of water led to the observation of 14 mmoles of nonanal and 2 mmoles of a minor isomer, presumably 4-methyloctanal, arising from the minor amount of secondary alkyl groups in the borane.[3,4] Consequently, it is quite clear that the initial reaction produces an intermediate, such as the enol borinate shown (I), which is converted to the free aldehyde only by water or some other material containing protolytic hydrogen.

The following procedure is representative. A 200-ml flask fitted with an inlet carrying a rubber septum cap, a magnetic stirring bar, and a condenser was flushed with nitrogen. In the flask was placed 40 mmoles of borane in 20 ml of tetrahydrofuran solution at room temperature. Then 120 mmoles of cyclohexene in 20 ml of tetrahydrofuran was added to form the tricyclohexylborane. The mixture was stirred at 50° for 3 hr to complete the hydroboration. Then 1.8 ml (100 mmoles) of water was added, followed by 5.3 ml (80 mmoles) of acrolein.[5] *n*-Decane was added to serve as an internal standard. The reaction mixture was allowed to stir for 1 hr at room temperature. Samples were removed at 10, 25, and 60 min and analyzed by glpc, indicating yields of 65, 71, and 77%, respectively. The identity of the product, isolated by preparative glpc chromatography, was confirmed as 3-cyclohexylpropanal by the pmr spectrum and preparation of the semicarbazone, mp 128–129°.[6]

Table I. Conversion of Olefins into 3-Alkylpropanals by Reaction of the Corresponding Organoboranes with Acrolein

		Yield, %[a,b] Time, min			
Olefin	Product, %	5	10	25	60
1-Butene	*n*-Heptanal, 85 4-Methylhexanal, 15	55			
2-Butene	4-Methylhexanal	75		89	96
Isobutylene	5-Methylhexanal		85	87	
1-Hexene	*n*-Nonanal, 85 2-Methyloctanal, 15	83		78	77
Cyclopentene	3-Cyclopentylpropanal		75		88
Cyclohexene	3-Cyclohexylpropanal		65	71	77
Norbornene	3-(*exo*-Norbornyl)propanal		67		80

[a] By glpc analysis. [b] The yield is based on the reaction producing I, with each mole of trialkylborane yielding 1 mole of aldehyde.

The experimental results are summarized in Table I.

As in the corresponding methyl vinyl ketone case, the acrolein appears to react preferentially with the secondary alkyl groups in the organoborane. Thus tributylborane from the hydroboration of 1-butene contains 6% of 2-butyl groups. Yet the reaction product contains 15% of 2-methylhexanal and 85% of heptanal. Thus most of the secondary alkyl groups present in the tributylborane have reacted. This selective reaction could be very helpful in destroying selectively the small amount of secondary alkyl derivatives produced in the hydroboration of terminal olefins, and we are exploring this possibility. It also suggests a means of achieving a far higher conversion of a given olefin to aldehyde product than the 33% now realized. This is being investigated.

In any case, the present procedure is so remarkably simple and evidently so general that it obviously has immediate utility in providing a major new route to aldehydes. Perhaps even more important at this time is the definite implication that this reaction of organoboranes with α,β-unsaturated derivatives is of very wide generality. We are currently exploring this possibility.[7]

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(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

(4) Although this minor component from the 1-hexene system has not yet been fully characterized, it was established that the minor component from 1-butene, also 15%, is identical with the product from 2-butene, 4-methylhexanal. Consequently, there can be little doubt that the minor component from the tri-*n*-hexylborane arises from the 6% of 2-hexyl groups present in the hydroboration product.

(5) It was convenient to use 100% excess of the reagent, although we have no evidence that the excess is necessary.

(6) A. Skita, *Ber.*, **48**, 1693 (1915), reports for 3-cyclohexylpropanal semicarbazone mp 128°.

(7) Research in progress with M. M. Rogić, M. W. Rathke, and G. W. Kabalka.

(8) National Science Foundation Postdoctorate Fellow at Purdue University, 1967–1968.

(9) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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Nonempirical Molecular Orbital Calculations on an α-Sulfinyl Carbanion

Sir:

Definite evidence has been obtained in at least one case that the electron pair in an α-sulfonyl carbanion is directed along the internal bisector of the OSO angle.[1] An exactly analogous conclusion was reached concerning an α-sulfinyl carbanion.[2] However, the generality of the former result has been questioned,[3] and the rigor of the nmr assignments used in the latter work may be in doubt.[4-6]

In an effort to gain further insight into the structure of an α-sulfinyl carbanion we have now made a detailed theoretical study of the hypothetical compound hydrogen methyl sulfoxide (I) and its derived carbanion (II).[7] The calculations were performed by the LCAO–MO–SCF method using Gaussian type functions (GTF) in the basis set.[8] A minimal basis set of 33 GTF was used for I and 32 GTF for II. These involved a single s-GTF on hydrogen, three s-, and one set of p-GTF on carbon and oxygen, and five s-, two sets of p-, and one set of d-GTF on sulfur.[9]

Figure 1 shows the total energy of I as a function of rotation about the C–S bond. It may be noted that minima and maxima appear at the skewed positions corresponding to a 21° rotation from the staggered

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(1) E. J. Corey and T. H. Lowry, *Tetrahedron Letters*, **13**, 793, 803 (1965).

(2) S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966).

(3) D. J. Cram, R. D. Trepka, and P. St. Janiak, *J. Am. Chem. Soc.*, **88**, 2749 (1966).

(4) K. W. Buck, A. B. Foster, W. D. Pardue, M. H. Quadir, and J. M. Webber, *Chem. Commun.*, 759 (1966).

(5) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).

(6) P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Commun.*, 550 (1967).

(7) The theoretical description of the α-sulfonyl system is due to H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

(8) For a description of the procedure and leading references see R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **46**, 4585 (1967).

(9) An IBM 7094-II computer was used for the calculations, each individual conformation requiring about 30 min of computer time. Similar calculations on methylsulfinyl carbanion (to be reported in our full paper) required about 60 min of computer time per conformation. Sufficient work was done on the latter system to show that the form of its potential energy surface is similar to that of II.

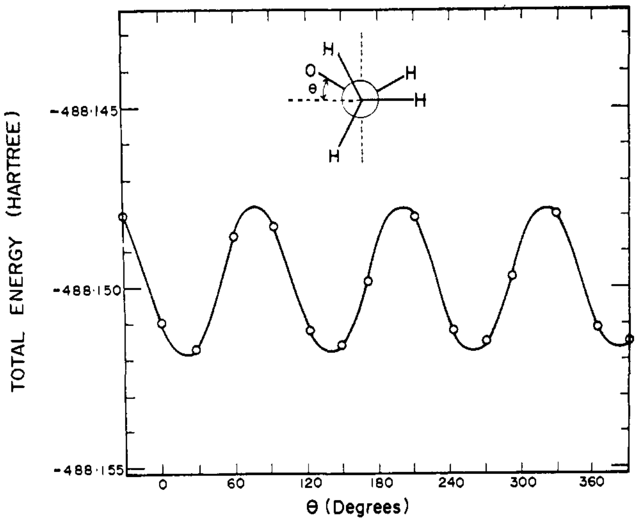
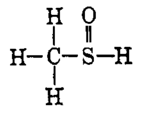


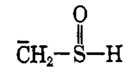
Figure 1. Total energy (in hartrees) of CH_3SHO as a function of rotation about the C–S bond.

(ethane type) and eclipsed (acetaldehyde type[10a]) conformations, respectively.[10b]



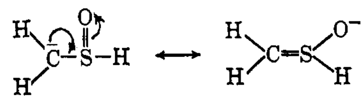
$H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{S}}{-}H$

I

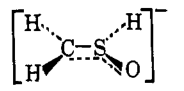


$\bar{C}H_2{-}\overset{O}{\overset{\|}{S}}{-}H$

II



III



IV

For the carbanion II the conformational energy surface was obtained for a 360° rotation (θ) about the C–S bond and a 15° change in the HCH angle (ϕ) on either side of planarity. The minimum was found to correspond to the experimental result[2] and HCH = 115°. Figures 2 and 3 are perpendicular cross sections through the energy minimum. Figure 2 shows the total energy of II as a function of θ for $\phi = 115°$. The maxima occur at carbanion *trans* to the lone pair on sulfur (higher) and carbanion nearly eclipsed with the lone pair (lower); the minima occur at carbanion *trans* to oxygen (higher) and *carbanion on the bisector of the internal O:S: lone pair angle* (*lowest*). Figure 3, the potential energy curve for inversion of this latter conformation, strongly suggests that a carbanion generated on the side opposite to oxygen and the lone pair would undergo spontaneous inversion.[11]

Figure 4 shows the variation of the overlap populations of the C–S and S–O bonds as a function of θ for I and II ($\phi = 115°$). It is apparent that the overlap population of the C–S bond increases and that of the S–O bond decreases in the conversion I → II and that there is a significant dependence upon θ. It would be convenient but quite misleading to represent this by the valence bond structures III, a more realistic structure being the nonplanar, charge-delocalized IV.

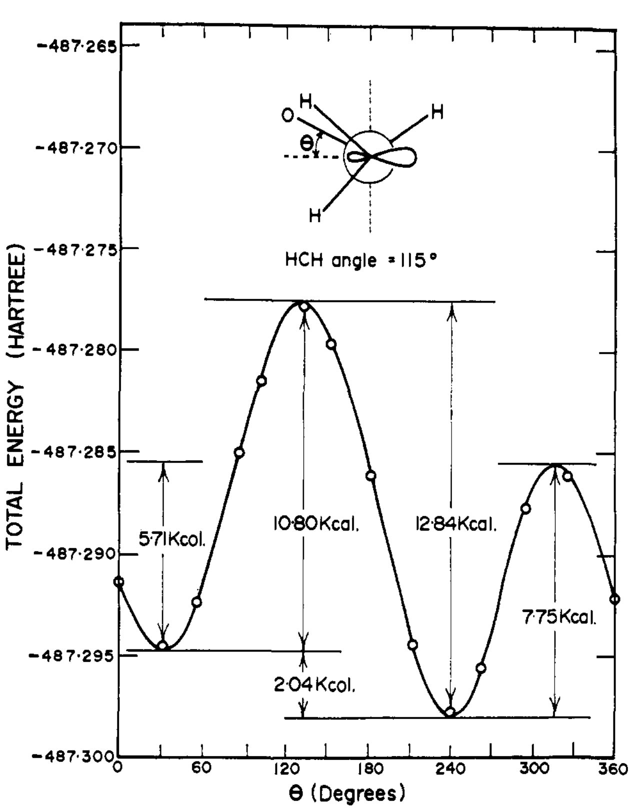


Figure 2. Total energy of $^{-}CH_2SHO$ *vs.* rotational angle (θ) about the C–S bond (ϕ = 115°).

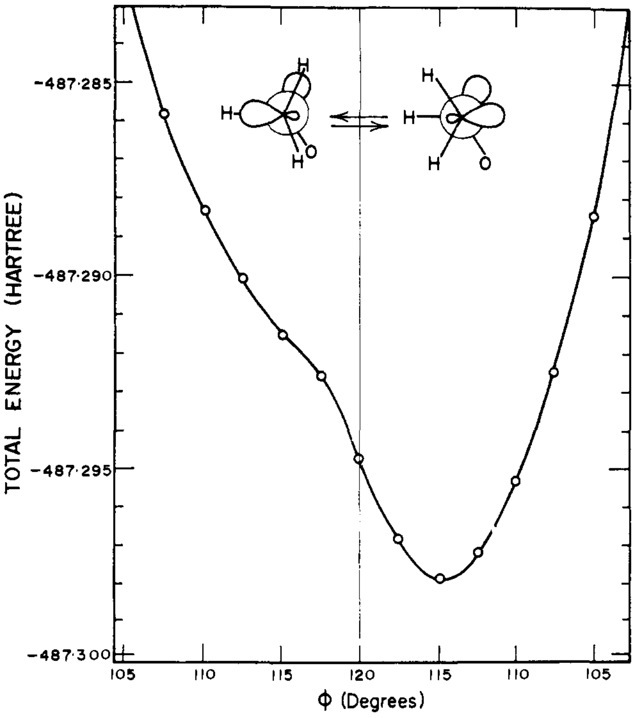


Figure 3. Total energy of $^{-}CH_2SHO$ *vs.* carbanion angle (ϕ) for the favored rotational conformer (θ = 60°, 240°).

It is also convenient but incorrect to invoke d-orbital participation from sulfur to explain this delocalization. *Inspection of the coefficient matrix reveals no d-orbital contributions to the higher occupied molecular orbitals.*

Finally, the calculations suggest that whether a proton in a sulfoxide exchanges with retention or inversion of

[10] (a) R. W. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.*, 26, 1695 (1957). (b) The rotational energy barrier is 2.51 kcal/mole.

[11] The electron density maps obtained for the lowest energy conformation show the molecular orbital containing the carbanion to be geometrically analogous to a pure sp^3 hybrid.

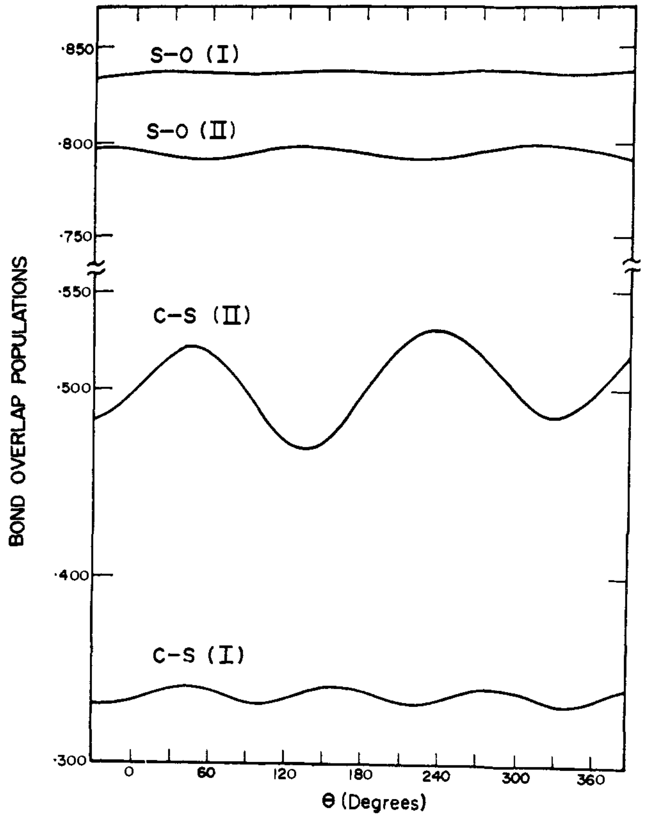


Figure 4. Bond overlap populations as a function of rotational angle (*θ*) about the C–S bond for I and II.

configuration will depend upon its specific environment in the molecule. We hope that experiments in progress will provide information on this point.[12]

Acknowledgments. We thank the Institute of Computer Science of the University of Toronto for making their facilities available to us and the National Research Council of Canada for financial support. Special thanks go from S. W. and A. R. to Professor D. J. Leroy for his kind hospitality.

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(12) The data of Cram and Pine[13] are consistent with this prediction. These workers found (*R*)-2-octyl phenyl (*S*)-sulfoxide[14] to undergo H–D exchange in DMSO by an inversion mechanism (k_e/k_α = 0.58); the epimeric (*R*)-2-octyl phenyl (*R*)-sulfoxide[14] exchanged by a retention mechanism (k_e/k_α = 1.4).

(13) D. J. Cram and S. H. Pine, *J. Am. Chem. Soc.*, **85**, 1096 (1963).

(14) The configurational assignments in Cram and Pine's paper have been reversed by the work of K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simons, and A. L. Ternay, *J. Am. Chem. Soc.*, **87**, 1958 (1965).

(15) Holder of a National Research Council Studentship 1966–1967.

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Cyclopentenone Photocycloaddition. A Reaction from a Higher Triplet State[1]

Sir:

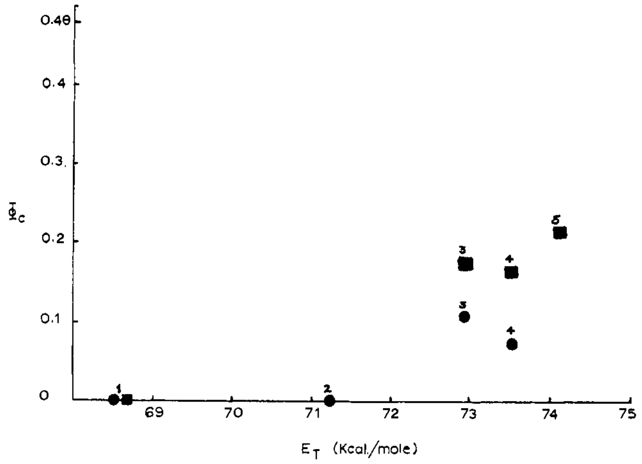

Figure 1. Quantum yields of cycloaddition (Φ_c) with sensitizers irradiated at 313 mμ. Concentration of sensitiser *ca.* 1 *M;* concentration of cyclopentenone 0.1 *M* (●), 0.3 *M* (■). Sensitizers: (1) benzophenone, (2) 4-bromoacetophenone, (3) 4-methylacetophenone, (4) acetophenone, (5) cyclopropyl phenyl ketone (uncorrected for triplet yield or transfer to cyclohexene).

There has been considerable interest expressed in the recent literature on the nature and multiplicity of the reacting species in the photocycloadditions of excited α,β-unsaturated ketones[2] and in particular those of cyclopentenone.[2a,b,3] It has been concluded in the latter case[2a,b] that a triplet is involved in dimerization. We report here evidence that in the addition of cyclopentenone to cyclohexene (which gives cyclobutane adducts of the type reported[3] for the addition to cyclopentene) the agent concerned is cyclopentenone in its T_2 state (or a species derived from it) and that the lowest triplet, T_1, is ineffective in cycloaddition.

The photocycloaddition of cyclopentenone to cyclohexene (solvent) proceeds in high quantum yield (Φ = 0.48).[4] Using benzophenone as a sensitizer (E_T $\sim$ 69 kcal/mole) no cycloaddition was observed (Φ < 0.01), but triplet energy was nonetheless transferred to the cyclopentenone. This was shown (a) by the fact that (0.11 *M*) benzophenone phosphorescence is quenched (in ether–ethanol 3:1, matrix at 77°K) by 2 *M* cyclopentenone, and (b) because the photoreduction of benzophenone by 2-propanol, a well-studied triplet process,[5] is quenched by the addition of cyclopentenone.[6] A linear Stern–Volmer plot (over a range of 0.005–0.1 *M* cyclopentenone) was obtained whose slope (55 M^{-1}) indicated close to diffusion-controlled quenching. On the assumption that benzophenone excites cyclopentenone to its lowest triplet this species apparently does not cycloadd. Direct irradiation of cyclopentenone in 2-propanol–cyclohexene gives cyclo-

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(1) Photochemical Synthesis. XX.

(2) (a) P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966); (b) H. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5671 (1966); (c) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964); (d) O. L. Chapman, "Organic Photochemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1967, p 304 *et seq.;* (e) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

(3) P. E. Eaton, *ibid.*, **84**, 2454 (1962).

(4) Irradiation at 313 mμ. The effect of the substrate and the solvent in cyclopentenone addition has been studied in some detail and a report will be submitted for publication.

(5) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961); A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2039, 2051 (1963); J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(6) M. Pfau, R. Dulou, and M. Vilkas, *Compt. Rend.*, 1817 (1962).