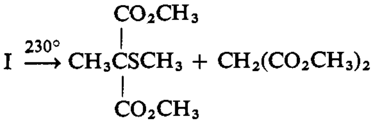
$$\mathrm{I} \xrightarrow[\text{in methanol}]{2537\ \text{Å}} \underset{\mathrm{V}}{CH_3OCH(CO_2CH_3)_2} + CH_2(CO_2CH_3)_2$$

When sulfonium ylide I was heated in a sealed tube at 230° for 3 hr, rearranged product[7] VI and dimethyl malonate were obtained. This fact is noteworthy since it



$$\mathrm{I} \xrightarrow{230°} CH_3\overset{CO_2CH_3}{\underset{CO_2CH_3}{C}}SCH_3 + CH_2(CO_2CH_3)_2$$

VI

is the first direct evidence of a thermal rearrangement of a sulfonium ylide, although there have been several reports suggesting rearrangements of unstable sulfur ylide intermediates.[8]

The relative reactivity of the sulfur atom in dimethyl sulfide was investigated. Product distributions from the photolysis of dimethyl diazomalonate in mixtures of cyclohexene and dimethyl sulfide are shown in Table I. Control experiments showed that the products are stable under the reaction conditions. The results indicate that bis(carbomethoxy)carbene reacts with dimethyl sulfide four times faster than with cyclohexene. Experiments with other olefins showed similar results (see Table II). Table II also shows the yields of reaction products from the photolysis of dimethyl diazomalonate in equimolar mixtures of dimethyl sulfide and other nucleophiles. In all cases, sulfonium ylide was separated and weighed, and reaction products from the other nucleophiles were determined by gas chromatography using an appropriate internal standard.

These observations suggest that dimethyl sulfide can be used as a more effective and more convenient acceptor of negatively substituted carbenes than olefins when the sulfonium ylides are stable under the reaction conditions, because of the high reactivity of dimethyl sulfide and the ease of isolating ylide products.

Because of the high yield of sulfonium ylides, the reaction will be useful for synthesis of ylides. Concerning scope and limitation, further extensive investigation is in progress.

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(7) The rearranged product (VI) was identified by the analysis of nmr spectra (3.75 ppm, $-CO_2CH_3$; 2.13 ppm, $-SCH_3$; 1.61 ppm, $-SCH_3$; intensity ratio 2:1:1) and an ir absorption maximum at 1745 cm^{-1}.

(8) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 304.

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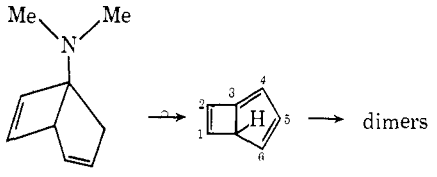
Bicyclo[3.2.0]hepta-1,3,5-triene

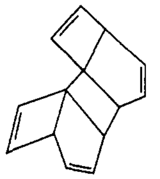
Sir:

The interesting results on the bicyclo[3.2.0]heptatrienyl system recently communicated to this journal by Breslow's group galvanize us to report our own closely related results which parallel those of Breslow except for the structure of the interesting dimer of bicycloheptatriene (**2**).[1]

Amine **1**[2] was converted by excess methyl iodide in ethanol (room temperature, 3 hr) to its methiodide salt and by hydrogen peroxide in methanol to its N-oxide. β eliminations on the former by sodium methoxide in DMSO (room temperature, 3 hr) and on the latter by pyrolysis at 120° both gave rise to the same *ca.* 50:50 mixture of isomeric hydrocarbon dimers, separated by vpc (silicone oil–chromosorb W, 160°). Both have m/e 180 and no $\lambda_{max} > 210$ mμ, but they are differentiated by their nmr spectra: dimer A, τ 3.7–3.9 (4 H, AB, J = 1.3 Hz, cyclobutenes), 4.2 (4 H, s, cyclopentenes), 6.45 (2 H, m, methines), 7.35 (2 H, m, methines); dimer B, τ 3.8 (4 H, s, cyclobutenes), 4.2–4.4 (4 H, AB, J = 2.9 Hz, cyclopentenes), 6.4 (2 H, m, methines), 6.7 (2 H, m, methines). The equivalence of the two cyclopentene and cyclobutene rings in both dimers and the presence of but two different types of methine hydrogen in each precludes, barring an inadmissible series of coincidences, the possibility that either of the present dimers is of the type suggested by Breslow's group. The nmr and uv data effectively rule out all reasonable dimeric structures except **3**, **4**, and **5** (all as *syn–anti* pairs).[3] Structure **5** is inconsistent with the very small (<2 Hz) coupling constant observed between the two types of hydrogen bound to saturated carbon. A much larger, geminal, splitting would be expected of **5**. Structures **3** and **4** would both result from olefin cycloaddition across the strained 3,4 double bond of triene **2**. Of these, **3** is preferred on the basis of the two-step mechanism of olefin cycloaddition and the expectation that more strain would be relieved if the two bridgehead (3) positions couple initially. Triene **2** has also been trapped as its diphenylisobenzofuran and cyclopentadiene adducts, which have structures analogous to **3**. Interestingly, triene **2**, though readily trapped by dienes, could not be trapped by reactive dienophiles such as dimethyl acetylenedicarboxylate and dimethyl fumarate. Thus, under our conditions, dienophilic properties are much more in evidence than dienylic properties in **2**.



1 **2**



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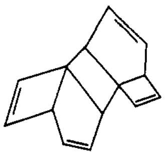

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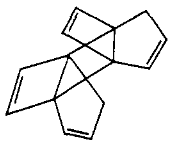

5

The results of our own deuterium-exchange experiments also differ from those reported by the Columbia group. No deuterium incorporation was found in the dimers when the methiodide of **1** was treated with potassium *t*-butoxide in DMSO-d_6, *t*-butoxide in *t*-butyl alcohol-O-*d*, or *t*-butoxide in THF–DMSO-d_6–

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(1) R. Breslow, W. Washburn, and R. C. Bergman, *J. Am. Chem. Soc.*, **91**, 196 (1969).

(2) A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *Chem. Commun.*, **23**, 1210 (1967).

(3) There is also another pair of stereoisomers of **5** having different relative dispositions of the cyclopentene double bonds.

t-butyl alcohol-O-*d* (the latter being the solvent mixture reported to yield 100% dideuterated dimer). Therefore, the fully conjugated anion is not formed, at least under our conditions.

Work aimed at the preparation of the cation, anion, and radical of the fully conjugated bicyclo[3.2.0]-heptatrienyl system is in progress.

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The *o*-Xylylene Anion Radical

Sir:

We are pleased to report a synthesis of the previously unknown anion radical of the elusive molecule, *o*-xylylene. The synthesis is exceedingly simple, but involves an unusual reaction type which could have applications to the synthesis of other anion radicals.

Benzocyclobutene, a valence isomer of *o*-xylylene, appears to undergo thermal valence isomerization to the latter at 200°. The ephemeral existence of *o*-xylylene can be inferred from Diels–Alder trapping experiments.[1]

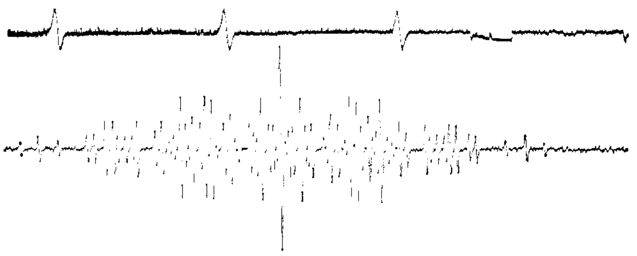
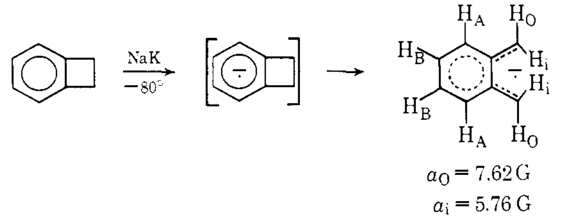


Figure 1. Esr spectrum of the *o*-xylylene anion radical in THF at −60° using NaK alloy. The computer simulation is virtually perfect. The upper trace is a simultaneously recorded spectrum of Fremy's salt.

Our thesis was that the anion radical of benzocyclobutene would undergo a similar, but much more rapid, isomerization, since *o*-xylylene should have a much higher electron affinity (the lowest vacant HMO has $E = \alpha - 0.29\beta$) than a benzene-like anion radical (LVMO, $E = \alpha - 1.00\beta$). Thus, if the isomerization could be brought about under sufficiently mild conditions, the *o*-xylylene anion radical might be detectable. In fact, when benzocyclobutene is contacted with K or NaK in THF or DME at −80°, the only radical which is observed, and this is formed virtually immediately, is the anion radical of *o*-xylylene, as the data and arguments below indicate.



$a_O = 7.62$ G
$a_i = 5.76$ G
$a_A = 5.23$ G
$a_B = 1.45$ G

The esr spectrum of the radical is reproduced in Figure 1. The hfs constants are listed below the structure. Splittings are observed from four nonequivalent pairs of protons, thereby immediately eliminating from consideration the benzocyclobutene anion radical, which can have at most three magnetically nonequivalent proton types. Moreover, the spectrum is unusually long for an anion radical (*ca.* 40 G), suggesting that some positions of fairly high spin density have more than one α proton attached, as would be the case with the benzylic positions of the *o*-xylylene anion radical. Thus, the splitting patterns and the spectrum length both constitute potent arguments for the assigned structure of the radical and against the benzocyclobutene anion radical.

The positional assignments given above are based upon HMO calculations and, in the case of $a_o > a_i$, upon the allyl radical analogy[2] and are thus tentative. If correct, the relatively large difference in splitting constants between H_i and H_o would be of considerable interest, and efforts are under way to substantiate the assignments as well as to determine the rotatory sense of the electrocyclic reaction presumably involved in the formation of the *o*-xylylene anion radical.

Acknowledgment. We wish to acknowledge support from the Welch Foundation and from the National Science Foundation, the latter for the purchase of an esr spectrometer.

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(1) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, 15 (1962).

(2) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7155 (1968).

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Perchloropolysilanes: Novel Reducing Agents for Phosphine Oxides and Other Organic Oxides[1]

Sir:

Perchloropolysilanes (Si_nCl_{2n+2}) constitute a class of compounds which have not been heretofore reported as reducing agents in organic synthesis, even though the possibility of such an application was foreshadowed by the earlier observation of Urry,[2] who noted the rapid reduction of antimony trichloride by hexasilicon tetradecachloride (Si_6Cl_{14}) in ether solution and recognized the potential of this compound "as a reducing agent for use in nonaqueous systems for reactions where hydride or metallic reducing agents are incompatible." We wish to communicate at this time what we believe to be the first reported deoxygenations of organic compounds with hexachlorodisilane (Si_2Cl_6) and octachlorotrisilane (Si_3Cl_8), the first two members of the perchloropolysilane series, and the particular usefulness of these reagents in the synthesis of optically active phosphines.

Optically active acyclic phosphine oxides[3] ($R_1R_2R_3PO$) are handily reduced by Si_2Cl_6 or Si_3Cl_8 with complete or nearly complete inversion of configuration.[4]

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(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 409 (1964).

(3) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968).