

125 mg.) was irradiated⁶ (best results in dilute pentane solution under nitrogen) with ultraviolet light (Hanovia medium-pressure quartz mercury-vapor lamp, 200 w., Pyrex filter) for 10 min. at 20°. The solution was concentrated to 5 ml. and cooled to -70° for several hours. The precipitated solid (ca. 60 mg.) was⁷ largely methyl *p*-isopropenylbenzoate (IV), m.p. 51-52°. Further concentration of the mother liquors gave crystals of II, which, however, were more or less contaminated with IV. A more satisfactory separation was achieved by rapid chromatography at -5° of the mother liquors over basic alumina (pretreated with diethylamine) and elution with 8:1 pentane-methylene chloride. Crystallization then gave pure II, m.p. 32-32.5°. *Anal.* Calcd. for C₁₁H₁₂O₂: C, 74.99; H, 6.82; mol. wt., 176. Found: C, 75.08; H, 6.92; mol. wt. (Rast, in dicyclopentadiene), 163. The ultraviolet absorption spectrum showed $\lambda_{\text{max}}^{\text{MeOH}}$ 238, 279, and 286 m μ (sh); log ϵ 3.95, 3.41, 3.41, and 3.39, respectively. The infrared spectrum (liquid film) showed strong bands at 1725, 1296, 1216, 1097, and 758 cm.⁻¹.

The n.m.r. spectrum (60 Mc./sec.) of II in carbon tetrachloride solution showed the following features given in τ -values (assignments shown in parentheses): 8.38, 6 protons (*gem*-dimethyl); 6.13, 3 protons (ester methyl); 2.84, quartet, 1 proton (H₅, $J_{\text{ortho}} = 6.6$ and $J_{\text{para}} = 1.9$ c.p.s.); 2.3, quartet, 1 proton (H₂, $J_{\text{para}} = 1.9$ and $J_{\text{meta}} = 0.7$ c.p.s.); 2.14, doublet,⁸ 1 proton (H₄, $J_{\text{ortho}} = 6.6$ c.p.s.). The assignments of the aromatic bands are based on the known^{9a} low-field shift of aromatic protons *ortho* to a carbomethoxy group and on the magnitude of J_{ortho} . It is interesting that J_{para} is greater than J_{meta} , the reverse of the usual order, and that J_{ortho} is a little smaller than normal.^{9b} Such variations are not unexpected, as there could be considerable distortion of the benzene ring in II.

The aromatic character (*e.g.*, the ring current effect) of the benzene ring is not greatly disturbed in II, as shown by the normal chemical shifts of protons H₂, H₄, and H₅, as well as by the similarity of the ultraviolet absorption spectrum of II to that of methyl benzoate. The equivalence of the *gem*-dimethyl protons in the n.m.r. spectrum of II, even at -150° (CCl₂F₂ solution), is consistent with a planar or a rapidly inverting, and therefore presumably nearly planar, structure for the benzocyclopropene skeleton.¹⁰

(6) The preparation of cyclopropenes by irradiation of pyrazolenines has been reported recently: G. L. Closs and W. Böll, *Angew. Chem. Intern. Ed. Engl.*, **2**, 399 (1963); G. Ege, *Tetrahedron Letters*, 1667 (1963).

(7) The structure was deduced from the n.m.r. spectrum and was confirmed by comparison of the photolysis product with a sample prepared from methyl *p*-isopropenylbenzoate by bromination with *N*-bromosuccinimide followed by dehydrobromination. Hydrolysis of IV gave *p*-isopropenylbenzoic acid, m.p. 160°; G. B. Bachmann, C. L. Carson, and M. Robinson, *J. Am. Chem. Soc.*, **73**, 1964 (1951), report the same melting point for this acid.

(8) Both components of the doublet were rather broad and thus obscured the small coupling due to J_{meta} which should also be present. This could be due to a very small long-range coupling of, *e.g.*, 0.3 c.p.s. with the *gem*-dimethyl group.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," Pergamon Press, New York, N. Y., 1959: (a) p. 63; (b) p. 85.

(10) The possibility of a nonplanar structure for benzocyclopropene has been discussed by Ullman and Buncel.⁴

Although II is stable for several hours at room temperature, it is completely destroyed in refluxing benzene after 15 min. The compound is very sensitive to acids, but not to bases. The transformation products and the rate of decomposition of II are being investigated; preliminary n.m.r. evidence shows that at least one of the products contains an isopropenyl group.

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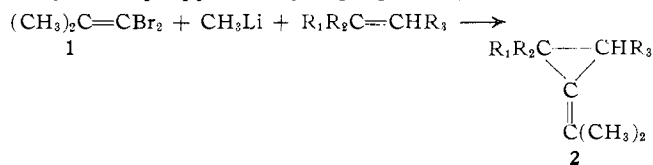
RECEIVED DECEMBER 14, 1963

The Synthesis of Methylene-cyclopropanes via an α -Elimination Reaction

Sir:

Methylene carbenes (R₂C=C:) have been suggested as intermediates in the formation of butatrienes from exocyclic vinyl halides and sodium amide¹ or phenyllithium.² With simpler 2,2-diaryl vinyl bromides rearrangement occurs to give diaryl acetylenes. Stereochemical evidence has been presented^{3,4} to prove that this reaction does not produce a methylene carbene. The formation of substituted methylenecyclopropanes in low yields by the reaction of vinyl chlorides, olefins, and potassium *t*-butoxide has recently been disclosed.⁵ This reaction is assumed to involve intermediate methylene carbenes.

We have found that aliphatic vinylidene bromides give α -elimination reactions with methyllithium. While 1,1-dibromopropene, methyllithium, and olefins gave methylacetylene; 1,1-dibromo-2-methylpropene (1), methyllithium, and olefins gave moderate yields (12-70%) of isopropylidene-cyclopropanes (2).



The reaction 1 \rightarrow 2 has been run successfully at -80 to +60°. A solution of methyllithium in ether was added slowly to an equimolar amount of 1 dissolved in a three- to tenfold excess of olefin. The products were isolated by standard separation and distillation procedures or by preparative scale vapor phase chromatography. The highest yields of 2 were obtained with nucleophilic olefins such as vinyl ethers. The reaction with ethyl isobutenyl ether gave a 59% yield of 2 (R₁ = R₂ = CH₃, R₃ = OCH₂CH₃), b.p. 85° (115 mm.). *Anal.* Calcd. for C₁₀H₁₈O: C, 77.9; H, 11.8. Found: C, 77.9; H, 12.0. Isopropylidene-cyclopropanes were also obtained from ethyl vinyl ether (70%), methyl vinyl ether (60%), cyclohexene (41%), isobutylene (35%), norbornene (22%), 2-methyl-2-butene (12%), and *trans*-2-butene (23%).⁶

All of the products 2 showed infrared absorption near 5.60 μ which was attributed to the strained double bond exocyclic to the cyclopropane ring. Two common features of the proton magnetic resonance spectra of 2 also assisted in the identification of the products: high-field resonances of the hydrogen atoms on the cyclopropane ring and long-range coupling (\sim 2 c.p.s.) between the ring hydrogens and the isopropylidene

(1) C. R. Hauser and D. Lednicer, *J. Org. Chem.*, **22**, 1248 (1957).

(2) D. Y. Curtin and W. H. Richardson, *J. Am. Chem. Soc.*, **81**, 4719 (1959).

(3) A. A. Bothner-By, *ibid.*, **77**, 3293 (1955).

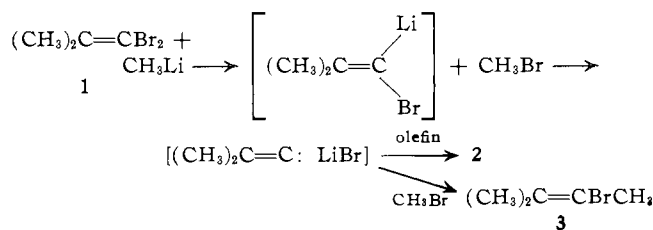
(4) D. Y. Curtin, E. W. Flynn, and R. F. Nystrom, *ibid.*, **80**, 4599 (1958).

(5) M. Tanabe and R. A. Walsh, *ibid.*, **85**, 3522 (1963).

(6) Satisfactory elemental analyses and spectral data were obtained for all these compounds.

hydrogens. Thus, the spectrum of the product obtained from isobutylene (**2**, R₁ = R₂ = CH₃, R₃ = H) showed the resonances of the ring methyls (singlet) at τ 8.85, the methylene (seven peaks) centered at τ 9.21, and the olefinic methyls (four peaks) centered at τ 8.24.

2-Bromo-3-methyl-2-butene (**3**) was formed in all the reactions of **1**, methyl lithium, and olefins. The yields of **3** were in inverse relation to those of the olefin adducts **2**. With weakly nucleophilic olefins, such as ethylene or vinyl chloride, only traces of methylenecyclopropanes were formed, and **3** was the major product. These results suggest that an intermediate is formed which can react with olefin or methyl bromide. The variation in yield of **2** with olefin structure is that expected of an electrophilic intermediate. It is suggested that lithium-bromine exchange occurs and is followed by, at least, partial loss of lithium bromide.⁷



Attempts to trap the α-halolithium intermediate by carbonation were unsuccessful. No products of insertion of the isopropylidene carbene into carbon-hydrogen bonds have yet been found.

(7) A more precise formulation of the intermediate cannot now be given. The extent to which a metal halide leaves an α-halo metal compound to produce a carbene is a problem with all α-eliminations: see G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963).

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The Quadricyclic Carbonium Ion. Solvolysis of 7-Quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane Derivatives

Sir:

Because of their relation to the 7-norbornadienyl system¹ we have examined carbonium ion-forming reactions of 7-quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane derivatives (I).² Confirming the recent report by Richey and Buckley³ we find that these molecules are remarkably reactive compared to their 7-norbornyl analogs (II). This dramatic rate enhancement naturally raises the question of how best to represent charge delocalization in the intermediate carbonium ion. We have attempted to prepare the fluoroborate of I in sulfur dioxide as we did from the diene chloride (IIIb)¹ but the n.m.r. spectrum, which appeared to be that of a mixture, was too complex to be of value.

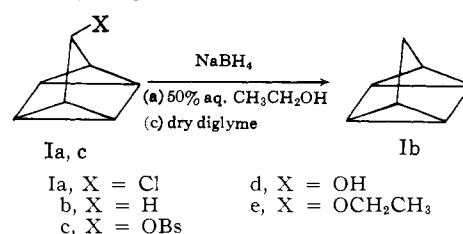
Subsequently, we solvolyzed the quadricyclic chloride (Ia) in 50% aqueous ethanol at 50° containing an excess of sodium borohydride to trap the intermediate carbonium ion according to Brown's procedure.⁴

(1) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962); P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3650 (1963).

(2) The quadricyclic compounds (I) were prepared by photolysis of the appropriate diene (III) (ref. 1) according to Hammond's procedure (ref. 6). Structures were established by n.m.r. analysis and by thermal conversion (170°) to the corresponding diene isomer (III). Satisfactory analyses were obtained for all new compounds.

(3) H. G. Richey, Jr., and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963).

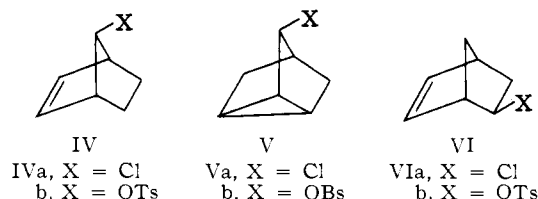
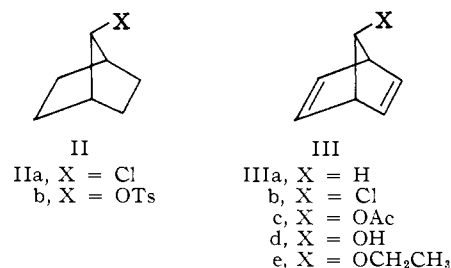
Careful analysis of the hydrocarbon fraction of the product by v.p.c. revealed only quadricyclene (Ib)^{5,6} and a trace (<1%) of an unknown material. Even



more remarkably, reaction of the *p*-bromobenzene-sulfonate (Ic) with sodium borohydride in dry diglyme⁷ at 40° produced only quadricyclene (Ib) along with a trace (<1%) of material with the same retention time as norbornadiene.

Solvolysis of quadricyclic chloride (Ia) in 50% aqueous ethanol at 46.3° gave a first-order rate constant of 1.03×10^{-5} sec.⁻¹. Comparison with *anti*-7-norbornenyl chloride (IVa)⁸ reveals that Ia is less reactive by a factor of only 100. While it is not possible to make a direct comparison with the corresponding saturated chloride (IIa),⁸ the tosylate (IVb) is reported to be *ca.* 10¹¹ times more reactive than IIb.⁹ Consequently, Ia is probably about 10⁸-10⁹ more reactive than 7-norbornyl chloride (IIa). These relative rate factors are in good agreement with those reported by Richey and Buckley.³ Interestingly, Ia is only *ca.* one-tenth as reactive as cyclopropylcarbinyl chloride under the same conditions.¹⁰

If Ia is solvolyzed in 50% aqueous ethanol containing a slight excess of sodium bicarbonate at 50°, the principal products are quadricyclic (Id,e) and account for 75% of the total yield (80-90%). However, under these conditions 18% of the product consists



of dienes (IIIId,e).¹¹ Two unidentified materials accounted for 7% of the product. One of these (*ca.* 3%) was highly unstable and visibly diminished with time. The diene isomer (III) is clearly of lower energy than

(4) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); *J. Am. Chem. Soc.*, **85**, 2324 (1963).

(5) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

(6) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(7) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(8) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(9) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

(10) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

(11) The mal reversion of Ia to IIIb is only 50% complete at 170° after 5 hr. in carbon tetrachloride solution. Thermal reversion is negligible below 100°.