hydrazone salt, is 35–40%. Azine is also formed, but does not easily escape the pyrolysis chamber and its yield could not be measured.

The presence of the monosubstituted benzenes implicates a mechanism involving radicals and a "cross-over" experiment confirms this. Thus, co-generation of **1** and **2** gives *p*-xylene, *p*-diethylbenzene, *p*-ethyltoluene, ethylbenzene, and toluene in the ratio 0.8:0.6: 1:3.6:2.8. The ratio of dialkylbenzenes to monoalkylbenzenes is 1:2.6. A cleavage of carbene to alkyl

1 + 2 ⟶
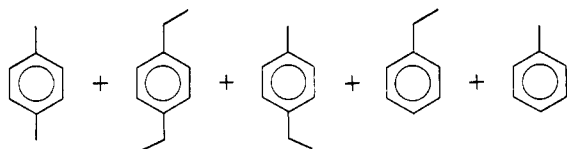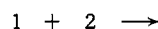
and aryl radicals is followed by recombination. As expected from the postulated mechanism, biaryls are also formed.

Intramolecular carbene–radical fragmentations have been claimed for cyclopropylcarbenes[7] and oxocarbenes.[8] The latter case presents particularly compelling stereochemical evidence for the reaction. The reactions of **1** and **2** are related in a vinylogous sense.
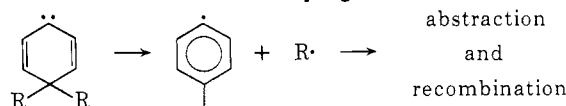
Although the present results show that the major course of reaction of **1** and **2** is cleavage to radicals, they do not preclude a small amount of conversion to *p*-dialkylbenzenes through intramolecular processes. Nor do they necessarily require that the formations of [7]-[9] and [6]paracyclophane[10] from carbenes related to **1** and **2** follow the same mechanism.

(7) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

(8) A. M. Foster and W. C. Agosta, *ibid.*, **95**, 608 (1973). See also R. J. Crawford and R. Raap, *Proc. Chem. Soc.*, 370 (1963).

(9) A. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **95**, 1680 (1973).

(10) A. D. Wolf, V. V. Kane, and M. Jones, Jr., unpublished results.

(11) National Science Foundation Predoctoral Fellow, 1971–1973.

(12) NDEA Fellow, 1967–1970.

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A Facile Synthesis of Strained Bridgehead Olefins *via* the Intramolecular Wittig Reaction[1]

Sir:

The synthesis of polycyclic compounds with a strained bridgehead double bond has recently received attention. These bridgehead alkenes have generally been

synthesized by elimination of XY from the appropriate precursor a (X = Y = halogen;[2] X = N$^+$(CH$_3$)$_3$OH$^-$, Y = H;[3,4] X = CH$_3$SO$_2$O, Y = H;[5] X = COO$^-$, Y = CH$_3$SO$_2$O;[6] or X–Y = –OCSO–[4]).
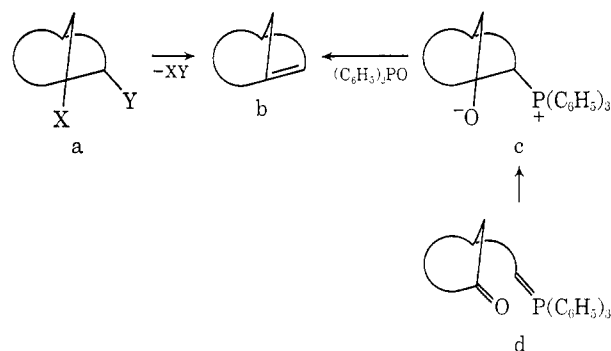
The intramolecular Wittig reaction (d → c → b) has not been utilized for the synthesis of bridgehead olefins. The results of Büchi and Wüest[7] indicate that compounds of type d should be easily available by the reaction of allyl ylides with cyclic α,β-unsaturated ketones. We would like to report our results of the application of this reaction in the synthesis of some new conjugated bridgehead olefins.

The reaction of cyclooct-1-en-3-one (**1**) with 2-butenylidenetriphenylphosphorane (**2b**) (from corresponding phosphonium bromide and potassium *tert*-butoxide) in tetrahydrofuran at room temperature gave diene **3b**[8] in 72% yield (bp 90–100° (10 mm); nmr (CCl$_4$) δ 5.5 (m, 2 H), 1.9–2.36 (m, 5 H), 1.75 (s, 3 H), 1.3–1.56 (m, 8 H); uv max (cyclohexane) 275 nm (ε 5700)). The structure of **3b** was proved by ozonolysis to 3-acetylcyclooctan-1-one (80% yield, bp 100° (0.1 mm), ir (film) 1710 cm^{-1}) which was identical with an independently synthesized sample.[9]

The reaction of **1** with ylides **2a** and **2c**, respectively, yielded (Scheme I) diene **3a** (yield 63%, bp 90–100° (5 mm); nmr (CCl$_4$) δ 5.7–6.0 (m, 2 H), 5.59 (br s, 1 H), 1.3–2.4 (m, 13 H); uv max (cyclohexane) 273 nm (ε 4700)) and diene **3c** (57% yield, bp 130–140° (0.5 mm); nmr (CCl$_4$) δ 7.0–7.4 (m, 5 H), 6.0 (AB q, 2 H, Δδ = 25.5 Hz, *J* = 5.0 Hz, higher field bands also show *J*′ ≤ 1 Hz); uv max (cyclohexane) 315 nm (ε 8700), 230 (ε 6100)).

The preferred formation of the dienes **3a–3c** instead of triene **6** in the Wittig reaction shows that the ylide reacted with **1** in a Michael-type fashion to yield **4**;

(2) (a) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, **21**, 2997 (1965); (b) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); (c) R. Keese and E. P. Krebs, *ibid.*, **11**, 518 (1972); (d) D. Lenoir, *Tetrahedron Lett.*, 4049 (1972); (e) D. Grant, M. A. McKervey, J. J. Rooney, N. C. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972).

(3) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 956 (1970).

(4) J. A. Chong and J. R. Wiseman, *J. Amer. Chem. Soc.*, **94**, 8627 (1972).

(5) C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 1343 (1973).

(6) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970).

(7) G. Büchi and H. Wüest, *Helv. Chim. Acta*, **54**, 1767 (1971).

(8) All compounds reported here with the exception of **7** gave satisfactory elemental analysis and consistent ir, nmr, and mass spectra. Diene **7** is very air sensitive and was characterized by the spectroscopic data including the high-resolution mass spectrum. The distillations were carried out using a Kugelrohr; the boiling points reported are the temperatures of the oven.

(9) Prepared *via* the general procedure of A. McCoubney, *J. Chem. Soc.*, 2931 (1951).

Scheme I

a, R = H
b, R = CH₃
c, R = C₆H₅
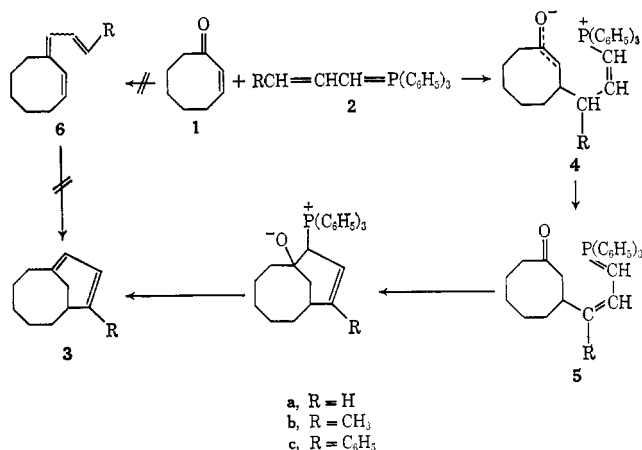
proton abstraction must yield ylide **5** followed by an intramolecular Wittig reaction to give the observed products **3a–3c**. The trienes **6a** and **6c** were synthesized independently[10] and were shown not to be intermediates in the formation of the bridgehead alkenes.

7   8   9   10
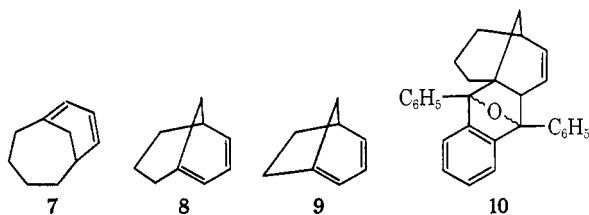
Bicyclo[4.3.1]deca-7,9-diene (**7**) was prepared from cyclohept-1-en-3-one and ylide **2a** in tetrahydrofuran at room temperature (yield 52%; bp 80–90° (3 mm); nmr (CCl₄) δ 5.84–5.98 (m, 2 H), 5.35 (br s, 1 H), and 1.2–2.3 (m, 11 H); uv max (cyclohexane) 274 nm (ε 2800)); this material is the most constrained bridgehead diene of this type which is readily isolable. The ultraviolet absorption maxima of **3a–3c** and **7** are in good agreement with data from analogous 1,3-cyclohexadiene derivatives,[11] showing no indication of distortion of the diene chromophore.

The foregoing results suggested that these reactions could be utilized for the synthesis of highly strained bridgehead alkenes such as bicyclo[3.3.1]nona-1,3-diene (**8**) and bicyclo[3.2.1]octa-1,3-diene (**9**). The reaction of cyclohex-1-en-3-one with ylide **2a** at room temperature gave in 63% yield a mixture of three isomeric dimers of **8** in a ratio of 72:24:4 (mass spectrum for $C_{18}H_{24}$, m/e 240).[12] The major component was obtained in pure form by chromatography on silica gel. When the reaction was performed in the presence of 1,3-diphenylisobenzofuran, two [4 + 2] cycloaddition adducts of structure **10** were obtained in a ratio of 2:1 (yield 67%; mass spectra m/e 390; isomer A, mp 198–199°; isomer B, mp 148–150°). Both isomeric adducts were hydrogenated over Pd–C in ethanol and isomer B upon dihydrogenation yielded a product identical with that derived from the reaction of bicyclo-

(10) **6a** and **6c** were synthesized by the reaction of 1-cyclooctenyllithium with acrolein and cinnamaldehyde, respectively, followed by dehydration (**6a**, bp 90–95° (1 mm); **6c**, mp 76–77°).

(11) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 45.

(12) The corresponding bicyclo[3.3.1]non-1-en is stable at room temperature and does not dimerize.[3,6]

[3.3.1]non-1-ene with the 1,3-diphenylisobenzofuran (mp 181–182°),[3] dihydro isomer A, mp 205–206°.

13   14
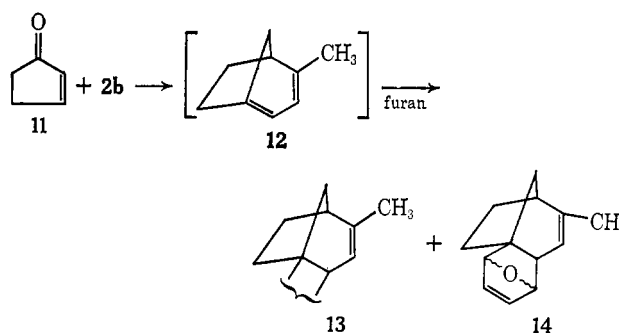
The reaction of cyclopent-1-en-3-one (**11**) with ylide **2b** in refluxing tetrahydrofuran gave in 86% yield the dimer **13** (mp 78–83°; mass spectrum for $C_{18}H_{24}$, m/e 240; nmr (CCl₄) δ 5.15 (br s, 1 H), 1.25–2.7 (m, 11 H)). When the reaction was run in the presence of furan, the diene product **12** was trapped as the [4 + 2] cycloaddition product **14** (yield 37% (and 30% dimer **13**), bp 65–70° (3 mm); mass spectrum for $C_{13}H_{16}O$, m/e 188; nmr (CCl₄) δ 5.9–6.5 (m, 2 H), 5.1–5.4 (d, 1 H), 4.4–4.8 (m, 2 H), 0.8–2.4 (m, 11 H)).

At first sight the formation of strained bridgehead alkenes is surprising, but it must be realized that the process proceeds in two steps. The first step is simple ring closure to yield a betaine, the formation of the single bond not greatly affecting the strain energy of the molecule. The second step is introduction of the strained double bond, a reaction which proceeds well owing to the efficiency of $(C_6H_5)_3PO$ as a leaving group.

(13) Stipendiat der Deutsche Forschungsgemeinschaft.

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1,4-, 1,5-, and 1,6-Dibromoalkanes from Ionic Reaction of Bromine with n-Butylcyclopropane

Sir:

Ionic brominations of cyclopropanes to produce 1,3-dibromides are possibly the most frequently cited aspect of cyclopropane chemistry; there is an unsatisfactory insight to be gained from these statements, for 1,3-dibromides are often minor products.

Ionic brominations of cyclopropanes are slow reactions if the ring is not heavily substituted with alkyl groups. For example, cyclopropane does not react with bromine without Lewis acid catalysis.[1] After 10-min reaction time at 0° in CCl₄ solvent there is no detectable reaction of ethylcyclopropane with bromine. This is unlike the radical chain bromination which is rapid at −78°.[2]

Further, the dibromides from ethylcyclopropane include significant amounts of 2,3-dibromopentanes (50%), which drives one to consider a variety of exotic explanations. Similarly, 2,3-dibromobutanes were obtained on bromination of methylcyclopropane. These

(1) N. C. Deno and D. N. Lincoln, *J. Amer. Chem. Soc.*, **88**, 5357 (1966).

(2) K. J. Shea and P. S. Skell, *J. Amer. Chem. Soc.*, in press.