decomposition of benzenediazonium chloride react with acrylonitrile to give **1**. Thus, the formation of **1** in our photochemical experiment is consistent with the hypothesis that excited chlorobenzene dissociates homolytically. The extra photoproducts **2** and **3** have been shown to be derived from **1** by photolysis in acetonitrile.

We therefore suppose that excitation of chlorobenzene gives rise to C_6H_5 and Cl, which react with $NaBH_4$ by the mechanism suggested or with acrylonitrile to give **1**.

Further evidence in support of our proposal is provided by an experiment in which iodobenzene (0.5 *M*) and $NaBH_4$ (1.0 *M*) in liquid ammonia and MeCN was reduced with sodium. Benzene was formed in 675% yield (calculated on Na consumed); replacement of the $NaBH_4$ by NaCl gave benzene in only 51% yield. Sodium is known[6,7] to transfer an electron to iodobenzene yielding $C_6H_5\cdot$ and I^-.

The quantitative photoreduction by $NaBH_4$ of 1- and 2-bromonaphthalene and 9-bromophenanthrene to the corresponding hydrocarbons was also inhibited by acrylonitrile and the hydrocarbons obtained in the presence of $NaBH_4$–D_2O contained no deuterium.

We note a marked similarity between the results of our photochemical experiments and those of Brown and Krishnamurthy,[8] who reduced halogenated benzenes in the dark with $LiAlH_4$ in tetrahydrofuran. It may be that the presence of peroxides in this solvent initiates a chain reaction with the consequences described above.

Acknowledgments. We gratefully acknowledge financial support of this work by Brasenose College, Oxford.

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(6) J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc.*, *Ser. A*, **293**, 246 (1966).

(7) A. R. Buick, T. J. Kemp, G. T. Neal, and T. J. Stone, *J. Chem. Soc. A*, 666 (1969).

(8) H. C. Brown and S. Krishnamurthy, *J. Org. Chem.*, **34**, 3918 (1969).

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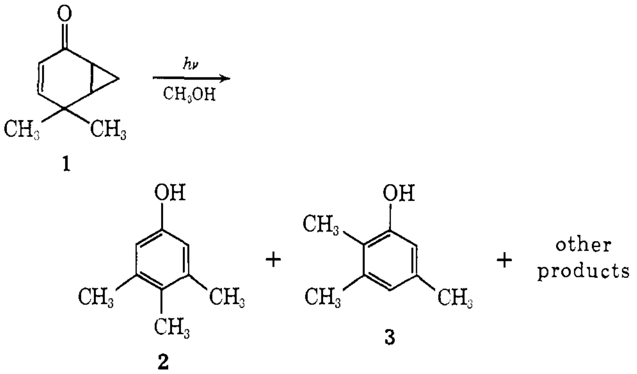
Photoisomerization of 5,5-Dimethylbicyclo[4.1.0]hept-3-en-2-one and 4,6,6-Trimethylbicyclo[3.1.0]hex-3-en-2-one[1]

Sir:



1

2

3

Irradiation of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (**1**) in methanol at room temperature gives among other products two rearranged phenols (**2** and **3**, *ca.* 50%, identified by ir and nmr comparison). These products are formed in a complex series of transformations which culminate in the thermal isomerization of the primary photoproducts of 4,6,6-trimethylbicyclo-[3.1.0]hex-3-en-2-one. Deuterium labeling has shown that the cyclopropyl methylene group of **1** becomes the third methyl group found in the phenolic products.[1] This observation and the results of Dauben's studies on the photochemistry of fused-ring cyclopropyl ketones[2] suggest that the first step in the rearrangement might be photoisomerization of **1** to 3,4,4-trimethyl-2,5-cyclohexadienone (**4**). Attempts to detect **4** during the irradiation of **1** were frustrated by the fact that **4** is destroyed photochemically far more efficiently than **1**. Irradiation of **4** in methanol at room temperature gives only **5**.[3] Irradiation of **5** in methanol at room temperature gives phenols **2** and **3** among other products. The sequence **4** → **5** → **2** and **3** is analogous to the rearrangements observed with 4,4-diphenyl-2,5-cyclohexadienone[4] and 4,4-dimethyl-2,5-cycohexadienone.[5] Irradiation of **5** as a neat film at 77°K gives primary product bands at 2107 and 1810 cm^{-1}.[6] Continued irradiation produced carbon monoxide at the expense of the 1810-cm^{-1} band. These observations together with the results of our earlier investigations[7] suggest that the 2107-cm^{-1} band is due to a ketene and the 1810-cm^{-1} band to a cyclopropanone. Irradiation of **4** at −78° in methanol–ether (1:2) gives (*via* **5**) the methanol adducts **6** and **7** and the ester **8**.[8] An analogous ester is observed in the irradiation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.[9] Irradiation of either **4** or **5** in furan–ether (1:4) at −78° gives a furan adduct **9**.[10] Similar irradiation of **10** gives adduct **11** (mp 113–115°). Adduct **11** was selected for X-ray analysis because it gave better crystals.

Diffractometer measured cell constants are $a = 15.24$ (2), $b = 6.47$ (1), and $c = 11.15$ (1) Å and $\beta = 115.2$ (2)° for the uniquely determined space group $P2_1/c$. A total of 2476 unique reflections with $\theta \leq 30°$ for Mo Kα radiation were measured and 2476 were judged observed.

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(1) Photochemical Transformations. LI. Abstracted in part from the Ph.D. Thesis of T. A. McDowell, Iowa State University, Ames, Iowa, 1971.

(2) W. G. Dauben, G. W. Shaffer, and E. J. Deving, *J. Amer. Chem. Soc.*, **92**, 6273 (1970); W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, 4415 (1967).

(3) Compound **5**: ν (neat) 1687, 1606 cm^{-1}; uv λ_{max}^{EtOH} 228 (ϵ 4770), 253 (ϵ 3790), 315 nm (ϵ 241); nmr δ (CCl_4) 1.1 (m, 1 H), 1.15 (s, 3 H), 1.23 (s, 3 H), 1.85 (m, 1 H), 2.05 (d, 3 H), 5.50 (m, 1 H). *Anal.* Found: C, 79.32; H, 8.89.

(4) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(5) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *ibid.*, **90**, 2990 (1968).

(6) Irradiation of 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (**10**) as a neat film at 77°K gives similar bands (2109, 1815 cm^{-1}).[1]

(7) O. L. Chapman, L. L. Barber, and J. D. Lassila, *J. Amer. Chem. Soc.*, **91**, 3664 (1969); O. L. Chapman, *Int. Union Pure Appl. Chem. Congr.*, *XXIIIrd*, *Spec. Lect.*, **1**, 311 (1971).

(8) Compound **6**; ir ν (neat) 1732, 1678 cm^{-1}; nmr δ (CCl_4) 1.02 (s, 3 H), 1.08 (s, 3 H), 1.75 (d, 3 H), 2.19 and 2.47 (q, $J_{AB} = 12$ Hz, 2 H), 3.32 (s, 3 H), 3.51 (m, 1 H), 5.45 (m, 1 H); parent ion *m/e* 168 (35%). Compound **7**: ir ν (neat) 1680, 1640 cm^{-1}; uv λ_{max}^{EtOH} 247 nm (ϵ 9620); nmr δ (CCl_4) 1.03 (s, 6 H), 1.82 (d, 3 H), 2.19 (s, 4 H), 3.60 (s, 3 H); parent ion *m/e* 168 (66%). *Anal.* Found: C, 71.13; H, 9.63. Compound **8**: ir ν (neat) 1742 cm^{-1}; uv λ_{max}^{EtOH} 244 nm (ϵ 21,500); nmr δ (CCl_4) 1.73 (s, 3 H), 1.82 (m, 6 H), 3.06 (s, 2 H), 3.62 (s, 3 H), 5.97 (m, 2 H). *Anal.* Found: C, 71.25; H, 9.37.

(9) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

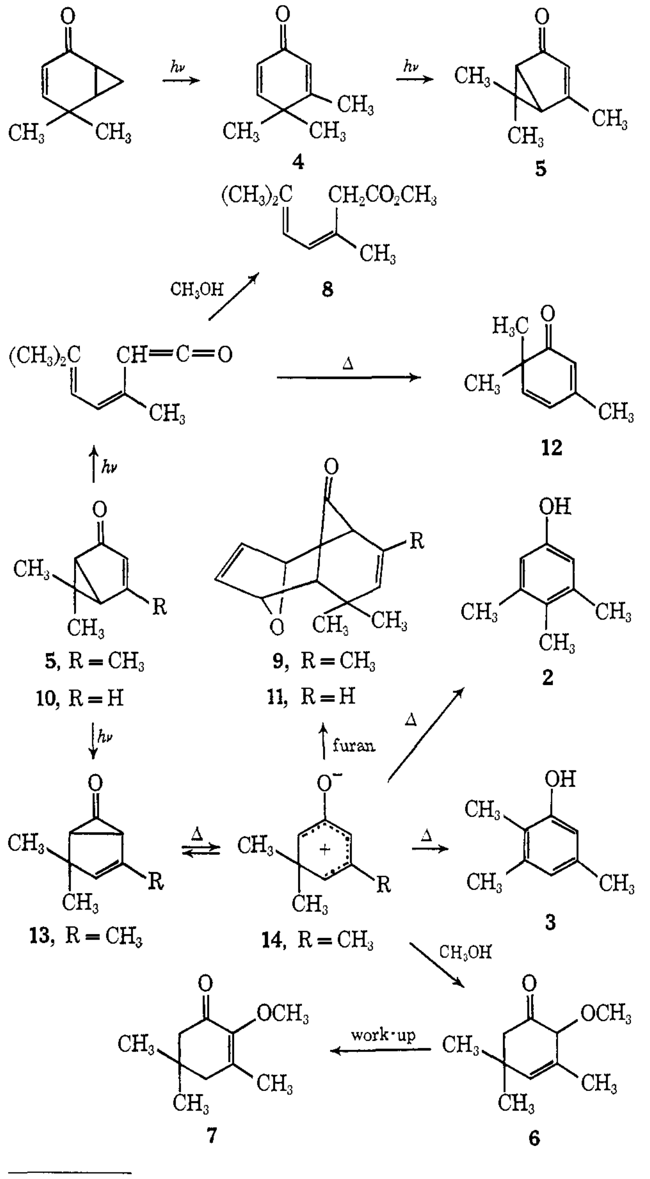
(10) Compound **9**: mp 68–70°; ir ν (CCl_4) 1737, 1720 cm^{-1}; λ_{max}^{EtOH} 284 nm (ϵ 128); nmr δ (CCl_4) 0.98 (s, 3 H), 1.24 (s, 3 H), 1.74 (d, 3 H), 1.96 (m, 1 H), 2.43 (m, 1 H), 4.61 (m 1 H), 4.83 (m, 1 H), 5.26 (m, 1 H), 6.25 (m, 2 H); parent ion *m/e* 204 (100)%. *Anal.* Found: C, 76.28; H, 7.78.

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



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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 ν (CCl_4) 1662, 1646, 1576 cm^{-1}; nmr δ (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.

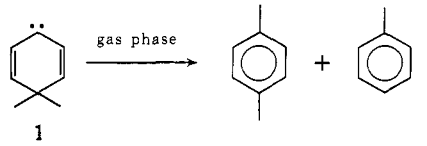
(15) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1972–1977.

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.