some hyperfine splitting by the phenyl hydrogens may be uncovered with further resolution.[14] In support of this, possible side band structure was noted in the spectrum of I from the present work. Further investigation of this point is planned.

Helpful discussions with Dr. W. M. Jones and Dr. W. S. Brey, Jr., of this department, are gratefully acknowledged.

[14] Reitz recently has resolved the e.s.r. spectrum of pentaphenylcyclopentadienyl into at least 33 lines separated by 0.3 gauss. The pattern observed is that expected for the ratios of spin densities in an odd-alternant radical such as the triphenylmethyl radical, but the magnitude of the splitting is best accounted for by twisted phenyl rings [D. C. Reitz, *J. Chem. Phys.*, **34**, 701 (1961)].

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA
MERLE A. BATTISTE

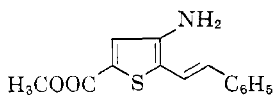
RECEIVED AUGUST 3, 1962

A DERIVATIVE OF BORAZARENE[1]

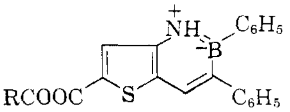
Sir:

We wish to report the first synthesis of a derivative of borazarene.[2] Reduction of methyl 2-styryl-3-nitrothiophene-5-carboxylate[3] with tin and hydrochloric acid gave methyl 2-styryl-3-aminothiophene-5-carboxylate (I), isolated as its acetyl derivative, m.p. 203–203.5°. *Anal.* Calcd. for $C_{16}H_{15}NO_3S$: C, 63.8; H, 4.98; N, 4.65. Found: C, 63.7; H, 4.9; N, 4.75. Condensation of (I) with phenyl dichlorobornite gave 2-carbomethoxy-5,6-diphenyl-5,4-borazarobenzothiophene (IIa). The product crystallized as pale yellow needles from a solution of benzene and methylene chloride, m.p. 200–201°, $\lambda_{\max}^{\text{EtOH}}$ 222 mμ (ε 20,100), 240 mμ (ε 17,1780), 286 mμ (ε 14,930), 310 mμ (ε 10,310), 355 mμ (ε 25,500). *Anal.* Calcd. for $C_{20}H_{16}NO_2BS$: C, 69.6; H, 4.69; N, 4.1. Found: C, 69.7; H, 4.69; N, 4.2.

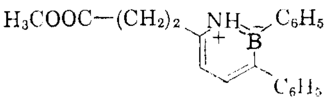
This is the first sulfur-containing heteroaromatic boron compound of this type to be reported. Hydrolysis of (IIa) with methanolic sodium hydroxide gave the corresponding acid (IIb), m.p. 205°. *Anal.* Calcd. for $C_{19}H_{14}NO_2BS$: C, 68.9; H, 4.23; N, 4.23. Found: C, 68.9; H, 4.15; N, 4.15.



I



IIa, R = CH₃
b, R = H



III

Attempts to desulfurize (II) with freshly prepared active Raney nickel[4] by the method of Blicke and Sheets[5] failed to give any new compound; however, reactions of (II) with samples of Raney nickel that had been prepared some months earlier gave excellent yields (80–85%) of 2,3-diphenyl-6-(2-carbomethoxy-ethyl)-2,1-borazarene (III), m.p. 110–110.5°, $\lambda_{\max}^{\text{EtOH}}$ 220 mμ (ε 18,450), 275 mμ (ε 10,970), 306 mμ (ε 15,850). *Anal.* Calcd. for $C_{20}H_{20}NO_2B$: C, 75.7; H, 6.39; N, 4.42. Found: C, 75.52; H, 6.39; N, 4.55. No change was observed in the ultraviolet spectrum of (III) in absolute ethanol in the presence of acid or alkali over a period of a week. The latter evidence, and the fact that the double bonds in the borazarene ring remained intact during the desulfurization of (II), indicate that (III) is an aromatic compound of considerable stability.

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[1] This work has been supported by the Atomic Energy Commission under Contract No. A.E.C. 889.

[2] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959), suggested that borazarobenzene should be given the trivial name borazarene. Since 2,1-borazarobenzene is expected on theoretical grounds to be much more stable than the 3,1- or 4,1-isomers, we suggest that the name "borazarene" apply only to the 2,1-isomer. The other isomers could be called β-borazarene and γ-borazarene (*cf.* tropolone, β-tropolone and γ-tropolone).

[3] I. J. Rinkes, *Rec. Trav. Chim.*, [4] **52**, 538 (1933).

[4] R. Mozingo, D. E. Wolfe, S. A. Harris and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

[5] F. F. Blicke and D. G. Sheets, *ibid.*, **71**, 4010 (1949).

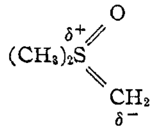
GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS
MICHAEL J. S. DEWAR
PETER A. MARR

RECEIVED JULY 27, 1962

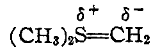
DIMETHYLSULFONIUM METHYLIDE, A REAGENT FOR SELECTIVE OXIRANE SYNTHESIS FROM ALDEHYDES AND KETONES

Sir:

As a result of the general synthetic utility of dimethyloxosulfonium methylide (alternatively dimethylsulfoxonium methylide) (I) as a reagent for the addition of methylene to double bonds which are receptive to nucleophiles,[1] a study of the related dimethylsulfonium methylide (II) seemed appropriate despite indications that sulfonium ylides derived from non-stabilized carbanions are subject to rapid spontaneous decomposition[2] while those in a highly stabilized condition, *e.g.*, 9-fluorenyl derivatives,[3] are of very limited synthetic import. This report summarizes the first returns of such an investigation including a practical method for the generation of the ylide II in a reasonably stable condition and the application of this substance as a reactive but *exceedingly selective* methylene transfer agent.



I


$$(CH_3)_2\overset{\delta+}{S}{=}\overset{\delta-}{C}H_2$$
II

Solutions of dimethylsulfonium methylide were prepared successfully by addition of a solution of trimethylsulfonium iodide with stirring to a solution of methylsulfinylcarbanion[4] in equivalent amount under nitrogen, as was the case with the oxosulfonium ylide I[1] except that it was necessary to conduct the reaction at lower temperatures (0 to −10° in dimethyl sulfoxide containing enough tetrahydrofuran to prevent freezing) be-

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[1] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).

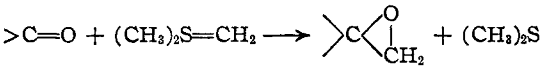
[2] *Cf.* V. Franzen, H.-J. Schmidt and C. Mertz, *Ber.*, **94**, 2942 (1961).

[3] A. W. Johnson and R. B. LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

[4] E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962).

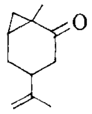
cause of the marked thermal instability of II. In contrast to the oxosulfonium ylide I which can be stored in tetrahydrofuran solution (under nitrogen) for several days at 25° without appreciable decomposition, the sulfonium ylide II decomposes with a half life of a few minutes at room temperature.[5] At 0° or below the stability of II is much greater, and since the process of ylide formation appears to be instantaneous, it is possible to conduct subsequent reactions without significant loss of the reagent by the immediate addition of the appropriate substrate with continued cooling.

The ylide II reacts with a wide variety of aldehydes and ketones by overall methylene transfer to form oxiranes, a process observed previously in many instances with the oxosulfonium ylide I. After a standard reaction time of 10 minutes at 0° and 30–60 minutes for warming to room temperature, the carbonyl compounds studied were consumed completely using 1.1 to 1.2 equivalents of ylide. Thus several compounds were converted to the corresponding oxiranes by selective addition of methylene to the carbonyl group: benzophenone

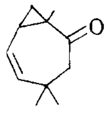


$$>C=O + (CH_3)_2S=CH_2 \longrightarrow >C\langle{}^{O}_{CH_2} + (CH_3)_2S$$

(84% yield), benzaldehyde (75%), cycloheptanone (97%), carvone (89%), eucarvone (93%), benzalacetophenone (87%) and pulegone (90%).[6] The only case studied in which the ketone–epoxide conversion was not observed with II was desoxybenzoin (enolate formation). However, an important difference between I and II can be discerned, *viz.*, that the sulfonium ylide selectively affords oxiranes even in the case of α,β-unsaturated carbonyl compounds which behave as Michael receptors with the oxosulfonium ylide. Thus, in contrast with the above results these ketones interact with I to form cyclopropanes: benzalacetophenone (95%),[1] carvone (81% to III) and eucarvone (88% to IV).[7]



III



IV

As expected from relative stabilities of I and II and from data on rates of base-catalyzed hydrogen-deuterium exchange for the corresponding conjugate acids,[8,9] the sulfonium ylide is a far more powerful methylene transfer agent than the oxosulfonium ylide. Thus, the reaction of 5 equivalents of II with 1,1-diphenylethylene effects 60% conversion to 1,1-diphenylcyclopropane, whereas there is no methylene transfer from I under the same conditions. Neither ylide reacts with tolane or *trans*-stilbene. The sulfonium ylide II converts benzalaniline to 1,2-diphenylazirane readily (91% yield) at low temperatures; the oxosulfonium ylide I reacts more slowly and gives a mixture of 1,2-diphenylazirane and acetophenone anil (ratio *ca.* 2:1).

The extension of this investigation to the transfer of substituted methylenes will be discussed in subsequent publications. It is already apparent that this approach presents new opportunities in organic synthesis because of the variegated uses of oxiranes and the many different sulfonium ylides potentially available; the complementary relationship to other reagents for methylene transfer[1,10,11,12] is clear.

This work was supported generously by a grant from the National Institutes of Health.

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[5] This interesting decomposition, which proceeds with the copious evolution of ethylene, will be described in greater detail in due course.

[6] 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. Previously known compounds were identified by comparison with authentic material.

[7] It is of note that the hydrogenation of IV with palladium-charcoal in methanol produces both 2,2,6,6-tetramethylcycloheptanone and 3,3,8-trimethylcycloöctanone (ratio 3:1).

[8] S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

[9] W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **77**, 521 (1955).

[10] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[11] U. Schöllkopf and A. Lerch, *Angew. Chem.*, **73**, 27 (1961).

[12] *Cf.* also W. Kirmse, *ibid.*, **73**, 161 (1961).

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.
E. J. COREY
MICHAEL CHAYKOVSKY

RECEIVED AUGUST 31, 1962

INTRAMOLECULAR BIFUNCTIONAL CATALYSIS OF AMIDE HYDROLYSIS

Sir:

In a previous communication from this laboratory[1] it was shown that a phenyl ester is highly activated if it is placed between two carboxyl groups, one of which is ionized. With an ester of this type the solvolysis rate has the bell-shaped pH dependence characteristic of many enzyme catalyzed reactions, and is a maximum at a pH corresponding to the maximum concentration of the singly ionized species. We have now demonstrated a similar effect with compound I whose pH-reactivity profile is shown in Fig. 1.

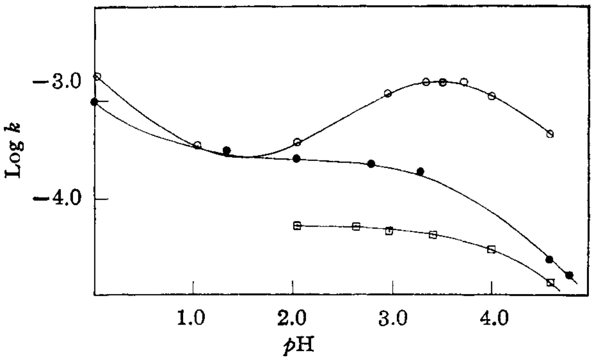

Fig. 1.—Hydrolysis of (I), *o*-carboxyphthalanilic acid, ⊙; (II), phthalanilic acid, ●; and (IV), *p*-carboxyphthalanilic acid, ⊡; at 25.8°; full drawn lines calculated using the constants in Table I.

It may be shown that the change of the *pseudo-first* order rate constant with hydrogen ion activity a_H should be given by

$$k_{obs} = \frac{(k_1K_1 + k_2K_2)a_H + k_3(a_H)^2}{(a_H + K_1)(a_H + K_2)} + k_4a_H \quad (1)$$

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[1] H. Morawetz and I. Oreskes, *J. Am. Chem. Soc.*, **80**, 2591 (1958).