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FRAGMENTATION OF SUBSTITUTED NORBORNADIENONE KETALS

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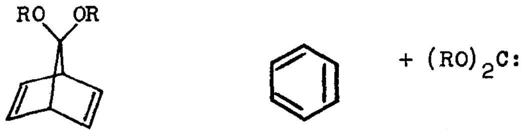
ALTHOUGH dialkoxycarbenes have received considerable attention in the chemical literature, there exists to our knowledge no well-authenticated preparation of a species of this class.[1,2] Interest in the properties and potential synthetic utility of dialkoxycarbenes compelled us to examine the thermal decomposition of substituted norbornadienone ketals. We hoped for aromatization of the bridged dihydrobenzene system (**1**) attended by expulsion of the bridge as a carbene (**2**):



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[1] See, *inter alia*, H. Scheibler *et al.*, J. prakt. Chem., **279**, 60, 70 (1958) and earlier papers; P. S. Skell and I. Starer, J. Am. Chem. Soc., **81**, 4117 (1959); J. Hine, A. D. Ketley and K. Tanabe, *ibid.*, **82**, 1398 (1960).

[2] E. J. Corey and R.A.E. Winter, *ibid.*, **85**, 2677 (1963).

Prepared by treatment of hexachlorocyclopentadiene with ethylene glycol sodium salt, 5,5-ethylenedioxy-1,2,3,4-tetrachlorocyclopentadiene, 3[3,4] (m.p. 65-67°; nmr,[5] singlet at 5.73τ), reacted with phenylacetylene (4) at 65-70°. The Diels-Alder adduct 5 was obtained in 66% yield. M.p. after purification 127.5-128.3°; nmr, 271 (aryl), 3.56 (vinyl), and 5.81τ(methylene protons). Decomposition of this substance was discernible at the melting point and proceeded smoothly at 140°. The virtually colorless residue proved to be 2,3,4,5-tetrachlorobiphenyl (6),[6] isolated almost quantitatively. Gaseous pyrolysis products, which accounted for 95% of the ketal bridge of 5, were separated by vapor chromatography on a silica gel

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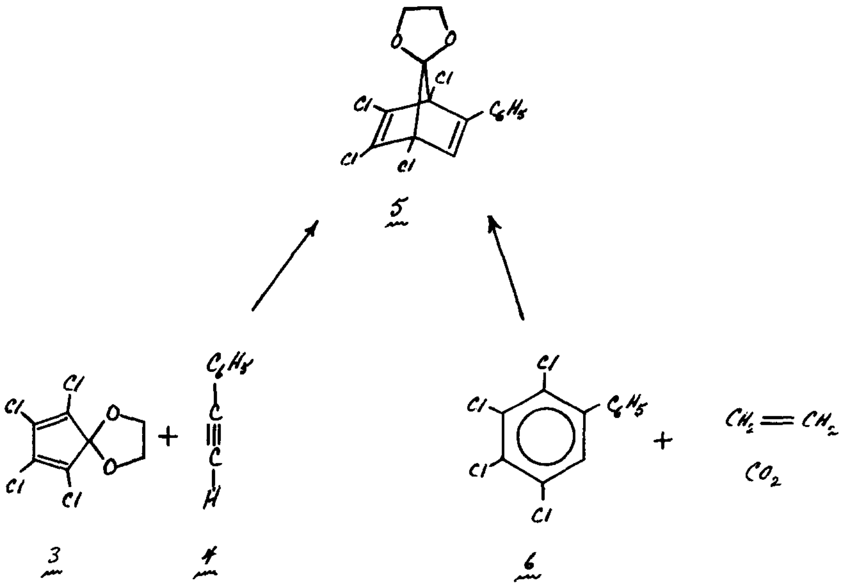
[3] Several simple ketals of tetrachlorocyclopentadienone (ref. 7) are readily accessible and stable, in contrast to their unsubstituted counterparts (C. H. De Puy, B. W. Ponder and J. D. Fitzpatrick, Angew. Chem., 74, 489 (1962); E. Vogel and E. G. Wyes, *ibid.*, 74, 489 (1962)).

[4] All new compounds prepared in this work gave satisfactory carbon and hydrogen analyses.

[5] NMR spectra were measured in carbon tetrachloride and calibrated with hexamethyldisiloxane (9.94τ) or tetramethylsilane (10.00τ) as internal standards. Relative peak areas were consistent with structural assignments in all cases.

[6] E. T. McBee *et al.*, J. Am. Chem. Soc., 77, 385, 6674 (1955).

column into equimolar amounts of carbon dioxide and ethylene, identified by their mass spectra. These results were clearly explicable in terms of a carbene intermediate in the decomposition,[2] but the possibility remained that formation of the three stable products occurred synchronously. Study of an open-chain ketal (8) shed some light on this question.



5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (7)[7] and excess phenylacetylene (4) were heated together at about 70°. Higher temperatures led to decomposition products, but under these conditions the Diels-Alder adduct 8 was isolated in 57% yield, m.p. 95.5-96.5° after recrystallization. Nmr, 2.79 (phenyl), 3.66 (vinyl), 6.50 and 6.54 τ(methoxyl protons). Effervescence accompanied the fast reaction of this compound with cold, concentrated sulfuric acid and the tetrachlorobiphenyl 6 crystallized immediately, as expected for the structure 8.

Like 5, adduct 8 was remarkably labile thermally. Decomposition in an inert atmosphere occurred vigorously, but without darkening at temperatures as low as 140°.[8] Pyrolysis at 150° of a concentrated solution of 8 in di-*n*-butyl phthalate gave in essentially quantitative yield three aromatic compounds separable by g.l.c.: the chloroesters 9 and a roughly equal quantity of the tetrachlorobiphenyl 6.[9] The structures of the former, which differed from 8 by the elements of methyl chloride, were determined by spectral, microanalytical, and degradative data. Among

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[7] J. S. Newcomber and E. T. McBee, *ibid.*, **71**, 949 (1949).

[8] It is interesting to note that *combustion* ensues when the adduct is heated to ~150° *in the air!*

[9] This substance had been isolated in low yield by McBee (ref. 6) from the reaction of 4 and 7 in refluxing benzene, but the fate of the ketal bridge had not been investigated.

the volatile products of pyrolysis methyl chloride was found in yields approximately equal to those of the chloroesters.[10] Of key significance was the isolation by g.l.c. of tetramethoxyethylene (10), presumably formed by dimerization of dimethoxycarbene.[11] The yield based on the quantity of biphenyl 6 produced was 70%.[12] A single sharp line at 6.50 τ constituted the nmr spectrum of 10. Extremely gentle acid hydrolysis transformed the compound into methyl dimethoxy-

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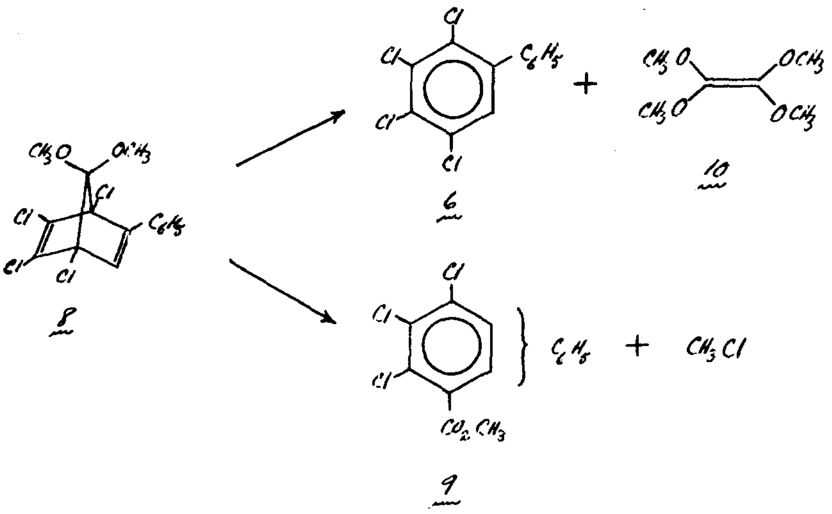
[10] Adducts (not isolated) of the dienes 3 and 7 with dimethyl acetylenedicarboxylate gave almost no 6 when pyrolyzed, the predominant products being esters analogous to 9 and methyl chloride. The reaction of 7 with the acetylenic ester was studied independently by J. Diekmann, J. Org. Chem., 28, 2880 (1963).

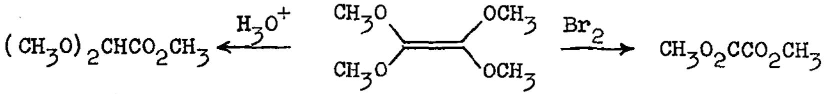
[11] Although a free radical pathway to 10 can be envisioned, the absence of aromatic coupling products casts grave doubts upon such a scheme.

[12] H. Feichtinger and H. Linden, Ger. pat. 1,105,862 (1961) (C.A., 56, 12803 (1962)), have reported that the reaction of 7 with $CH_3CO_2CH_2C{\equiv}CCHROCOCH_3$ (R=H, CH_3) leads to the corresponding benzene derivatives with loss of the ketal bridge as carbon monoxide and dimethyl ether. We found no dimethyl ether and very little carbon monoxide among the thermal decomposition products of 8 even when the reaction was run in dilute solution.



8 6 10 9

acetate (11), identical with an authentic sample. As anticipated, bromine oxidized the ethylene to dimethyl oxalate (12).



$(CH_3O)_2CHCO_2CH_3 \xleftarrow{H_3O^+} (CH_3O)_2C{=}C(OCH_3)_2 \xrightarrow{Br_2} CH_3O_2CCO_2CH_3$

11 10 12

Preliminary attempts to intercept the hypothetical carbene with olefins have met with failure, a result most simply interpreted as evidence for a high degree of internal stabilization in the divalent species.[13] Efforts to obtain direct physical evidence for dimethoxycarbene are currently under way.

The competition between bridge opening and bridge loss observed in the decomposition of 8 contrasts sharply with the clean bridge loss characteristic of 5. This contrast strongly suggests that ethylene, carbon dioxide and tetrachlorobiphenyl 6 are formed simultaneously in the fragmentation of 5. Absence of the dimer of ethylenedioxycarbene among the products lends support to this proposal.

Other data bearing on the mechanisms for decomposition of 5, 8 and related adducts will be discussed in a full publication.

Acknowledgment. - The authors wish to thank both the National Science Foundation and the National Institutes of Health for generous financial support.

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[13] Recently it has been shown that bis-[alkylthio]-carbenes are remarkably resistant to trapping by simple olefins (U. Schöllkopf and E. Wiskott, Angew. Chem., 75, 725 (1963); D. M. Lemal and E. H. Banitt, Tetrahedron Letters, in press.