m.p. 133°,[24] m.p. 139.5–141°,[25] which had an infrared spectrum identical with the published[23] spectrum of bicyclo[3.2.1]octane.

Hydrolysis of 16.—Vinyl bromide **10** (2 g.) was shaken with 80% sulfuric acid (300 ml.) at 0° for 1.5 min. and then the mixture was hydrolyzed with ice. The hydrolysate was partially neutralized with sodium bicarbonate and then was extracted with ether. The extract was washed with bicarbonate solution, dried and analyzed by gas chromatography C20M, 200°, with naphthalene as an internal standard, collecting the following products: **16** (21%) $t_R = 0.52$, **17** (17%) $t_R = 0.65$, an unidentified ketone (0.4%; assuming a molecular weight of 122; infrared, 1745 cm.$^{-1}$) $t_R = 0.72$, and **19** (22%) $t_R = 1.28$.[27] In a similar experiment employing a reaction time of 5 min. the per cents were **16** (5%), **17** (12%), unidentified ketone (2.7%), and **19** (25%). Physical constants for **17** and **19** are given subsequently.

3-Bromotricyclo[3.2.1.0^{2,7}]octene-3 (**17**).—**17** has $n^{25}\text{D}$ 1.5471. Infrared: 3040, 1612, 850, 833, 695 cm.$^{-1}$. N.m.r.: 0.92 δ (2H) doublet, $J = 11.8$ c.p.s. (*syn*-C-6, -C-8); 1.4–1.8 δ (4H) complex; 1.93 δ (1H) multiplet (C-2); 2.55 δ (1H) multiplet (C-5); 5.97 δ (1H) sharp quartet, $J_1 = 7.3$ c.p.s., $J_2 = 2.9$ c.p.s. (C-4).

Anal. Calcd. for C_8H_9Br: C, 51.92; H, 4.90. Found: C, 51.68; H, 4.89.

Bromide **17** (10 mg.) was shaken with 2 ml. of 80% sulfuric acid for 5 min.; then the mixture was hydrolyzed and processed as before. Analysis by gas chromatography (C20M, 212°, with naphthalene as an internal standard) established the following yields: **16** (3%), **17** (56%), and **19** (21%).

Tricyclo[3.2.1.0^{2,7}]octanone-3 (**19**).—This compound appeared to be free of impurities (gas chromatography) but did not solidify upon standing. It is very hygroscopic; $n^{25}\text{D}$ 1.5074. Infrared: 3030, 2920, 2860, 1710, 1450, 1410, 1340, 1325, 860 cm.$^{-1}$. Ultraviolet (heptane): λ_{max} 192 mμ (ϵ 7090). N.m.r.: 1.35–2.3 δ complex, no signals at lower field. The mass spectrum showed a molecular ion peak at mass number 122 in agreement with the indicated molecular formula.

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 79.20, H, 8.41.

The 2,4-dinitrophenylhydrazone of **19** melted at 210–211° (recrystallized from alcohol).

Anal. Calcd. for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67. Found: C, 55.59; H, 4.69.

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(27) Retention times relative to naphthalene = 1.00, C20M, 218°; **6** has $t_R = 0.61$.