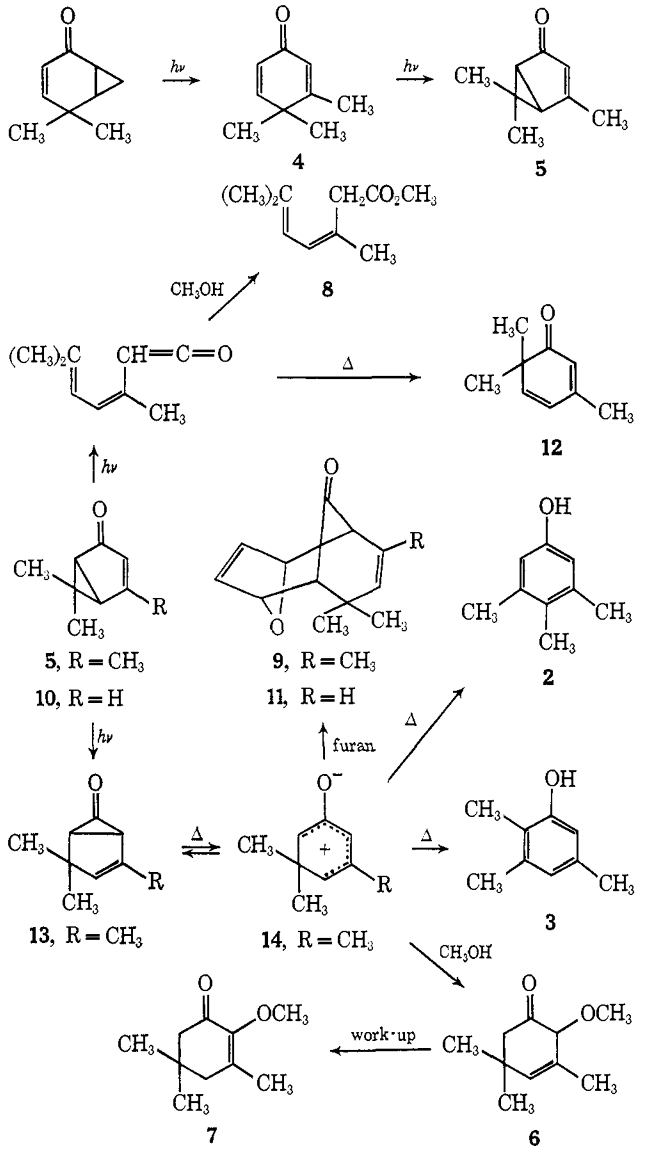
Nonhydrogen atoms were easily located on a three-dimensional E synthesis with signs given by Sayre's equation.[11] Full-matrix least-squares refinements smoothly converged to the present minimum of $R = 0.098$ for the observed reflections.[12] All bond distances and angles agree well with generally accepted values.

Irradiation of **4** at room temperature in cyclohexane gives **5** which in turn gives 3,6,6-trimethyl-2,4-cyclohexadienone (**12**)[13] among other products. This dienone dimerizes slowly at room temperature and is analogous to that observed in the irradiation of **10** in cyclohexane.[5]

The transformations described above can be understood in terms of the mechanism shown in Chart I. It is a moot question whether the primary product at room temperature is the cyclopropanone (**13**) or the zwitterion (**14**).[7,14] The cyclopropanone is definitely a primary photoproduct at 77°K. Compelling evidence has been described for a zwitterion intermediate in the formation of phenolic products from 6,6-diphenylbicyclo[3,1.0]hex-3-en-2-one.[14] The key to trapping zwitterion **14** with furan or methanol is the greater thermal coefficient of methyl migration relative to the furan and methanol addition reactions. At room temperature and above methyl migration is heavily favored. At low temperatures furan and methanol trapping are favored.[7]

**Chart I**



**Acknowledgment.** This research was supported by Grant No. AM-14624 from the National Institute for Arthritis and Metabolic Disease, U. S. Public Health Service, and Grant No. GP28152X from the National Science Foundation.

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[11] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942); J. Karle and H. Hauptman, *Acta Crystallogr.*, **9**, 635 (1956); R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

[12] W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

[13] Compound **12**: ir $\nu$ ($CCl_4$) 1662, 1646, 1576 $cm^{-1}$; nmr $\delta$ ($CCl_4$) 1.12 (s, 6 H), 2.04 (d, 3 H), 5.77 (m, 1 H), 5.92 (q, 1 H), 6.23 (d, 1 H); parent ion $m/e$ 136 (93%). *Anal.* Found: C, 79.47; H, 9.01.

[14] H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 7806 (1972), and references cited therein.

[15] Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1972–1977.

**O. L. Chapman,* J. C. Clardy**[15]
**T. L. McDowell, H. E. Wright**
*Department of Chemistry and*
*Ames Laboratory of the Atomic Energy Commission*
*Iowa State University*
*Ames, Iowa 50010*

*Received February 22, 1973*

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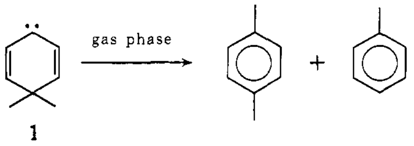
## 4,4-Dialkylcyclohexadienylidenes in the Gas Phase. Carbene–Radical Fragmentations[1]

*Sir:*

In 1969 we described the reactions of 4,4-dimethylcyclohexadienylidene (**1**) in solution.[2] Here we report the remarkable gas-phase rearrangements of **1** and the related 4,4-diethylcyclohexadienylidene (**2**).

Generation in the gas phase avoids the rapid intermolecular reactions typical of carbenes[3,4] and favors intramolecular processes. It might be anticipated that **1**, a $C_8H_{10}$ isomer, would find its ultimate repose in



xylene, but, remarkably, decomposition of 4,4-dimethyldiazocyclohexadiene in a flow system at 380° yields only the para isomer and toluene in the ratio 1:2.1.[5,6] Similarly, **2** gives *p*-diethylbenzene and ethylbenzene in the ratio 1:3.7. In both the above cases, the overall yield of aryl- and diarylbenzenes, based on starting tosyl-

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[1] Support from the National Science Foundation in the form of Grant GP-30797X and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with thanks.

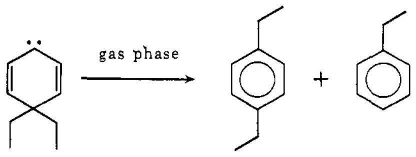
[2] M. Jones, Jr., A. M. Harrison, and K. R. Rettig, *J. Amer. Chem. Soc.*, **91**, 7462 (1969).

[3] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

[4] M. Jones, Jr., and R. A. Moss, Ed., "Carbenes," Wiley, New York, N. Y., 1973.

[5] The diazo compound was generated by the flash pyrolysis of the lithium salt of the tosylhydrazone of 4,4-dimethylcyclohexadienone. Pyrolysis of the isolated diazo compound in a flow system gave similar results, although the amount of toluene was smaller.

[6] No *o*- or *m*-xylene could be detected by gas chromatography under conditions where a few per cent would have been easily found.

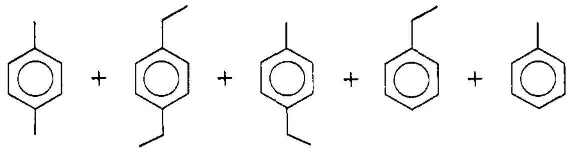


2

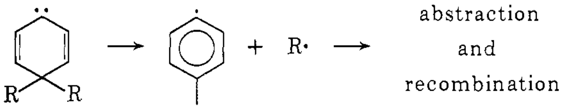
hydrazone salt, is 35–40%. Azine is also formed, but does not easily escape the pyrolysis chamber and its yield could not be measured.

The presence of the monosubstituted benzenes implicates a mechanism involving radicals and a "crossover" 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 and aryl radicals is followed by recombination. As expected from the postulated mechanism, biaryls are also formed.

1 + 2 ⟶



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.

**Thomas E. Berdick,[11] Ronald H. Levin[12]**
**Anthony D. Wolf, Maitland Jones, Jr.***
*Department of Chemistry, Princeton University*
*Princeton, New Jersey 08540*

*Received March 9, 1973*

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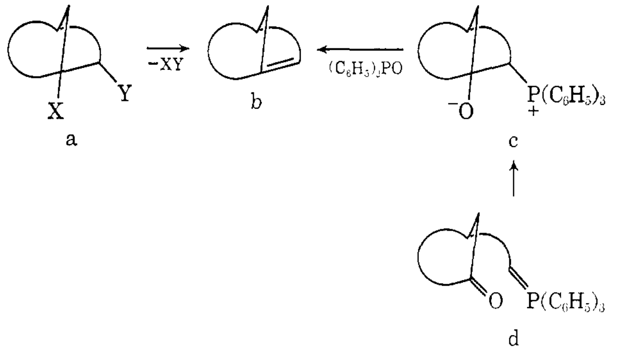
## A Facile Synthesis of Strained Bridgehead Olefins *via* the Intramolecular Wittig Reaction[1]

*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 = $N^+(CH_3)_3OH^-$, Y = H;[3,4] X = $CH_3SO_2O$, Y = H;[5] X = $COO^-$, Y = $CH_3SO_2O$;[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 $\alpha,\beta$-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 ($CCl_4$) $\delta$ 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 ($\epsilon$ 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 ($CCl_4$) $\delta$ 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 ($\epsilon$ 4700)) and diene **3c** (57% yield, bp 130–140° (0.5 mm); nmr ($CCl_4$) $\delta$ 7.0–7.4 (m, 5 H), 6.0 (AB q, 2 H, $\Delta\delta$ = 25.5 Hz, $J$ = 5.0 Hz, higher field bands also show $J' \leq 1$ Hz); uv max (cyclohexane) 315 nm ($\epsilon$ 8700), 230 ($\epsilon$ 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**;

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[1] This work was supported by the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, Grant No. AM-00709.

[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).