complex molecules whose rates of reaction have been discussed above.

Finally, it should be emphasized that our proposal that charge separation in the transition state is not a factor in controlling reaction rates for hydrogen abstractions by radicals is not merely a semantic alternative. The "polar effect" argument would predict $\rho \simeq 0$ for abstractions from substituted toluenes by the methyl radical; for abstractions by the *tert*-butyl radical ρ should be zero or positive. On the other hand, we predict $\rho \simeq -0.6$ for abstractions by methyl and as high as $\rho \simeq -1.4$ for abstractions by *tert*-butyl, near 50° on the basis of Figure 1.[52] Some data are available for the reaction of methyl radicals with substituted toluenes. From gas-phase measurements with toluene, *m*-xylene, and *p*-xylene between 100 and 250°,[53] we can extrapolate a very rough estimate of $\rho = -0.76 \pm 0.20$ at 60°. The liquid phase data of Pryor[54] and of Szwarc[55] are also limited in the range of σ values examined. A linear regression analysis of Pryor's seven points gives a poor correlation coefficient and a better fit with σ^+: $\log (k/k_0) = -0.14\sigma^+ - 0.016$ ($r = 0.83$)[56] at 100°. Szwarc's data provide four points at 0° and they exhibit superior linearity and correlate better with σ: $\log (k/k_0) = -0.57\sigma - 0.003$ ($r = 0.992$). Although the latter value of ρ is in agreement with our prediction, additional data are clearly needed for abstractions by alkyl radicals from toluenes.

Experimental Section

Materials. Reagent grade commercial materials were used. They were checked for purity by gas chromatography, the toluene was washed with concentrated H_2SO_4, and all hydrocarbons were passed through 80–100 mesh activated alumina before use. *tert*-Butyl hypochlorite was prepared from the alcohol with a twofold excess of commercial sodium hypochlorite solution neutralized with HCl, at 0°; it was extracted in the appropriate solvent, washed with sodium bicarbonate and water, and dried over $MgSO_4$.

Reactions were run in ampoules as previously described.[14,57] Relative reactivities were determined by the method of excess hydrocarbon,[14,57] with chlorobenzene as an internal standard. Each hydrocarbon was approximately 1.1 *M* and the hypochlorite 0.8 *M*. The analyses were performed with 15 ft × 1/8 in. packed columns of diisodecyl phthalate. It was established that the phenethyl chlorides did not decompose under the analytical conditions used.

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[52] Figure 1 predicts BDE $\simeq$ 107 kcal/mol for the para C–H bond in nitrobenzene, a reasonable estimate compared to 112 ± 2 for benzene.

[53] W. A. Sanders and R. E. Rebbert, *J. Phys. Chem.*, **67**, 170 (1963).

[54] W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969).

[55] A. E. Eachus, J. A. Meyer, J. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 3646 (1968).

[56] A value of $r < 0.9$ is in the so-called region of noncorrelation: G. R. Wiley and S. I. Miller, *J. Org. Chem.*, **37**, 767 (1972).

[57] A. A. Zavitsas and S. Ehrenson, *J. Amer. Chem. Soc.*, **87**, 2841 (1965).

Tricyclo[3.2.1.0^{1,5}]octane. A 3,2,1-Propellane[1]

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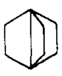
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received December 11, 1971*

Abstract: The synthesis of tricyclo[3.2.1.0^{1,5}]octane, the first hydrocarbon to possess carbons with "inverted" tetrahedral geometry, is described. It is unusual in its high reactivity toward oxygen as well as other chemical reagents. Despite its high strain it is quite unreactive thermally. Attempted syntheses of smaller ring propellanes are described. Whereas the dissolving metal reduction of 1,5-dibromobicyclo[3.2.1]octane leads to ring closure, the corresponding reaction with 1,4-dibromobicyclo[2.2.2]octane gives 1,4-dimethylenecyclohexane, and that of 1,4-dichloronorbornane gives norbornane. The reaction of the three dihalides with sodium–potassium alloy in cyclohexane gave only free-radical coupling products.

We have found it useful to consider several classes of compounds having bond angle distortion.[3] In the first class (I) we have compounds with a single constrained angle per carbon. Examples would be cyclopropane and cyclobutane. A second class (II) would contain compounds in which two angles are constrained at one or more carbons. Bicyclo[1.1.1]pentane and spiropentane would be examples. The third class (III) contains compounds in which three angles are constrained at one or more carbons. This class includes compounds **1**–**3**. Additional constraint may be realized in a compound such as **4**.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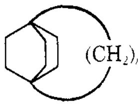

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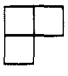
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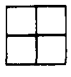
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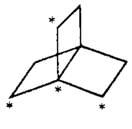
Whereas most of the strained compounds in classes I and II are easily considered in terms of the cyclopropane model proposed by Coulson and Moffitt,[4] the compounds in class III present some interesting aspects. In the case of **1**, which might better be drawn as



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[1] This investigation was supported by the U. S. Army Research Office.

[2] National Institutes of Health Predoctoral Fellow, 1968–1970. This has been taken from part of the Ph.D. Thesis of G. J. B., 1970.

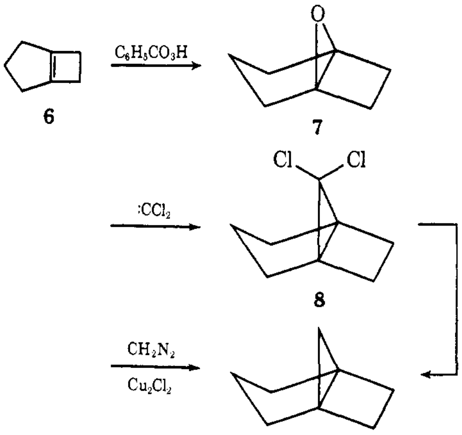
[3] K. B. Wiberg, J. E. Hiatt, and G. J. Burgmaier, *Tetrahedron Lett.*, 5855 (1968).

[4] C. A. Coulson and W. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

it can be seen that four starred atoms must lie close to a plane. The symmetry of the molecule would require that the orbitals from the bridgehead carbon be sp^2, leaving a p orbital to form the central bond.[5] Thus, the internal bond should be p–σ. Furthermore, no bonds would be found on one side of the plane formed by the starred atoms.

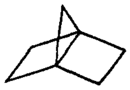
In the case of compound **2** (with a relatively short external bridge) and compounds **3** and **4**, a relatively unstrained (in terms of bond angles) geometry can be achieved only by significant contribution from 3d orbitals in the bonds formed by the bridgehead or central atoms. Thus, compounds of types **1–4** provide opportunities for learning more about the nature of bonding at carbon. We now wish to report on the properties of a compound related to **1**, and we shall later consider the other members of the group.

Our initial goal was an isomer of **1**, which might be expected to be less highly strained, tricyclo[3.2.1.0^{1,5}]octane (**5**).[6] In principal, it should be possible to prepare compounds of this class by an addition reaction on $\Delta^{1,5}$-bicyclo[3.2.0]heptane (**6**). The reaction of **6** with peroxy acids was found to give the oxa derivative **7**[3] and the addition of dichlorocarbene gave the 8,8-dichloro derivative **8**. The hydrocarbon itself could be prepared by the reduction of **8**, or by the cuprous chloride catalyzed reaction of **6** with diazomethane.[7]



The structures of **5** and **7** have been determined by electron diffraction[8] and the structure of **8** has been determined by X-ray diffraction.[9] In each case it was found that a plane passed through the three methylene carbons attached to the bridgehead intersected the central C–C bond. Thus, these compounds contain "inverted tetrahedron" at the bridgehead. The geometrical condition is not much different than that in **1**, leading to the conclusion that the central bond in these compounds also should be essentially a pure p–σ bond.

The heat of formation of **7** has been determined to be +6.4 kcal/mol.[10] Making use of the Franklin group equivalents,[11] the calculated value for **7** is −53.2 kcal/mol, leading to a strain energy of 60 kcal/mol. It is known that the strain energies of cyclopropane and ethylene oxide are the same,[12] and so the strain energy of **5** must have a similar value. This may be compared with the strain in one of its components, bicyclo[2.1.0]pentane (**9**) (53 kcal/mol).[13] The fusion of the five-membered ring onto **9** then raised the strain energy by only about 7 kcal/mol. These data permit one to estimate the strain energies of **1** and **10**. In the case of **10**, the fusion of a four-membered ring onto **9** should raise the strain energy by 23 kcal/mol (the strain in cyclobutane less one torsional interaction already present in **9**) plus an increment for the extra distortion. This must be at least 5 kcal/mol, and 10 might be a more reasonable estimate. Thus, a value of 86 kcal/mol would be estimated. Since cyclopropane and cyclobutane rings have similar strain energies, a corresponding value would be expected for **1**. With a strain energy comparable to a C–C bond dissociation energy, both **1** and **10** would be expected to be considerably less stable and more reactive than **5**.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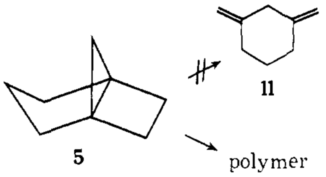
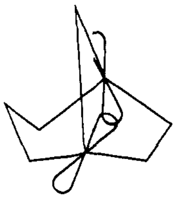
The hydrocarbon **5** is remarkably unreactive in thermolysis. In diphenyl ether solution, it had a half-life of about 20 hr at 195°, and gave a polymer as the product rather than 1,3-dimethylenecyclohexane. The polymer appeared from its nmr spectrum to be formed by bridgehead–bridgehead coupling of a series of molecules of **5**. The low thermal reactivity of **5** is not unreasonable. The only process which would lead to major strain relief is the cleavage of the central bond. However, because of the rigid structure, the bridgehead orbitals cannot get far from each other, and will therefore always have significant overlap.





As a result of this interaction, the cleavage of the outer cyclobutane ring bond to give **11** is symmetry forbidden. Similarly, the usual consequence of cleaving a cyclopropane C–C bond, hydrogen migration to give an olefin, is not possible since this would create a highly strained bridgehead double bond.

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(5) Bonding in compounds of this type has recently been discussed by W.-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 779 (1972), and by M. D. Newton and J. M. Schulman, *ibid.*, **94**, 773 (1972).

(6) The preparation of this compound was reported in preliminary form: K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Lett.*, 317 (1969). It has also been reported by Gassman, Topp, and Keller.[7]

(7) P. A. Gassman, A. Topp, and K. W. Keller, *ibid.*, 1093 (1969).

(8) Private communication from R. Bohn and S.-T. Li, University of Connecticut.

(9) K. B. Wiberg, G. J. Burgmaier, K.-W. Shen, S. J. LaPlaca, and W. C. Hamilton, *J. Amer. Chem. Soc.*, **94**, 3209 (1972).

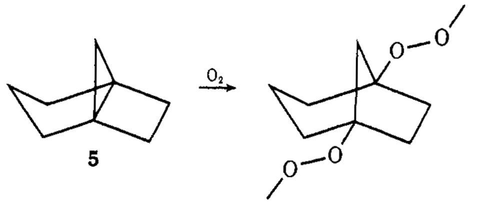
(10) K. B. Wiberg, G. J. Burgmaier, and E. C.Lupton, Jr., *ibid.*, **91**, 3372 (1969).

(11) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

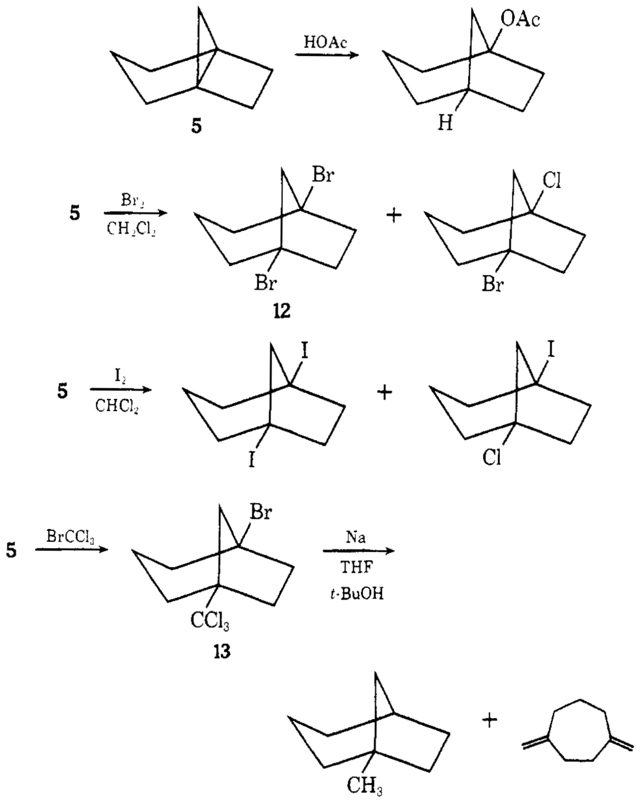
(12) A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, **61**, 71 (1965).

(13) R. B. Turner in "Kekule Symposium," Butterworths, London and Washington, D. C., 1959, p 67.

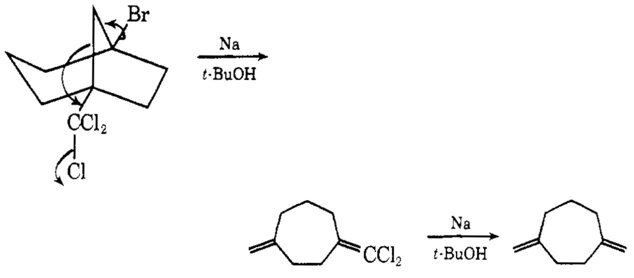
Although **5** is unreactive thermally, it is highly reactive toward chemical reagents. It reacts spontaneously with oxygen at room temperature to give a 1:1 copolymer having an average molecular weight of 1700. The structure is indicated by the mass spectrum which had fragments corresponding to 1:2 hydrocarbon–oxygen and 2:4 hydrocarbon–oxygen. The nmr spectrum also indicated the cleavage of the central bond (no cyclopropyl or olefinic protons).



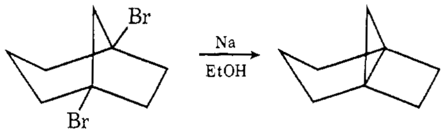
The reaction of **5** with acetic acid occurred very rapidly at room temperature and gave the bridgehead acetate. This may be contrasted with the reaction of bicyclo[2.1.0]pentane which proceeds relatively slowly at 50° in the presence of an acid catalyst.[14] The reaction of **5** with bromine in methylene chloride occurred instantaneously (at about −50°) and gave a mixture of 1,5-dibromocyclo[3.2.1]octane and 1-bromo-5-chlorobicyclo[3.2.1]octane. The reaction must be two-step in which the 5-bromobridgehead radical or cation is formed. This then either reacts with bromine or abstracts a chlorine from methylene chloride. Iodine reacts in a similar fashion.



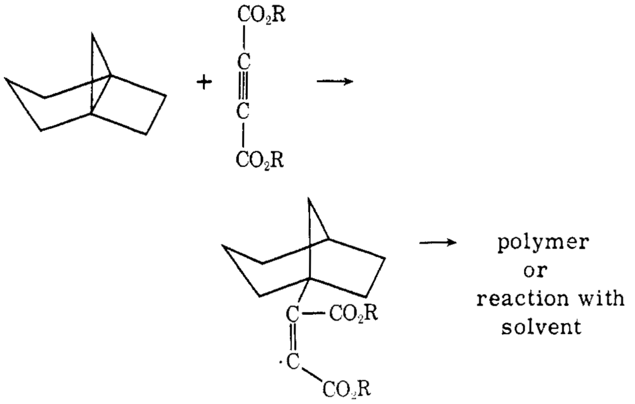
Bromotrichloromethane underwent a spontaneous addition to **5** at room temperature in the dark and in the absence of oxygen. This is presumably a chain reaction although the nature of the initiation step is not clear. Besides the major product **13** a 2% yield of the dibromide **12** also was obtained suggesting that the 5-bromobridgehead radical is formed in the initiation step and that it abstracts bromine from the bromotrichloromethane. The structure of **13** was shown by its reduction to 1-methylbicyclo[3.2.1]heptane and 1,4-dimethylenecycloheptane. The latter is formed *via* a fragmentation reaction, possibly at the trichloride stage.



The hydrocarbon **5** may be recovered from the dibromide by a dissolving metal reduction. Despite the favorable geometry for a Grob-type fragmentation reaction,[15] 1,3-dimethylenecyclohexane was not formed in significant amount.



The tricyclooctane **5** is reactive toward reagents such as acetylenedicarboxylic ester. In carbon tetrachloride, much of the product results from addition of the solvent across the central bond. In the absence of a reactive solvent, the product is polymeric. Presumably the first step is reaction at the central bond forming a diester in a fashion similar to bicyclo[2.1.0]pentane.[16] The diradical thus formed cannot easily close because of the expected high strain in the tricyclic product. Rather, reaction with solvent leading to a chain reaction or polymerization occurs.



It can be seen that **5** has the properties expected for a compound with a very weak central bond and relatively high strain. It appears comparable in its reactivity to the dehydroadamantane (**14**) reported by Pincock and Torupka,[17] and it is interesting to note that

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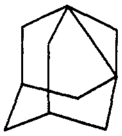
(14) R. T. LaLonde and L. S. Forney, *J. Amer. Chem. Soc.*, **85**, 3767 (1963).

(15) C. A. Grob and P. W. Schiess, *Angew. Chem.*, **79**, 1 (1967); C. A. Grob, *ibid.*, **81**, 543 (1969).

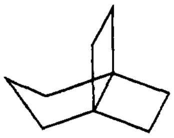
(16) P. G. Gassman and K. Mansfield, *Chem. Commun.*, 391 (1965).

(17) R. E. Pincock and E. J. Torupka, *J. Amer. Chem. Soc.*, **91**, 4593 (1969).

their hydrocarbon may be formed *via* a closure of a dibromide and that it also reacts spontaneously with oxygen as well as with acetic acid and halogens. The tricyclooctane and the dehydroadamantane appear to be the only saturated hydrocarbons in which a carbon–carbon bond is easily cleaved by oxygen and attests to their unusual bonding character.


14

Eaton and Nyi[18] have prepared the higher homologs of **5**, tricyclo[3.2.2.0^{1,5}]nonane (**15**),[19] and tricyclo[4.2.2.0^{1,6}]decane (**16**). These hydrocarbons appear to be stable toward oxygen. They react with bromine at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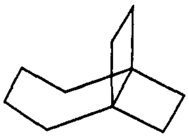
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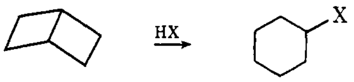
room temperature over the course of 10–20 min and thus are much less reactive than the tricyclooctane **5**.

It is interesting to note the relationship between bicyclo[2.1.0]pentane (**17**), bicyclo[2.2.0]hexane (**18**), and the tricyclic compounds. As far as reactivity toward electrophiles is concerned, cyclopropane, bicyclo[2.1.0]pentane, and tricyclo[3.2.1.0^{1,5}]octane form one series of increasing reactivity and cyclobutane, bicyclo[2.2.0]hexane, and tricyclo[3.2.2.0^{1,5}]nonane form another series of increasing reactivity. However, each member of the former series is considerably more reactive than the corresponding member of the latter series.

The difference is not due to thermodynamic factors. As an example, the strain energy (SE) of **17** is known to be 53 kcal/mol,[13] and the strain energy of **18** cannot be much less.[20] The strain relief on reaction would then be

17, SE = 53 kcal/mol SE = 6 kcal/mol

ΔSE = 47 kcal/mol



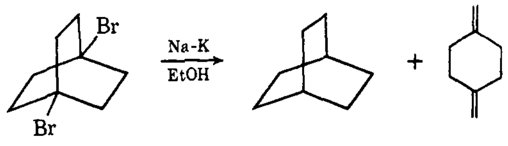
18, SE = 52 kcal/mol SE = 0 kcal/mol

ΔSE = 52 kcal/mol

Thus, **18** has a thermochemical advantage over **17**. Despite this, **18** is much less reactive than **17** in electrophilic addition reactions.

The difference in reactivity probably results from the difference in bonding between cyclopropane and cyclobutane. The difference in bonding appears to persist throughout the two groups of compounds.

The compounds which would be of greater interest are tricyclo[2.2.2.0^{1,4}]octane (**1**) and tricyclo[2.2.1.0^{1,4}]heptane (**10**) because of their anticipated higher strain. One possible approach for the preparation of these compounds is the intramolecular Wurtz reaction which was successful with the dibromide **12**, as well as with 1,3-dibromoadamantane.[17] Under the same conditions, the corresponding halides **19** and **20** failed to give the desired products. Rather, **19** gave a Grob fragmentation to 1,4-dimethylenecyclohexane and **20** gave only reduction. It is possible that the desired hydrocarbons



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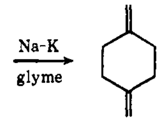

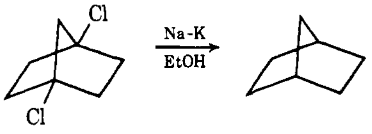

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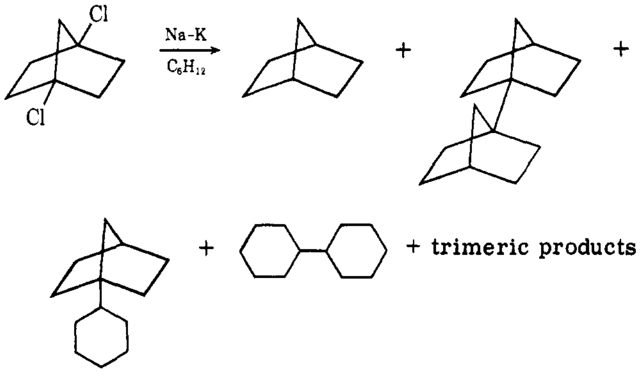
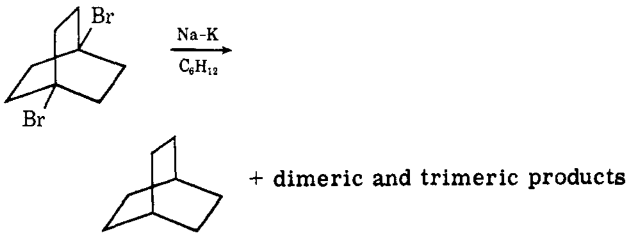
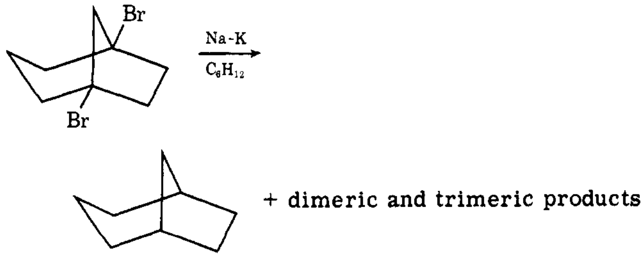
were formed as intermediates in the reactions, and reacted further to give the observed products. However, there is no evidence supporting such a view.

Another way in which to carry out the Wurtz reactions is to use an inert solvent such as cyclohexane. In this case, only free-radical coupling products were found. In the case of 1,4-dichloronorbornane, the products shown above were isolated and identified.







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[18] P. E. Eaton and K. Nyi, *J. Amer. Chem. Soc.*, **93**, 2787 (1971).

[19] A tetracyclic derivative of **15** has also been prepared: K. B. Wiberg, G. J. Burgmaier, and P. Warner, *ibid.*, **93**, 246 (1971).

[20] C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

The trimeric products appeared from their mass spectra to contain both three norbornyl rings and two norbornyl and one cyclohexyl ring. The presence of cyclohexyl rings was confirmed by carrying out the reaction in cyclohexane-d_1 and observing the mass spectra parent peaks shift upward by one mass unit.

In the other two cases, only the parent hydrocarbon was isolated. The structures of the dimers and trimers were deduced from the mass spectra and appeared to correspond to the products formed from 1,4-dichloronorbornane.

Experimental Section

8,8-Dichlorotricyclo[3.2.1.$0^{1,5}$]octane. Using a drybox, 4.3 g (80 mmol) of freshly prepared finely powdered sodium methoxide was transferred to a 100-ml flask equipped with a magnetic stirrer, gas inlet tube, and dropping funnel. A solution of 30 g (32 mmol) of $\Delta^{1,4}$-bicyclo[3.2.0]heptene in 50 ml of olefin-free pentane was added. The flask was cooled to ice temperature and flushed with nitrogen. Freshly distilled ethyl trichloroacetate (10.7 g, 56 mmol) was added dropwise over a 15-min period with stirring, and stirring was continued for an additional 8 hr at 0°.

After adding 20 ml of water, the pentane layer was separated, washed with saturated salt solution, and dried over potassium carbonate. The solvent was removed by careful distillation through a 35-cm packed column. The crude residue was cooled to $-80°$ and filtered giving 2.6 g (46%) of slightly yellow crystals. Purification could be effected by vacuum sublimation at 50° to give white crystals, mp 29–30°.

The nmr spectrum had a broad multiplet from τ 6.80 to 7.75. The mass spectrum indicated the presence of two chlorines in the molecular ion giving *m/e* 176, 178, and 180 with a relative ratio of 100:68:12 (calcd 100:65.3:10.6). A sample was used in an X-ray crystallographic study which confirmed the assigned structure. The dichloride is best stored in a freezer under an inert atmosphere.

Anal. Calcd for $C_8H_{10}Cl_2$: C, 54.3; H, 5.7; Cl, 40.1. Found: C, 54.1; H, 5.5; Cl, 40.4.

Tricyclo[3.2.1.$0^{1,5}$]octane. Method One. Into a flask equipped with a magnetic stirrer, addition funnel, and Dry Ice–acetone condenser was distilled (from sodium) 15 ml of liquid ammonia. The flask was flushed with nitrogen and cooled in a Dry Ice–acetone bath, and 0.75 g (32.5 mg-atom) of freshly cut clean sodium was added. A solution of 2.30 g (13 mmol) of 8,8-dichlorotricyclo-[3.2.1.$0^{1,5}$]octane in 10 ml of dry glyme (from lithium aluminum hydride at reduced pressure) was slowly added to the stirred reaction mixture. Stirring was continued for an additional 3.5 hr, after which time 1.75 g of ammonium chloride was added carefully. The reaction mixture was allowed to warm to 0° and the ammonia was allowed to evaporate. After adding 15 ml of water the organic layer was separated. The aqueous layer was washed with four 5-ml portions of pentane, and the combined organic layers were washed with three 15-ml portions of water. After drying over potassium carbonate, the pentane was removed by careful distillation through a 35-cm packed column. The volatile portion of the residue was transferred to a storage vessel using a vacuum line. Gas chromatography indicated only one product along with residual pentane. The yield ranged from 30 to 45%. An analytical sample was collected by gas chromatography. The product must be stored in an inert atmosphere.

The product had an nmr spectrum with an AB quartet (J = 6 Hz) centered at τ 9.32 (2 H) and a multiplet from 7.85 to 8.78 (10 H). The mass spectrum had a molecular ion with *m/e* 108.

Anal. Calcd for C_8H_{12}: C, 88.2; H, 11.2. Found: C, 88.6; 88.5; H, 11.1, 11.0.

Method Two. The diazomethane generator consisted of a 500-ml round-bottomed three-necked flask with smooth joints. A helium inlet tube extended from one side joint to the bottom of the flask. The large center joint was used for the introduction of *N*-methylnitrosourea (NMU), and the remaining joint held an outlet tube which was connected to a potassium hydroxide drying tower and then to a glass tube which extended to just above the stirring bar in the reaction flask. The reaction flask consisted of a 25-ml Erlenmeyer flask with an extended neck to which a side arm had been attached. The extended neck of the flask held the diazomethane inlet tube, and the side arm held an efficient Dry Ice condenser and drying tube.

The generator was charged with 100 ml of 50% potassium hydroxide solution, 50 ml of water, and 25 ml of decalin. The reaction vessel was charged with 12.4 g (0.132 mol) of $\Delta^{1,5}$-bicyclo-[3.2.0]heptane in a small amount of pentane. To the solution was added 300 mg of cuprous chloride, and the stirring was started. Approximately every 10 min, 1 g (10 mmol) of NMU was added to the generator while a slow helium flow was maintained through the system. After 30 g of NMU had been added, an additional 100 mg of cuprous chloride was introduced.

The reaction was followed by gas chromatography (12 ft × $^3/_8$ in. 20% Dow 710 on 50–60 Anaprep column at 60°). After the addition of 42 g of NMU, the reaction appeared to be 80% complete. The reaction solution was filtered and the precipitate was washed with pentane. The combined filtrate from two runs was distilled giving 29.5 g having bp 35° (20 mm). Gas chromatography indicated 17.0 g (58%) of product and 2.7 g (9%) of unreacted starting material. Preparative gas chromatography gave 13.5 g of pure material which was identical with that obtained using method one. It could be stored indefinitely in a freezer under vacuum.

Thermolysis of Tricyclo[3.2.1.$0^{1,5}$]octane. A mixture of 50 mg of diphenyl ether and 50 ml of tricyclo[3.2.1.$0^{1,5}$]octane was sealed under vacuum in an nmr tube. No change in nmr spectrum was noted when heated at temperatures up to 150°. After heating at 190° for 20 hr the ratio of cyclopropyl protons to the other methylene protons changed from 2:10 initially to 2:19, indicating that slightly less than half of the material had undergone reaction. No vinyl absorption appeared. The tube was opened and the only material with glc retention time less than diphenyl ether was starting material. Thus, the hydrocarbon has a half-life of about 20 hr at 190° and leads high molecular weight products.

Thermolysis of 8-Oxatricyclo[3.2.1.$0^{1,5}$]octane. A sample was sealed in an nmr tube and was heated in an oil bath. A slow reaction occurred at 150° leading to new nmr bands in the cyclopropyl region. The tube was then heated at 190° following the reaction by nmr. Only one product was formed, and this was identified as spiro[2.4]heptanone-4 by comparison with an authentic sample. The half-life at 190° was 4.5 hr.

Thermolysis of 8,8-Dichloro[3.2.1.$0^{1,5}$]octane. A sample of the dichloride was dissolved in diphenyl ether, added to an nmr tube, and sealed under vacuum. After 10 min at 125° the material had become very dark and quite viscous. Polymerization had apparently occurred, but the nature of the reaction is not known.

Reaction of Tricyclo[3.2.1.$0^{1,5}$]octane with Oxygen. To a 5-ml flask was added 100 mg of glc-pure hydrocarbon. After standing in air for 1 hr, the liquid had become cloudy, and after 2 days, it had turned into a white crystalline solid. The nmr spectrum showed a broad multiplet from τ 7.60 to 8.82 with a major peak at 8.42. There were no vinyl proton bands or bands corresponding to O–C–H protons. The solid had mp 158–163° dec. The average molecular weight was found to be 1700 by osmometry. Combustion analysis indicated an oxygen (O_2) to hydrocarbon ratio of 0.9:1.0.

The high-resolution mass spectrum of the polymer was not reproducible, being dependent on the probe temperature. The highest bands were at *m/e* 281.17412 corresponding to two hydrocarbon molecules, four oxygen atoms, and a hydrogen, and *m/e* 280.16547 derived from the other by the loss of hydrogen.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.5; H, 8.6; O, 22.8. Found: C, 69.7; H, 9.1; O, 21.3.

Reaction of Tricyclo[3.2.1.$0^{1,5}$]octane with Methyl Acetylenedicarboxylate. A mixture of 320 mg (2.3 mmol) of distilled and degassed methyl acetylenedicarboxylate and 245 mg (2.3 mmol) of the hydrocarbon was prepared using a vacuum line. As the flask warmed up to room temperature, an exothermic reaction occurred and the temperature increased to 70°. Volatile material was removed under vacuum giving 62 mg (20%) of unreacted hydrocarbon, and leaving 500 mg of a yellow viscous product. The average molecular weight was found to be 506 by osmometry (a 1:1 adduct would have mol wt 250). The nmr spectrum showed a vinyl singlet at τ 4.24 (1 H), methoxy protons at 6.2 and 6.3, a broad triplet from 5.9 to 6.5 (5 H) and a broad multiplet from 7.5 to 8.9 (7 H). When the reaction was carried out in carbon tetrachloride as the solvent, it was incorporated into the product.

Reaction of Tricyclo[3.2.1.$0^{1,5}$]octane with Acetic Acid. To 500 mg of glacial acetic acid was added 100 mg of freshly distilled hydrocarbon. Reaction occurred immediately with considerable warming. Gas chromatography indicated a single product which was identified as 1-acetoxybicyclo[3.2.1]octane by comparison with an authentic sample.

Reaction of Tricyclo[3.2.1.$0^{1,5}$]octane with Bromotrichloromethane. Using a vacuum line, 20 ml of bromotrichloromethane and 235 mg of pure hydrocarbon were transferred to a 50-ml flask. The flask was allowed to warm to room temperature in the absence of light. An exothermic reaction occurred at about room temperature. After the flask had cooled, the volatile material was removed by bulb-to-bulb distillation leaving 600 mg (90%) of white crystalline product. It could be sublimed at 70–80° (0.1 mm) and it could be recrystallized from pentane. Gas chromatography (12 ft × $^3/_8$ in. 20% Dow 710 on 50–60 Anaprep column at 220°) indicated the crude product to be about 90% pure. One impurity (2%) had the same retention time as 1,5-dibromobicyclo[3.2.1]octane (see below). It was collected by glc and identified by comparison with an authentic sample.

The purified product had mp 73.0–73.5°. The analysis indicated a 1:1 adduct of the hydrocarbon with bromotrichloromethane. The highest *m/e* peak in the mass spectrum corresponded to the loss of a bromine atom from the nonobservable molecular ion.

Anal. Calcd for $C_9H_{12}BrCl_3$: C, 35.3; H, 3.9; Br, 26.1; Cl, 34.7. Found: C, 35.5, 35.5; H, 3.7, 3.8; Br, 26.1; Cl, 34.7.

A mixture of 9.6 g of *tert*-butyl alcohol, 6.1 g of sodium which had been cut into small pieces, and 500 mg of crude 1-bromo-5-trichloromethylbicyclo[3.2.1]octane was heated at reflux with stirring for 17 hr. The reaction mixture was cooled to ice temperature and 20 ml of methanol was added to destroy excess sodium. Ice chips and water were then added. The layers were separated and the aqueous layer was extracted with three 20-ml portions of ether. The combined organic layers were washed with water and dried over sodium sulfate. Most of the solvent was removed by distillation through a 30-cm Vigreux column. The residue was analyzed by gas chromatography which indicated two products.

The product with the shorter retention time (25%) appeared to be 1-methylbicyclo[3.2.1]octane. It had a parent peak in the mass spectrum at *m/e* 124 with a typical hydrocarbon fragmentation pattern. The nmr spectrum consisted of τ 9.01 (3 H, CH_3 s), 8.00–8.93 (12 H, unresolved m), and 7.83 (1 H, br s). The nmr pattern was quite similar to that of other bicyclo[3.2.1]octane derivatives.

Anal. Calcd for C_9H_{16}: C, 87.0; H, 13.0. Found: C, 86.7, 86.9; H, 13.1, 12.9.

The product with a longer retention time (30%) was identified as 1,4-dimethylenecycloheptane. It had a parent peak at *m/e* 122. The nmr spectrum had bands at τ 8.09–8.60 (2 H symmetric series of at least ten peaks centered at 8.34), 7.58–7.92 (4 H, m), 7.73 (4 H, s), and 5.53 (4 H, s). The ir spectrum had double bond absorption at 1640 cm^{-1}, and had a band at 890 cm^{-1} which is typical for a terminal methylene.

Anal. Calcd for C_9H_{14}: C, 88.5; H, 11.6. Found: C, 88.2, 88.5; H, 11.6, 11.4.

1,5-Dibromobicyclo[3.2.1]octane. A solution of 1.46 g (9.3 mmol) of bromine in 5 ml of methylene bromide containing 100 mg of potassium carbonate was cooled to −50°. To this was added 100 mg (0.9 mmol) of freshly distilled tricyclo[3.2.1.0^{1,5}]octane in 5 ml of methylene bromide over the course of 10 min at −50°. The solution was allowed to warm to room temperature. Distillation of the solvent followed by sublimation of the residue at 60° and 0.1 mm gave 150 mg of white crystalline dibromide. Gas chromatography indicated the material to be pure. An analytical sample was prepared by recrystallization from pentane, mp 59–60°.

The mass spectrum gave molecular ions with *m/e* 266, 268, and 270 having relative ratios corresponding to a dibromide. The nmr spectrum consisted of a broad multiplet from τ 7.00 to 8.45. The absence of lower field bands indicates that the bromines are on tertiary carbons. Further evidence for the structure comes from the observation that the dibromide may be converted back to the tricyclooctane (see below).

Anal. Calcd for $C_8H_{12}Br_2$: C, 35.9; H, 4.5; Br, 59.6. Found: C, 36.0; H, 4.6; Br, 59.9.

When the reaction was carried out in methylene chloride as the solvent, approximately half of the product was the corresponding 1-chloro-5-bromo derivative as shown by its parent peak in the mass spectrum and analysis. The reaction with iodine proceeded in the same fashion giving both the diiodide and the chloroiodide.

Reaction of 1,4-Dichlorobicyclo[2.2.1]heptane with Sodium–Potassium Alloy. A mixture of 1.25 g of freshly prepared sodium–potassium alloy (20:80), 5 ml of dry cyclohexane, and 500 mg of 1,4-dichlorobicyclo[2.2.1]heptane[21] was heated at reflux for 24 hr with stirring. The volatile material was transferred using a vacuum line, and was analyzed by vpc (12 ft × $^3/_8$ in. 20% Dow 710 at 140°). The first component was norbornane (36%), the second was 1-chlorobicyclo[2.2.1]heptane (2%), and the third was 1,4-dichlorobicyclo[2.2.1]heptane (4%).

The residue from the distillation was mixed with 5 ml of pentane and ethanol was added to destroy the metal. Analysis of the pentane solution indicated the presence of an additional 39 mg of norbornane giving a total yield of 55%. Higher molecular weight products also were present. The latter could be sublimed at 50–100° (0.1 mm). Analysis by vpc using the Dow-710 column at 200° indicated at least eight components. Two of the products were identified as 1,1′-bisnorbornyl and bicyclohexyl by comparison with authentic samples. One of the higher molecular weight products was present in large enough quantity to be isolated. The mass spectrum had a parent peak at *m/e* 272 along with strong P − 29 and P − 83 peaks, the latter corresponding to loss of cyclohexyl. This suggested that the compound was 1-cyclohexyl-4-(1-norbornyl)norbornane. The mass spectrum of the sublimate with the inlet at room temperature had parent peaks and fragmentation patterns expected for 1,1′-bisnorbornyl- and 1-cyclohexylnorbornane. If the inlet temperature was raised to 100°, parent peaks and fragmentation patterns expected for 1-cyclohexyl-4-(1-norbornyl)norbornane and 1-(1-norbornyl)-4-(1-norbornyl)-norbornane were also observed.

The reaction also was carried out using cyclohexane-d_1 as the solvent. The same products were formed as described above except that in the mass spectrum the parent peaks for those components which should have a cyclohexane ring were displaced upward by one mass unit.

Reaction of 1,4-Dibromobicyclo[2.2.2]octane with Sodium–Potassium Alloy. To a mixture of 1.5 g of freshly prepared sodium–potassium alloy and 5 ml of dry cyclohexane was added 0.5 g of 1,4-dibromobicyclo[2.2.2]octane.[22] The mixture was rapidly stirred at reflux for 21 hr. After cooling, the volatile materials were transferred to another flask on a vacuum line. Vpc analysis using cyclooctane as an internal standard indicated that 65% of bicyclo[2.2.2]octane had been formed. Only a trace of 1,4-dimethylenecyclohexane was found. It was independently shown that the diene was stable under the reaction conditions.

The nonvolatile residue was suspended in pentane and the metal was destroyed with ethanol at ice temperature. The pentane solution was separated and the solvent was removed leaving a residue which could be partially sublimed at 50–100° (0.1 mm). The mass spectrum, with the inlet at room temperature, had peaks at *m/e* 218, 192, and 166 which suggested the presence of 1,1′-bisbicyclo[2.2.2]octane, 1-cyclohexylbicyclo[2.2.0]octane, and bisbicyclohexyl. The nmr spectrum was consistent with this assignment. When the temperature of the inlet was raised to 100°, parent peaks and fragmentation patterns consistent with mixed trimers were obtained.

Reaction of 1,4-Dibromobicyclo[2.2.2]octane with Sodium in 1,2-Dimethoxyethane. A mixture of 100 mg of 1,4-dibromobicyclo[2.2.2]octane, 0.17 g of freshly cut sodium, and 2 ml of dry 1,2-dimethoxyethane was heated at reflux for 2 hr. The volatile material was transferred using a vacuum line and was analyzed by vpc ($^3/_8$ in. × 12 ft 20% Dow 710 at 130°). The major product was 1,4-dimethylenecyclohexane (50% yield) along with about 1% of bicyclo[2.2.2]octane.

Reaction of 1,5-Dibromobicyclo[3.2.1]octane with Sodium–Potassium Alloy. A mixture of 250 mg of 1,5-dibromobicyclo[3.2.1]-octane, 5 ml of cyclohexane, and 1 g of sodium–potassium alloy (20:80) was heated for 21 hr and worked up as described above. The volatile fraction contained only one compound other than solvent. It was identified as bicyclo[3.2.1]octane. Higher molecular weight products of the types described above were found in the nonvolatile fraction.

Reaction of 1,5-Dibromobicyclo[3.2.1]octane with Sodium in 1,2-Dimethoxyethane. A mixture of 100 mg of 1,5-dibromobicyclo[3.2.1]octane, 2 ml of dry dimethoxyethane, and 0.17 g of freshly cut sodium was stirred at room temperature for 4 hr, and worked up as described above. Gas chromatographic analysis of the volatile fraction indicated only tricyclo[3.2.1.0^{1,5}]octane (65%), identified by comparison with an authentic sample.

The reaction also was carried out using ethanol in cyclohexane instead of dimethoxyethane. In this case the volatile fraction contained 95% tricyclo[3.2.1.0^{1,5}]octane and 5% bicyclo[3.2.1]-octane.

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[21] C. F. Wilcox, Jr., and J. G. Zajacek, *J. Org. Chem.*, **29**, 2209 (1964).

[22] We thank Dr. K. Shen for providing us with a sample of 1,4-dibromobicyclo[2.2.2]octane. It was prepared by the brominative decarboxylation of bicyclo[2.2.2]octane-1,4-dicarboxylic acid.