That biphenylene (**5**) is a result of benzyne dimerization was assured since **5** obtained by decomposing **1′** in excess benzene-d_6 was found to be deuterium free, *m/e* 152, C–D stretch absent in the infrared.

None of the other metal ions (Tl^+, Cu^+, Cu^{2+}, Hg_2^{2+}, Hg^{2+})[11] screened thus far altered the course of the benzyne–benzene reaction. The study is being extended however, to transition metals and their complexes in anticipation that an isolable benzyne complex may result.[12]

amounts of biphenyl-d_{10} were formed *via* benzene-d_6 thermal dimerization;[10b] biphenyl-d_6:biphenyl-d_{10} ~0.1. Biphenylene was not detected. Acenaphthylene and acenaphthene are formed *only* by thermal rearrangement of **3**. Based on *isolated* and *characterized* hydrocarbon products, it can be concluded that at 690° the major reaction of benzyne with benzene is 1,4 addition (~75%) to give **2**, followed by loss of acetylene to give thermally stable naphthalene. The balance is electrophilic attack (*vide supra*) to give **4** (~10%) and **3** (~15%) (which rearranges (60%) to form acenaphthene, which in turn is partially dehydrogenated to acenaphthylene) and pyrolysis (40%) to naphthalene. These results are somewhat different from earlier reports[2a] (D. F. Lindow, unpublished data). (b) *Cf.* G. M. Badger, *Progr. Phys. Org. Chem.*, **3**, 1 (1966).

(11) The absence of any effect is a strong argument against benzyne attacking a benzene–metal complex.

(12) The assistance of L. R. Rice and D. F. Lindow in carrying out some of the initial experiments is gratefully acknowledged.

Lester Friedman
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

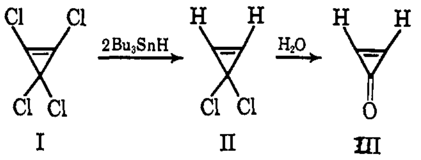
Received March 6, 1967

Cyclopropenone

Sir:

Studies of various cyclopropenones, including diphenylcyclopropenone,[1] the earliest example, and the more recent monoalkylcyclopropenones,[2] have fully established the unusual stability of this strained system. Most chemical properties of importance have also been investigated on these derivatives.[1-3] However, although the parent ketone III is clearly of interest, it has resisted our synthetic attempts to prepare it by the methods used to make substituted derivatives. We have now succeeded in synthesizing unsubstituted cyclopropenone.

Reaction of tetrachlorocyclopropene[4] (I) with 2 equiv of tri-*n*-butyltin hydride at room temperature in paraffin oil produced a volatile mixture[5] of chlorocyclopropenes containing 3,3-dichlorocyclopropene (II) (nmr: δ 8.0), 1,3-dichlorocyclopropene (δ 7.2, 4.5, J_{AB} = 2 cps), and mono- and trichlorocyclopropene isomers. The distilled mixture was taken up in CCl_4 and cautiously hydrolyzed with cold water (or D_2O). The aqueous phase contained as the only detectable signal (the solvent peak could be moved by adding potassium phosphate or removed by using D_2O) a sharp singlet at δ 9.0 which we assign to the protons of cyclopropenone (III).



The nmr spectrum unambiguously establishes this structure. Thus the singlet shows ^{13}C satellites with the very large coupling ($J_{^{13}C-H}$ = 230 cps) characteristic of a cyclopropene[6] or acetylene. The latter is, of course, excluded by the chemical shift of δ 9.0; this also excludes nonketonic cyclopropene structures since 1,3,3-trimethylcyclopropene has its vinyl proton at δ 6.7 and the 3,3-dichlorocyclopropene signal is at δ 8.0, while methylcyclopropenone is at δ 8.7. The ^{13}C satellites of III appear, as expected, as a doublet (J_{H-H} = 3 cps).

The aqueous solution of III shows broad infrared absorption centered at 1850 cm^{-1}. On standing it slowly ($t_{1/2}$ at 25° >1 week) is hydrolyzed to acrylic acid.[8] Treatment with alkali produces a dark polymer, but the compound is stable to a variety of strong mineral acids. Although III is very polar, it can be extracted from the water solution with methylene chloride or ethylene chloride by salting out. The protons in III are still at δ 8.9–9.0, there are no other signals in the nmr, and the infrared spectrum shows a strong cyclopropenone doublet[9] at 1835 and 1870 cm^{-1} and no absorption in the O–H region. Thus III is apparently present as the free ketone, rather than a *gem*-diol, even in aqueous solution.

Attempts to isolate III by removal of solvent, distillation, or vapor phase chromatography under a variety of conditions have so far failed, leading to at least partial polymerization of the compound; the parent ketone is apparently more sensitive than its derivatives. However, the low reactivity of III compared with cyclopropanone,[10] and in particular its retention of the unhydrated carbonyl group in water solution, confirm our previous conclusion that the cyclopropenone system has considerable conjugative stabilization.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health, and thank Mr. John Groves for several experimental contributions.

(1) R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959); M. E. Vol'pin, Y. D. Koreshkov, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, 506 (1959); R. Breslow, T. Eicher, A. Krebs, R. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965).

(2) R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966).

(3) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

(4) S. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966).

(5) Although the allylic chlorines must be most reactive, the resulting conjugated cyclopropenyl radical may pick up hydrogen on any ring position and the cyclopropenyl chlorides undergo rapid allylic isomerizations. Under appropriate conditions the essentially pure mixture of dichlorides can be prepared. On treatment with $AgBF_4$ in a variety of solvents Mr. John Groves has found that this affords chlorocyclopropenium ion, with an nmr singlet at δ 9.6 ($J_{^{13}C-H}$ = 242 cps, J_{H-H} = 2 cps).

(6) Methylcyclopropenone[2] has $J_{^{13}C-H}$ = 213 cps and 1,3,3-trimethylcyclopropene[7] has $J_{^{13}C-H}$ = 218 cps.

(7) G. L. Closs, *Proc. Chem. Soc.*, 152 (1962).

(8) Identified by comparison of vpc, nmr, and mass spectra with those of an authentic sample.

(9) The spectra in aqueous and nonaqueous solution mirror those for alkylcyclopropenones[2] and indicate that the carbonyl group is still present in water, albeit hydrogen bonded.

(10) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966).

Ronald Breslow, Gordon Ryan
Department of Chemistry, Columbia University
New York, New York 10027

Received May 5, 1967

Singlet Oxygen Reactions from Photoperoxides

Sir:

It has been known for some time that aromatic hydrocarbons such as anthracene, rubrene, and tetra-