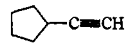
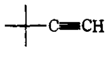
Table I. Yields of Dienes Derived from Various Alkynes

Alkyne	Hydroalumination temp, °C[a]	Diene	Yield, %[b,c]
$C_4H_9C{\equiv}CH$	50	*trans,trans*-5,7-Dodecadiene	73 (78)
	50	1,4-Dicyclopentyl-*trans,trans*-1,3-butadiene	68 (83)
	25	2,2,7,7-Tetramethyl-*trans,trans*-3,5-octadiene	67 (87)
$C_2H_5C{\equiv}CC_2H_5$	70	4,5-Diethyl-*trans,trans*-3,5-octadiene	71

[a] In each case hydroalumination was carried out with diisobutylaluminum hydride in *n*-hexane for 4 hr. [b] The values in parentheses were obtained by glpc analysis using an internal standard. The other values are isolated yields. [c] The nmr, ir, uv, and mass spectral data were in agreement with the assigned structures.

stituted alkynes. Thus, treatment with cuprous chloride of the monohydroalumination product obtained from 3-hexyne yielded 71% 4,5-diethyl-*trans,trans*-3,5-octadiene. This novel dimerization procedure therefore complements the more time consuming synthesis of tetrasubstituted 1,3-dienes *via* dienylalane intermediates.[2]

The simplicity of the present procedure for the preparation of trans,trans dienes is illustrated by the following example. A dry 250-ml flask equipped with a thermometer, a condenser, a magnetic stirrer, and a side arm capped with a rubber septum was flushed with nitrogen. To the flask, which was kept under a static pressure of nitrogen, was added 8.2 g (0.10 mol) of 1-hexyne, 40 ml of *n*-hexane, and 18.6 ml (0.10 mol) of diisobutylaluminum hydride while maintaining the temperature during the addition at 25–30° by means of a water bath. The solution was stirred at room temperature for 30 min, then heated at 50° for 4 hr. After cooling the reaction mixture to room temperature, the *n*-hexane was removed under reduced pressure and 80 ml of dry tetrahydrofuran was added at 0°. Dry cuprous chloride (12.0 g, 0.12 mol) was added over a period of 10 min while maintaining the temperature between 25 and 35° (water bath). The resultant dark reaction mixture was kept for an additional 50 min at ambient temperature before being poured slowly into a mixture of 5% H_2SO_4 (100 ml) and *n*-pentane (100 ml) which had been precooled in an ice bath.[5] The organic phase was separated, and the aqueous layer was extracted repeatedly with *n*-pentane. The combined extracts (containing some of the black precipitate) were washed with aqueous sodium bicarbonate, then dried over anhydrous magnesium sulfate. Distillation gave 6.05 g (73%) of *trans,trans*-5,7-dodecadiene: bp 76° (3 mm); $n^{25}D$ 1.4635; uv (cyclohexane) 231 (ϵ 31,200), 226 (sh), and 237 mμ (sh).[6]

Although we have not established the nature of the intermediates undergoing dimerization, it is probable that the vinylalanes react with cuprous chloride to give the vinylcopper(I) compounds which then decompose to give the diene products. The formation of the 1,3-dienes by this reaction sequence is reasonable in light of the previously observed thermal decompositions of vinylcopper(I) compounds derived from vinyllithium[7] and vinylmagnesium derivatives[8] to dienes.

It is apparent that the facile conversion of the readily available vinylalanes of defined stereochemistry into other vinylmetallic compounds having different reactivities toward organic and inorganic reagents should be exceedingly useful in organic syntheses. We are currently exploring exchange reactions involving vinylalanes and various metal salts other than cuprous chloride.

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(5) The same isomeric purity of the diene was observed when the reaction mixture was decomposed with water.

(6) The corresponding *cis,cis*-dodecadiene is available by reduction of the appropriate diyne with dialkylboranes [G. Zweifel and N. L. Polston, *J. Amer. Chem. Soc.*, **92**, 4068 (1970)], whereas the cis,trans diene can be prepared from 1-hexyne *via* the hydroboration–iodination reaction (ref 3).

(7) G. M. Whitesides and C. P. Casey, *ibid.*, **88**, 4541 (1966).

(8) T. Kaufmann and W. Sahm, *Angew. Chem., Int. Ed. Engl.*, **6**, 85 (1967).

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Equilibrium Acidities in Dimethyl Sulfoxide

Sir:

The presence of methylsulfinyl carbanion, the conjugate base of dimethyl sulfoxide, in solutions of potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) has been inferred from kinetic data and trapping experiments, but previously it has not been possible to detect this anion spectroscopically in such solutions. The demonstration of the existence and measurement of the concentration of this species are of great importance in understanding the chemistry of solutions of alkoxides in DMSO, a medium widely used in base-catalyzed reactions.[1] We wish to report the direct observation, by means of Raman spectroscopy, of methylsulfinyl carbanion in DMSO.

Corey and Chaykovsky first prepared methylsulfinyl carbanion (dimsyl, $CH_3SOCH_2^-$) and they observed addition of this ion to benzophenone in DMSO.[2] Russell observed similar addition products in basic solutions prepared from potassium *tert*-butoxide in DMSO.[3] Products of $CH_3SOCH_2^-$ reactions in alkoxide solutions have also been found by Walling,[4a] Ledwith,[4b] and Schriesheim[4c] and their coworkers. Kinetic evidence for the presence of $CH_3SOCH_2^-$ has been obtained by the observation of the rapid exchange of the protons of DMSO in the presence of *tert*-butoxide.[5]

None of the above evidence provides much insight, however, into the amount of $CH_3SOCH_2^-$ present in alkoxide solutions in DMSO. Ritchie and Uschold[6,7]

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(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(2) E. J. Corey and M. Chaykovsky: (a) *J. Amer. Chem. Soc.*, **84**, 866 (1962); (b) *ibid.*, **87**, 1345 (1965).

(3) G. A. Russell, E. G. Jantzen, H.-D. Becker, and F. J. Smentowski, *ibid.*, **84**, 2652 (1962); G. A. Russell and H.-D. Becker, *ibid.*, **85**, 3406 (1963); G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

(4) (a) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963); (b) A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964); (c) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, 30, 3233 (1965).

(5) J. I. Brauman, N. J. Nelson, and D. C. Kahl, *J. Amer. Chem. Soc.*, **90**, 490 (1968); J. I. Brauman and N. J. Nelson, *ibid.*, **90**, 491 (1968).

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

$$\textit{tert}\text{-BuO}^-\text{K}^+ + \text{CH}_3\text{SOCH}_3 \rightleftharpoons \textit{tert}\text{-BuOH} + \text{CH}_3\text{SOCH}_2{}^-\text{K}^+ \quad (1)$$

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.

$$\text{CH}_3\text{SOCH}_2{}^- + \text{Ph}_3\text{CH} \rightleftharpoons \text{CH}_3\text{SOCH}_3 + \text{Ph}_3\text{C}^- \quad (2)$$

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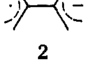
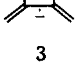
Reduction of *cis*- and *trans*-Tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene with Lithium. Cleavage of the Central Bond of a 1,3-Diene[1]

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,



2



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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).