

Fig. 2.—N.m.r. spectrum of isodicyclopentadiene in CCl_4 with tetramethylsilane as an internal reference. The spectrum integrals are given above each major band. The insert is a ten-fold expansion of the olefin resonance.

Structures III and IV both appear consistent with the observed ultraviolet spectrum, λ_{max} (*n*-pentane) $268 \text{ m}\mu$ ($\log \epsilon = 3.64$).¹¹

That the double bonds in isodicyclopentadiene are located as shown in II is indicated by the appearance of the n.m.r. spin-spin splitting pattern of the olefinic protons (Fig. 2). The cracking reaction which leads to dihydropentalene must, therefore, proceed by initial isomerization of isodicyclopentadiene to V, which then undergoes a reverse Diels-Alder reaction (eq. 1). The facility of double bond isomerization in the cyclopentadiene series is expected on the basis of known precedents.¹⁴

Acknowledgments.—We are grateful to Larry Parker and Barbara Wirth for assisting in the organic syntheses, and to the National Science Foundation (NSF G-15561) and the Socony Mobil Oil Co. for financial support.

(11) For cyclopentadiene in *n*-heptane $\lambda_{\text{max}} = 244 \text{ m}\mu$ ($\log \epsilon = 3.40$),¹² while for dimethylfulvene in iso-octane $\lambda_{\text{max}} = 265 \text{ m}\mu$ ($\log \epsilon = 3.9$).¹³

(12) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 1803 (1958).

(13) M. T. Murphy and A. C. Duggan, *J. Am. Chem. Soc.*, **71**, 3347 (1949).

(14) For example, the reaction of indene with maleic anhydride which yields a normal Diels-Alder adduct of isoindene¹⁵; the reverse Diels-Alder reactions of dicyclopentadienol-1¹⁶ and its acetate¹⁷ which yield mixtures of double bond isomers.

(15) K. Alder, F. Pascher and H. Vagt, *Chem. Ber.*, **75**, 1501 (1942).

(16) M. Rosenblum, *J. Am. Chem. Soc.*, **79**, 3179 (1957); K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

(17) R. E. Vanelli, Dissertation (Harvard, 1950); C. J. Norten, Dissertation (Harvard, 1955).

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RECEIVED JANUARY 26, 1962

METHYLSULFINYL CARBANION

Sir:

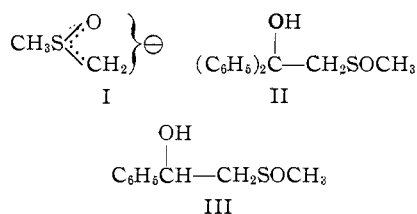
Little is known about the chemical reactivity of carbanions substituted by a single alkylsulfinyl

group although there is evidence that the interaction of this function with adjacent negative charge produces appreciable stabilization, intermediate in degree between that associated with nitro, carbonyl, sulfonyl, *etc.*, on the one hand and hydrogen (*vs.* alkyl) on the other.¹ We have found that the parent member of this class, methylsulfinyl carbanion (I), the conjugate base of dimethyl sulfoxide, is simply generated, highly reactive and sufficiently promising in a wide variety of applications to warrant preliminary mention here. For various reasons including the great reactivity of the anion no attempt has been made as yet to obtain it in the form of crystalline salts. The present investigations were carried out with freshly prepared solutions of sodium methylsulfinylcarbanion in dimethyl sulfoxide which were formed from reaction of powdered sodium hydride with excess dry dimethyl sulfoxide (500–600 ml. per mole of sodium hydride) at 65–70° under nitrogen with stirring until evolution of hydrogen is complete (*ca.* 45 minutes).² The formation of anion was verified by reaction with an equimolar amount of benzophenone to give the hydroxy sulfoxide II, m.p. 148–148.5°, in 86% yield; analogous reaction with benzaldehyde afforded III as a mixture of diastereomers, m.p. 78–123°.³

(1) See, for example, (a) H. H. Szmant in "Organic Sulfur Compounds," Vol. I, edited by N. Kharasch, Pergamon Press, New York 22, N. Y., 1961, pp. 154–169; (b) A. Schöberl and A. Wagner in "Methoden der Organischen Chemie (Houben-Weyl)," 4th Ed., Georg Thieme Verlag, Stuttgart, Vol. IX, p. 211 (1955); (c) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957).

(2) The sodium salt also can be made using sodium amide; the lithium salt is available starting from lithium hydride. Dimethylsulfoxide was dried by distillation from calcium hydride under reduced pressure (*ca.* 1 mm.).

(3) Acceptable elemental analyses have been obtained for all new compounds reported herein along with sufficient physical data (infrared, ultraviolet, and nuclear magnetic resonance spectra) to define structure.



The methylsulfinyl carbanion is strongly basic as is shown by its rapid reaction with triphenylmethane to produce a deep red solution of triphenylcarbanion. An approximate equilibrium constant for this reaction was determined by deuteration of mixtures from known amounts of the starting reagents with excess deuterium oxide and measurement of the ratio triphenylmethane: triphenylmethane- d_1

$$K_{\text{eq}} = \frac{[(\text{C}_6\text{H}_5)_3\text{C}^-][\text{CH}_2\text{SOCH}_3]}{[\text{CH}_2\text{SOCH}_3^-][(\text{C}_6\text{H}_5)_3\text{CH}]} = 21 \pm 4 (25^\circ)$$

Equilibrium for this proton transfer is attained in less than 15 minutes at 25°.

The reactivity of I is sufficient to effect the conversion of phosphonium salts to ylides thereby permitting an extremely simple and convenient modification of the Wittig reaction. Thus, the interaction of sodium methylsulfinylcarbanion with one equivalent of ethyl triphenylphosphonium bromide at room temperature led to formation of ethylidene-triphenylphosphorane as shown by color change and by the reaction with benzophenone (0.85 equivalent) to give 1,1-diphenylpropene-1, m.p. 49°,⁴ in 97.5% yield after 3 hours at 25° and 1.5 hours at 60°.

Chlorobenzene reacts at room temperature with an excess of sodium methylsulfinyl carbanion (6.7 equivalents) with spontaneous evolution of heat to yield methyl benzyl sulfoxide, m.p. 55–56°⁵; when a smaller excess (2.5 equivalents) of the anion is employed considerable amounts of methyl benzhydryl sulfoxide, m.p. 115–116°, result. In view of the strongly basic nature of the carbanion it is quite possible that substitution occurs *via* benzyne, in which case applications of I in this area can be envisioned.

We have not as yet had occasion to study the base-catalyzed generation of other types of reactive species, *e.g.*, carbenes, with this system. However, it might be noted that the reaction of benzyl chloride with sodium methylsulfinyl carbanion at room temperature produces *trans*-stilbene as the major product (together with an oily mixture of sulfoxides).

In spite of the high reactivity of the anion I in carbonyl addition as evidenced by the rapid formation of II from benzophenone, reaction with enolizable ketones seems to occur preferentially by proton transfer affording enolates which are stable to further attack by the reagent, the starting ketone being recovered unchanged after acidification. Such proton transfer predominates heavily with desoxybenzoin, cyclohexanone, 4-phenylcyclohexanone and norcamphor but to a lesser extent with camphor, which affords substan-

tial amounts (28%) of carbonyl addition product (as a mixture of isomers, m.p. 94–130°).

The fact that the anion I is even more basic than trityl anion together with the recently published findings that base-catalyzed reactions occur at greatly enhanced rates in dimethyl sulfoxide as solvent^{6,7} can be taken as an indication of the potency of the methylsulfinyl carbanion-dimethyl sulfoxide system. Further studies of I and also of some other sulfinyl carbanions are in progress.

We are indebted to the National Institutes of Health for a grant which supported this work.

(6) D. J. Cram, B. Rickborn and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

(7) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

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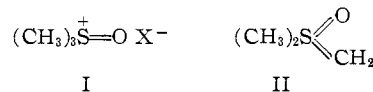
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RECEIVED JANUARY 8, 1962

DIMETHYLSULFOXONIUM METHYLIDE

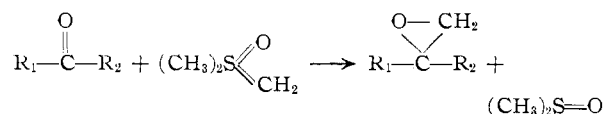
Sir:

We have observed that the readily accessible trimethylsulfoxonium halides^{1,2} (I) undergo proton transfer to strong base with formation of a reactive substance of considerable utility in synthesis which can reasonably be formulated as dimethylsulfoxonium methylide (II) on the basis of chemical data.



Solutions of II in dimethyl sulfoxide were prepared from the iodide or chloride I by stirring with one equivalent of powdered sodium hydride under nitrogen at room temperature (rapid evolution of hydrogen, exothermic). The ylide II also can be obtained in tetrahydrofuran by reaction of the more readily soluble chloride I in that solvent with powdered sodium hydride at reflux.

One of the most striking properties of II is its reactivity toward ketones and aldehydes which in many instances takes the form



Epoxides have been produced by this process from benzophenone (90%), 4-phenylcyclohexanone (72%), cycloheptanone (71%) and benzaldehyde (56%). Most of these reactions were carried out with a small excess of II at 25° for one hour, then a further hour at 50°.³ Certain ketones appear resistant to the transformation, in particular desoxybenzoin and Δ^4 -cholestenone, probably as a consequence of an enhanced tendency to form enolate ions by proton transfer to II.⁴

(1) R. T. Major and H. J. Hess, *J. Org. Chem.*, **23**, 1563 (1958).

(2) R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958).

(3) Satisfactory analytical data were obtained on all products described herein.

(4) Such resistance to epoxide formation may disappear under other conditions, a point now under investigation. However, it may prove useful in cases where selectivity is required.

(4) A. Klages, *Ber.*, **35**, 2646 (1902).

(5) S. Hünig and O. Boos, *Ann.*, **570**, 23 (1953).