inferred $K = 3.3 \times 10^{-5}$ for the reaction between alkoxide and DMSO, eq 1, by observing the equilibrium

$$tert\text{-BuO}^-K^+ + CH_3SOCH_3 \rightleftharpoons tert\text{-BuOH} + CH_3SOCH_2^-K^+ \quad (1)$$

ratio of triphenylmethide to triphenylmethane in basic solutions prepared both from $CH_3SOCH_2^-$ and from *tert*-butoxide. We have now examined directly the equilibrium represented in eq 1. A solution of *tert*-BuO^-K^+ in DMSO, formally 0.57 *M*, actually contains 0.2 *M* $CH_3SOCH_2^-$ at equilibrium.[8] Thus $K \cong 7.7 \times 10^{-3}$, a value which differs substantially from that obtained previously.[6] The discrepancy in results[9] is most easily accounted for by postulating a dependence of the apparent equilibrium constant on concentration, the previous work having been carried out at much lower concentrations, *ca.* 10^{-3} *M*.

The observation that the alkoxide–alcohol ratio appears to be roughly invariant with total concentration suggests that the equilibrium described in eq 1 is not an adequate description of the system. If the active concentration of $CH_3SOCH_2^-$ remained roughly constant, however, then the results at all concentrations could be accommodated. Such behavior would be expected if the $CH_3SOCH_2^-$ were aggregated and only monomeric species were active in the equilibrium. Aggregation effects in kinetic measurements in DMSO are well documented,[10] but effects in equilibrium measurements have not previously been observed. The aggregation model requires that the alkoxide behave normally in the concentration range observed; kinetic measurements[10] suggest that this would indeed be the case.[11]

Aggregation of $CH_3SOCH_2^-$ would also explain the magnitude of the equilibrium constant ($K \cong 200$) obtained by Corey and Chaykovsky[2b] for the reaction between triphenylmethane and $CH_3SOCH_2^-$ in DMSO, eq 2. Using ultraviolet techniques, Steiner and Gilbert[13] obtained a value of $K = 1.3 \times 10^4$. Ritchie and Uschold[5] found a value of $K = 1.6 \times 10^4$. As there were some doubts[14] about the validity of the D_2O quenching method used by Corey, the discrepancy was not explored.

$$CH_3SOCH_2^- + Ph_3CH \rightleftharpoons CH_3SOCH_3 + Ph_3C^- \quad (2)$$

We have reexamined eq 2 at relatively high (0.1 *M*) concentration by direct measurement of the concentrations of Ph_3CH and Ph_3C^- by nmr, and find $K \cong 250$ in agreement with Corey and Chaykovsky.[2b] Thus, in this equilibrium, the ratio of Ph_3C^- to Ph_3CH remains relatively independent of concentration, a result similar to that found for eq 1. It is satisfying that the phenomenon appears in this case as well; the data in both experiments are accommodated by the same aggregation model.

The observation of unusually large amounts of $CH_3SOCH_2^-$ in concentrated alkoxide solutions is significant in terms of the equilibrium composition of these solutions. It helps to account for the anomalously high apparent acidity of DMSO under these conditions of high base concentration, and for the great ease with which $CH_3SOCH_2^-$ can be trapped. Finally, it helps in understanding some of the discrepancies previously observed in these systems.

Acknowledgment. We are grateful to the National Science Foundation (GP-10621) and to donors of the Petroleum Research Fund, administered by the American Chemical Society (2917-A4), for support of this work.

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(6) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 2960 (1967).

(7) Ledwith and McFarlane[4b] attempted to measure this equilibrium by means of uv spectroscopy. However, their solutions were prepared from potassium metal, and it has been demonstrated (D. E. O'Connor and W. I. Lyness, *J. Org. Chem.*, **30**, 1620 (1965)) that solutions prepared in this way contain many impurities. Thus the uv band assigned to $CH_3SOCH_2^-$ may belong to another species, or may result from the overlapping of a band for $CH_3SOCH_2^-$ and a band for some other substance. The results obtained by Ledwith and McFarlane are incompatible with the results obtained by Steiner and by Ritchie in similar experiments using uv spectroscopy.

(8) Solutions of $CH_3SOCH_2^-$ prepared from potassium amide in DMSO contain a Raman band at *ca.* 860 cm^{-1} which is absent in the spectrum of DMSO. (Ritchie and Uschold[6] have observed an ir band for $CH_3SOCH_2^-Cs^+$ at *ca.* 850 cm^{-1}.) This band is also present in the Raman spectrum of a solution of *tert*-BuO^-K^+ in DMSO. The band can barely be observed in solutions made from 0.65 *M tert*-BuO^-K^+ and 1.95 *M tert*-BuOH. That the band is not due to alkoxide is deduced from its substantial diminishment in solutions of *tert*-BuO^-K^+ in DMSO containing appreciable amounts of *tert*-BuOH. By comparing the relative peak heights of the 860 cm^{-1} band and two bands of DMSO, we estimate *ca.* 0.2 *M* $CH_3SOCH_2^-$ in a solution made from 0.57 *M tert*-BuO^-K^+. Measurements were made with a Spex Ramalog, using the 4880-Å line of an argon laser for excitation.

(9) The difference in results is substantially greater than experimental error. In both experiments, the measurable amounts of species present require that the observed *K* be approximately correct.

(10) A. Schriesheim and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **84**, 3160 (1962); J. E. Hofmann, R. J. Muller, and A. Schriesheim, *ibid.*, **85**, 3000 (1963). For similar effects in other solvents see T. E. Hogen-Esch and J. Smid, *ibid.*, **89**, 2764 (1967); A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *ibid.*, **84**, 244 (1962); A. Streitwieser, Jr., R. A. Caldwell, M. R. Granger, and P. M. Laughton, *J. Phys. Chem.*, **68**, 2916 (1964).

(11) On the other hand, the rate of proton exchange between DMSO and $CH_3SOCH_2^-$ appears[12] to be first order in $CH_3SOCH_2^-$ in the concentration range 0.1–1 *M*. This solvent–lyate reaction may, however, be a poor model for comparison.

(12) J. I. Brauman and N. J. Nelson, *J. Amer. Chem. Soc.*, **88**, 2332 (1966).

(13) E. C. Steiner and J. M. Gilbert, *ibid.*, **85**, 3054 (1963).

(14) C. D. Ritchie and R. Uschold, *ibid.*, **86**, 4488 (1964). Also see ref 4b and 13. Control experiments have subsequently demonstrated that quenching carbanion solutions by slow addition to a well-stirred excess of D_2O is a valid method: D. F. McMillen, Ph.D. Dissertation, Stanford University, 1967.

(15) Alfred P. Sloan Fellow, 1968–1970; to whom correspondence should be addressed.

(16) National Science Foundation Predoctoral Fellow, 1966–1970.

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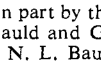
Reduction of *cis*- and *trans*-Tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene with Lithium. Cleavage of the Central Bond of a 1,3-Diene[1]

Sir:

The esr spectrum obtained during the electrolysis of 1,2-dimethylenecyclobutane (**1**) was initially interpreted by Bauld and Stevenson[2a] as arising from the radical anion of 2,2′-diallylene (**2**).[3] Subsequently,



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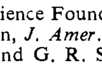

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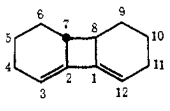
(1) Supported in part by the National Science Foundation (GP8181).

(2) (a) N. L. Bauld and G. R. Stevenson, *J. Amer. Chem. Soc.*, **91**, 3675 (1969); (b) N. L. Bauld, F. Farr, and G. R. Stevenson, *Tetrahedron Lett.*, 625 (1970).

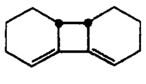
(3) Following Berthier,[3b] we will refer to the parent species (C_6H_8) as 2,2′-diallylene, and use the general term diallylene for molecules of this type. (b) G. Berthier, *J. Chim. Phys. Physicochim. Biol.*, **52**, 141 (1955).

based on electrolysis–esr results obtained with methyl derivatives of **1**, Bauld, Farr, and Stevenson[2b] have revised this interpretation and now conclude that in all cases the esr signals they observe arise from the radical anions of the parent substances, *e.g.*, **3**.[4]

We have examined the possibility of such ring opening employing "chemical" reduction of *trans*- and *cis*-**4**.[5] Upon reduction with sodium in liquid ammonia, *trans*-**4**

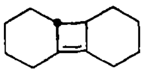


trans-**4**



cis-**4**

gives **5**,[5a] while *cis*-**4** gives **6**. The difference in the course of reduction might be rationalized after the fact,



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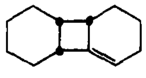

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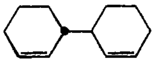
but the important point here is the complete absence of ring-opened products. This absence might simply mean that the radical anions of the dienes are quenched so rapidly by proton transfer from ammonia that opening cannot compete. Hence we examined aprotic reduction.

Treatment of a dilute solution of *trans*-**4** in anhydrous ether with a large excess of lithium dispersion at 25–35° followed by removal of excess lithium and quenching with water did in fact lead to ring opening. But the product, in yields as high as 97%, was *dl*-3,3′-bicyclohexenyl (**7**), a compound which can result only by *cleavage of the* C^1–C^2 *bond, the central bond of the 1,3-diene system of trans*-**4**.



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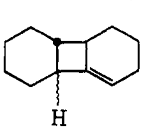
This result suggested that the 2,2′-dilithium derivative of **7** had been formed, a possibility which was established by quenching with deuterium oxide.[6] When various changes[7] in the reaction conditions were examined, in addition to **7** (generally the major product), varying amounts of **5**, **8**, and **9** were obtained. The last



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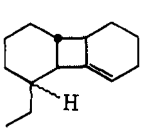

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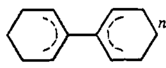
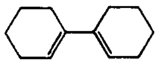
three products can be explained in terms of addition to the radical anion and/or the dianion of *trans*-**4**.[8] We believe that if opening to a diallylene radical anion **10** had occurred, **10** would have been reduced to the dianion **11**. Protonation of **11** should give 1,1′-bicyclohexenyl (**12**), but glc analysis established that no more than 1% of the latter could have been formed.



10, $n = 1$ **11**, $n = 2$



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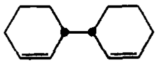
Reduction of *cis*-**4** under a variety of conditions has given **6**, **13**, and **14** as the major products. Although the product ratios have varied with the conditions,



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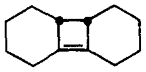

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meso-3,3′-bicyclohexenyl (**13**), the product of "abnormal" cleavage, typically has been obtained in 15–25% yields. The maximum amount of **12** that could have been formed in any case was less than 2% (generally <1%).

Orbital symmetry considerations show that the allowed opening of both the mono- and dianion of a 1,2-dimethylenecyclobutane to the corresponding diallylene ion (*e.g.*, **10** or **11**) is conrotatory. Thus *trans*-**4** would be expected to open more readily than *cis*-**4**. But neither compound opens in the diallylene sense. This failure to open could mean that the reactions would be endothermic—a probable event for the monoanions, but possibly not for the dianions. However, even if the opening were exothermic, it could be slow. If the dianion of *trans*-**4** were regarded as the product of the 1,4 addition of lithium (3,12-dilithio-**5**), opening might be expected to be slow inasmuch as the (allowed, exothermic) isomerization of **5** to **12** has an activation energy of 29 kcal/mol.[9]

While the opening of four-membered rings in organometallic compounds has been observed before,[10] the remarkable carbon–carbon bond cleavage leading to **7** and **13** has little precedent. We believe that this bond breaking occurs at the dianion stage. Support for this view comes from the observation that reduction of *trans*-**4** at −78° (with activated lithium) followed by quenching at that temperature gives **5**, **8**, and **9**, but no **7**. Warming to room temperature prior to quenching gives major amounts of **7**, indicating that the dianion of *trans*-**4** is formed at −78° but opens only at higher temperatures.

The breaking of the C_1–C_2 bond of the dianion of **4** (either isomer) reflects orbital energies and ring strain. While putting two electrons into an antibonding orbital of **4** increases the bond order between the central carbon atoms, it *decreases* the net π bonding of the diene system; in effect, partial bond breaking occurs. Additionally, opening the four-membered ring must relieve strain to the extent of at least 25 kcal/mol.

Applying orbital symmetry considerations to the opening of a 1,2-dimethylenecyclobutane dianion to the corresponding divinyl dianion indicates that nonrotatory and disrotatory openings are forbidden, but that conrotatory opening is allowed. Structural re-

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(4) The high hyperfine splittings attributed to the ring methylenes of 3 and the magnetic equivalence of all eight protons remain to be explained.

(5) (a) W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, **92**, 5469 (1970); (b) W. R. Moore, L. N. Bell, and G. P. Daumit, submitted for publication.

(6) The dilithium reagent attacks the solvent fairly rapidly, but 100% deuterium incorporation was obtained when the reduction was carried out in the presence of several equivalents of *n*-butyllithium, which apparently stabilizes the dilithium reagent.

(7) The lithium was activated by reaction with a 1,2-dibromoalkane; one or more of the following were added: tetrahydrofuran, lithium bromide, lithium iodide, ethylene, isobutylene; and the reaction was performed at −78°.

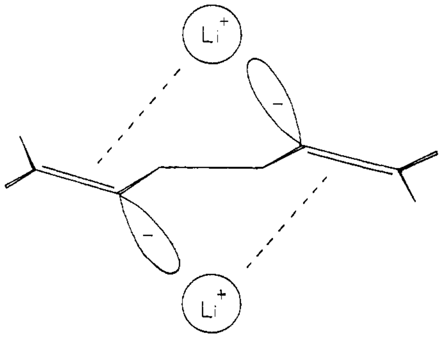
(8) Compound **9** results from the addition of ethylene to either the mono- or dianion of *trans*-**4**.

(9) R. Criegee and H. G. Reinhardt, *Chem. Ber.*, **101**, 102 (1968).

(10) E. A. Hill, H. G. Richey, and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963).

strictions, especially for *trans*-**4**, cause conrotatory opening of dienes **4** to be mainly a scissors-opening motion with rotation about the C_7–C_8 bond.

Actually, the dianions are not "free"; they must be tightly coordinated with lithium ions. Such coordination could facilitate bond breaking. If a dimethylenecyclobutane dianion were coordinated with two lithium ions, both centered on the diene system, but one above and one below the molecular plane, con-



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rotatory opening (to a dihedral angle of *ca.* 45°) would lead to a quadrupole-like structure, **15**, an arrangement which should be energetically highly favorable. Additionally, in **15** each lithium ion would be close to and thus should be coordinated by the π electrons of the adjacent double bond.

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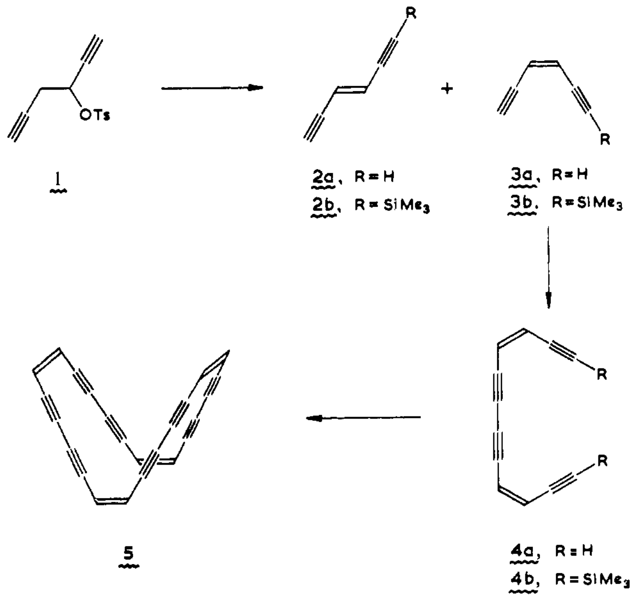
1,3,7,9,13,15,19,21-Octadehydro[24]annulene and Its Anions[1]

Sir:

We report the synthesis of the nonplanar 1,3,7,9,-13,15,19,21-octadehydro[24]annulene (**5**), and its conversion to the planar-delocalized radical anion **6** and dianion **7**. The aromatic character of the 26 out-of-plane π-electron dianion **7**, the first dianion of a dehydroannulene to be prepared,[2] is in contrast to the nonaromatic character of the neutral 26π-electron system tridehydro[26]annulene.[3]

A mixture of *trans*- and *cis*-3-hexene-1,5-diyne (**2a**–**3a**, ~3:2) in ether solution, prepared from 1,5-hexadiyn-3-ol *p*-toluenesulfonate (**1**) as described previously,[4] was treated with ethylmagnesium bromide (~1.7 mol equiv) in tetrahydrofuran and then with chlorotrimethylsilane (~1.8 mol equiv) at room temperature. Distillation, followed by chromatography of the stereoisomeric



mono(trimethylsilyl) derivatives on silica gel, gave 25% (based on **1**) of the trans compound **2b** [liquid, >98% pure by glc; $\lambda_{\max}^{\mathrm{EtOH}}$ 249 sh (ϵ 15,200), 254 sh (18,400), 261 (26,800), and 276 nm (25,600)][5] and then 14% (based on **1**) of the cis compound **3b** [liquid, >98% pure by glc; $\lambda_{\max}^{\mathrm{EtOH}}$ 249 sh (ϵ 10,200), 254 sh (11,400), 261 (16,400), and 276 nm (15,600)].[5,6] Substances **2b** and **3b** were much more stable than **2a** and **3a**, and are convenient derivatives for separation, storage, and further transformations.

Compound **3b** in acetone containing *N,N,N′,N′*-tetramethylethylenediamine and cuprous chloride was coupled by shaking with oxygen at room temperature.[7] Chromatography on silica gel gave 70% of the "dimer" **4b** as a yellow oil, homogeneous to tlc: $\lambda_{\max}^{C_6H_{12}}$ 257 sh (ϵ 18,700), 265 (22,400), 279 (20,900), 295 (24,800), 302 sh (18,700), 312 (22,300), 317 (22,300), 324 sh (18,700), 340 (30,400), and 366 nm (29,700); mass spectrum, *m/e* 294.127 (calcd for $^{12}C_{18}{}^{1}H_{22}{}^{28}Si_2$: 294.126).[5]

Removal of the protecting groups of **4b** by the silver nitrate–potassium cyanide method[8] led to the unstable dienetetrayne **4a** [$\lambda_{\max}^{\mathrm{ether}}$ (>300 nm) 302.5 (ϵ 15,800), 310 sh (12,100), 323.5 (22,000), and 347 nm (21,200)[9]], which was coupled directly in ether and pyridine (1:1) with cupric acetate[10] at room temperature for 2 hr. Chromatography on alumina then yielded 20% (based on **4b**) of the octadehydro[24]annulene (**5**) as yellow-orange crystals (bright yellow in concentrated solution): explosion point ~130° (capillary); $\lambda_{\max}^{\mathrm{ether}}$ 243 (ϵ 50,600), 248 (50,400), 307 sh (27,400), 317 sh (29,500), 329 (38,900), 341 (38,300), and 352 nm (45,100); $\nu_{\max}^{\mathrm{CHCl_3}}$ 2110 (w) cm^{-1} ($C{\equiv}C$); nmr spectrum (THF-d_8, 100 MHz), τ 3.85 (sharp s). The solid substance was

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[1] Unsaturated Macrocyclic Compounds. LXXV. For part LXXIV, see G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, in press.

[2] For the synthesis of the radical anions of dehydroannulenes, see H. A. Staab and F. Graf, *Tetrahedron Lett.*, 751 (1966); *Chem. Ber.*, **103**, 1107 (1970); N. M. Atherton, R. Mason, and R. J. Wratten, *Mol. Phys.*, **11**, 525 (1966).

[3] C. C. Leznoff and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 4247 (1967). See also M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 685 (1965).

[4] W. H. Okamura and F. Sondheimer, *ibid.*, **89**, 5991 (1967).

[5] The nmr and infrared spectra, as well as the elemental analysis or high-resolution mass spectrum, were in accord with the assigned structure.

[6] Further amounts of **3b** could be obtained by photolysis of **2b** in pentane with a Hanovia low-pressure mercury vapor lamp at 0°, which led in ~80 , yield to an equilibrium mixture of **2b** and **3b** (~2:3).

[7] See A. S. Hay, *J. Org. Chem.*, **27**, 3320 (1962); R. Eastmond and D. R. M. Walton, *Chem. Commun.*, 204 (1968).

[8] J. F. Arens and H. M. Schmidt, *Recl. Trav. Chim. Pays-Bas*, **86**, 1138 (1967).

[9] The ϵ values represent minimum ones, due to the instability of the substance.

[10] See G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).