constant is very close to that of benzene ($\kappa$ = 2.2).[24] That solvent dielectric constant is not the controlling factor[22] is indicated by the finding that ions are not produced for any of these systems in tetrahydrofuran ($\kappa$ = 7.4). Further study is planned to determine the influence of medium on the transition between excited complex, ion pair, and free ions in other systems.[25]

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(24) J. Timmermans, "The Physico-chemical Constants of Binary Systems in Concentrated Solutions," Vol. I and II, Interscience, New York, N. Y., 1959.

(25) Support of this work by the UNC Materials Research Center and the U. S. Public Health Service (Grant No. GM 15,238-05) is gratefully acknowledged.

(26) Alfred P. Sloan Foundation Fellow.

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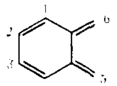
## Stereospecific Synthesis of the (*E,E*)- and (*Z,E*)-5,6-Diphenyl-*o*-xylylene Dianions. Stereochemistry of Cycloreversion of the *cis*- and *trans*-3,4-Diphenylbenzocyclobutene Anion Radicals

*Sir:*

*o*-Xylylene (**1**) and its (*Z,E*)- and (*E,E*)-5,6-diphenyl derivatives **2** and **3** have been reliably inferred as transient intermediates near room temperature,[1,2] but no electronated species (*e.g.*, anion radicals or dianions) have been observed in this series. The present report describes a stereospecific synthesis of the dianions of **2** and **3** (**2**$^{2-}$ and **3**$^{2-}$). These are by far the most stable *o*-xylylene derivatives yet observed and, indeed, are the only ones known in which the *o*-xylylene structure is more thermodynamically stable than the contending benzocyclobutene one. The synthesis is additionally significant because it elucidates, for the first time, the preferred rotational stereochemistry of an electrocyclic reaction of an anion radical.



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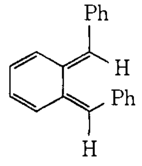

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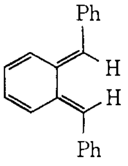

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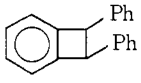

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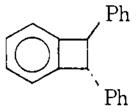

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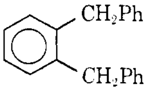

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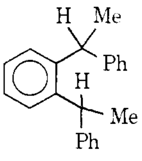

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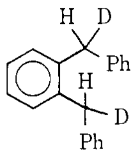

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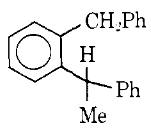

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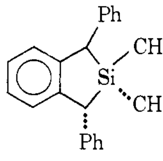

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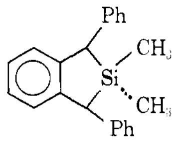
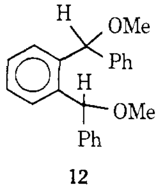


**11**



**12**

*cis*- and *trans*-3,4-diphenylbenzocyclobutene (**4** and **5**, respectively) were prepared by the method of Carpino.[3] Birch reduction (Na–NH$_3$–EtOH) of each gave *o*-dibenzylbenzene (**6**) in quantitative yield, indicating facile cleavage of the 3,4 bond of the cyclobutane ring of the anion radicals of **4** and **5** (**4**$^{\cdot -}$ and **5**$^{\cdot -}$) even at −78°. Attempts to observe **4**$^{\cdot -}$ and **5**$^{\cdot -}$ (esr) by the usual alkali metal–ethereal solvent procedures were totally unsuccessful, thus confirming the instability of these anion radicals and, together with the Birch reduction results, suggesting that they cyclorevert rapidly to **2**$^{\cdot -}$ and/or **3**$^{\cdot -}$ which are rapidly converted to the diamagnetic dianions. Therefore, **2**$^{2-}$ and **3**$^{2-}$ were sought. The reactions of **4** and **5** with potassium in 2-methyltetrahydrofuran (MTHF) at −78° *in vacuo* were complete within 2 hr. That the resulting deep red solutions contained essentially only the desired dianions was indicated by quenching them with excess methyl iodide and with D$_2$O. The dimethyl and dideuterio compounds **7** and **8** were formed in >90% yield. The absence of monomethyl product **9** was further confirmed by independent synthesis. The two diastereoisomers of **7** were produced in *ca.* the same proportions from either **4** or **5** and have nmr (CDCl$_3$) $\tau$ 2.4–30 (14 H, m), 5.6 (2 H, q, $J$ = 7 Hz), 8.4 (6 H, d, $J$ = 7 Hz, 25% of this diastereoisomer), 8.6 (6 H, d, $J$ = 7 Hz, 75%); mass spectrum $m/e$ 286 (M).

The dianions from **4** and **5** can be confidently assigned the *Z,E* (**2**$^{2-}$) and *E,E* (**3**$^{2-}$) structures, respectively, on the basis of their reactions with dimethyldichlorosilane (−78°, MTHF, vacuum line). The dianion from **4** gave silanes **10** (84%) and **11** (16%) in >90% total yield, while that from **5** yielded **10** (30%) and **11** (70%), also in very high yield. Silane **10** has nmr (CS$_2$) $\tau$ 2.7–3.15 (14 H, m), 6.15 (2 H, s), 9.9 (6 H, s), mass spectrum $m/e$ 314 (M), while **11** has nmr (CS$_2$) $\tau$ 2.6–3.1 (14 H, m), 6.35 (2 H, s), 9.6 (3 H, s), 10.4 (3 H, s); and mass spectrum $m/e$ 314 (M). The methyl groups of the cis adduct **11** are nonequivalent whereas those of the trans adduct **10** are equivalent. Since any preference in the quenching reactions should be for suprafacial rather than antarafacial addition, the reaction sequences must be $\mathbf{4} \rightarrow \mathbf{4}^{\cdot -} \rightarrow \mathbf{2}^{\cdot -} \rightarrow \mathbf{2}^{2-} \rightarrow \mathbf{10}$ and $\mathbf{5} \rightarrow \mathbf{5}^{\cdot -} \rightarrow \mathbf{3}^{\cdot -} \rightarrow \mathbf{3}^{2-} \rightarrow \mathbf{11}$. Both cycloreversions (of **4**$^{\cdot -}$ and **5**$^{\cdot -}$) are therefore at least predominantly conrotatory. Note that the reactions of **2**$^{2-}$ and **3**$^{2-}$ with the silane are probably stepwise and thus not completely stereospecific.

Further confirmation of the dianion structural assignments and evidence that both cycloreversions are highly stereospecific are provided by nmr studies of the dianions in THF-$d_8$ (vacuum line preparation, sealed tube studies at −78° to room temperature). Dianion **2**$^{2-}$ has nmr $\tau$ 2.8 (4 H, m, meta), 3.5 (6 H, m, para, ortho), 4.1 (4 H, m, $H_{1,2,3,4}$), 5.77 (1 H, s, $H_5$ (outside benzylic proton)), 6.28 (incompletely resolved from solvent peak, s, $H_6$); **3**$^{2-}$ has nmr $\tau$ 2.7 (4 H, m, meta), 3.4 (6 H, m, ortho, para), 3.93 (2 H, m, $H_{2,3}$), 4.40 (2 H, m, $H_{1,4}$), 5.77 (2 H, s, $H_{5,6}$). The positional assignments, except for the benzylic protons, are based in part

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(1) N. L. Bauld, C.-S. Chang, and F. R. Farr, Jr., *Tetrahedron Lett.*, 2443 (1972).

(2) R. Huisgen and H. Seidl, *ibid.*, 3381 (1964).

(3) L. A. Carpino, *J. Amer. Chem. Soc.*, **84**, 2196 (1962).

on MO calculations and are thus tentative. The large upfield shifts of all the aromatic protons except the meta ones are noteworthy. More significantly, $H_{5,6}$ are equivalent in $\mathbf{3}^{2-}$ but not in $\mathbf{2}^{2-}$. Each of the two dianions can be obtained free of the other if the reaction vessel and later the nmr tube are kept close to −78°.

Two alternate, convenient, highly stereoselective syntheses of $\mathbf{2}^{2-}$ have also been achieved. Reaction of *o*-dibenzylbenzene with excess butyllithium in MTHF at room temperature gives, along with smaller amounts of the monoanion, mainly $\mathbf{2}^{2-}$ as shown by methyl iodide quenching and reaction with dichlorodimethylsilane (83% **10**, 17% **11**). Similarly, reaction of diether **12** with potassium in MTHF at 0° gives $\mathbf{2}^{2-}$. Quenching with silane again gives 87% **10** and 13% **11**. These experiments strongly suggest that $\mathbf{2}^{2-}$ is more stable than $\mathbf{3}^{2-}$ despite steric factors. Presumably the greater attractions between the two contact metal gegenions and the more proximate negative charge on an inside phenyl substituent engender this interesting order of stabilities.

Conrotation is in accord with orbital symmetry analysis,[4,5] but neither this approach nor the experiment is consistent with a simplified frontier orbital analysis. The odd electron in a diphenyl-*o*-xylylene anion radical occupies an s orbital, leading to an expectation of disrotation, according to the latter analysis. This appears to be the first instance in which the frontier orbital approach has been shown to lead to an erroneous prediction. In general, *cycloreversions of anion radicals can only be ideally "allowed" for that rotational mode allowed for their neutral precursors, and then only when the orbitals occupied by the odd electron also correlate.* In many cases, therefore, neither mode will be ideally allowed,[6] though some preference may still exist.

**Acknowledgment.** We thank the National Science Foundation (GP-17596) for support.

[4] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

[5] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395, 2046, 2511 (1965); *Angew. Chem.*, **81**, 787 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[6] The cyclobutene anion radical → 1,3-butadiene anion radical cycloreversion is not ideally allowed in either rotational sense.

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*Received May 26, 1972*

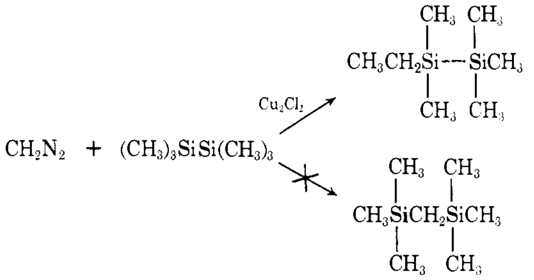
## Carbon–Hydrogen Insertion in the Copper-Catalyzed Decomposition of Diazomethane in Hexamethyldisilane. A Silicon α Effect

*Sir:*

The possibility that silylene $SiH_2$ might insert into a silicon–silicon bond[1–3] led us to investigate the analogous methylene insertion. In order to be able to carry out experiments without rigorously excluding oxygen, we chose hexamethyldisilane as the reaction substrate. This compound has the advantage of not containing silicon–hydrogen bonds. In addition to high reactivity toward oxygen, silicon–hydrogen bonds have been shown to be 8.9 times as reactive as carbon–hydrogen bonds toward photochemically generated methylene.[4] Therefore, the replacement of silicon–hydrogen bonds by methyl groups was expected to diminish the importance of side reactions which might compete with silicon–silicon insertion.

To maximize the selectivity among competing reaction pathways, the relatively impotent carbenoid species resulting from the copper-catalyzed decomposition of diazomethane[5,6] was chosen for the initial experiments. Diazomethane was swept in a nitrogen stream from a cooled decalin reservoir into a magnetically stirred suspension of 500 mg of cuprous chloride in 2 ml of hexamethyldisilane over a 5-hr period. The reaction mixture was maintained at room temperature and shielded from light. A condenser cooled to 14° retarded evaporation of the reaction mixture.

Vapor chromatographic analysis using several stationary phases detected only a single product formed in *ca.* 5% yield (based on diazomethane). Upon isolation the product proved to be ethylpentamethyldisilane rather than the hoped-for 2,4-disila-2,2,4,4-tetramethylbutane.


$$\mathrm{CH_2N_2} + \mathrm{(CH_3)_3SiSi(CH_3)_3} \xrightarrow{\mathrm{Cu_2Cl_2}} \mathrm{CH_3CH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3}$$
$$\mathrm{CH_2N_2} + \mathrm{(CH_3)_3SiSi(CH_3)_3} \not\rightarrow \mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3}$$

The product was identified by comparison of its physical properties (vapor chromatographic retention times, and infrared, nuclear magnetic resonance, and mass spectra) with those of an authentic sample prepared by standard techniques.[7]

Since the observed reaction product is also formed upon photolysis of diazomethane in hexamethyldisilane,[8] and since copper-catalyzed decomposition of diazomethane has not previously been observed to give carbon–hydrogen (or silicon–carbon) insertion,[9] it was necessary to preclude stray light as the source of a spurious result, and to differentiate between carbon–hydrogen and silicon–carbon insertion as the pathway leading to the observed product.

When the reaction of diazomethane with hexamethyldisilane was repeated (several times) in the absence of catalyst but otherwise under conditions identical with those which produced ethylpentamethyldisilane, *no* product was detected. With the chromatographic sensitivity employed, a yield as low as 0.25% would certainly have been found. When the catalyzed decomposition of diazomethane was carried out in cyclohexane and methylcyclohexane in place of hexa-

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[1] M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

[2] P. P. Gaspar and P. Markusch, *Chem. Commun.*, 1331 (1970).

[3] P. P. Gaspar and B. Jerosch Herold in "Carbene Chemistry," W. Kirmse, Ed., 2nd ed, Academic Press, New York, N. Y., 1971, Chapter 13.

[4] J. Mazac and J. W. Simons, *J. Amer. Chem. Soc.*, **90**, 2484 (1968).

[5] W. von E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963).

[6] W. von. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[7] M. Kumada, K. Tamao, T. Takubo, and M. Ishikawa, *J. Organometal. Chem.*, **9**, 43 (1967).

[8] Unpublished work of R. T. Conlin and P. P. Gaspar.

[9] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 86.