as opposed to measurements of the thermodynamic stability of adducts with respect to their constituents, which depend on a reorganization energy. For example, upon protonation, a_N(I) increases by a factor of 1.37 to a_N(V) = 21.8 ± 0.2,[4] whereas a_N(I) increases by a factor of 1.28 upon complexation with aluminum chloride. Further information is gained by consideration of the size of a suitably normalized coupling constant to the central nucleus of the Lewis acid.[5] Steric hindrance from the nitroxide methyl groups may be taken account of by using different aliphatic nitroxides which are still less hindered. Also, structural differences in the aromatic and aliphatic nitroxides lead to markedly different changes in coupling constants upon protonation.[4,9] Exploring these differences upon adduct formation gives us yet another probe into the electronic structure of the Lewis acid adducts.

Acknowledgment. We are indebted to Professor D. F. Shriver for many invaluable discussions and to D. Barry for synthesizing the parent nitroxides. This research was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Material Research Center.

(9) H. Hogeveen, H. R. Gersmann, and A. P. Praat, *Rec. Trav. Chim. Pays-Bas*, **86**, 1063 (1967).

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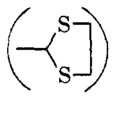
Neighboring Sulfur Participation in the Acetolysis of Benzyl Chlorides[1]

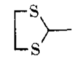
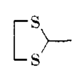
Sir:

Neighboring sulfur participation has long been known in the case of the solvolysis of β-chloroethyl sulfides.[2] However, similar participation has never been reported for benzyl chlorides having sulfur-containing *ortho* substituents. We now report rates of acetolysis of some *ortho*- or *para*-substituted benzyl chlorides and striking rate enhancement by the *o*-dithiacyclopentyl group.



Substituted benzyl alcohols were synthesized by conventional methods and converted into the corresponding chlorides by thionyl chloride in benzene with the use of a small amount of 2,6-lutidine. All of the chlorides were checked for purity by analysis and nmr spectra: *o*-dithiacyclopentylbenzyl chloride (V) (*Anal.* Calcd for $C_{10}H_{11}S_2Cl$: Cl, 15.36. Found: Cl, 15.24) nmr (τ) 2.10 (m, 1 H, Ar), 2.75 (m, 3 H, Ar), 3.98 (s, 1 H, CH), 5.30 (s, 2 H, CH_2), 6.57 (m, 4 H, CH_2CH_2); *p*-dithiacyclopentylbenzyl chloride (VI) (*Anal.* Calcd for $C_{10}H_{11}S_2Cl$: C, 52.05; H, 4.80; S, 27.79; Cl, 15.36. Found: C, 52.31; H, 4.98; S, 27.86; Cl, 15.32) nmr (τ) 2.67 (m, 4 H, Ar), 4.45 (s, 1 H, CH), 5.51 (s, 2 H, CH_2), 6.63 (m, 4 H, CH_2CH_2).

Table I. Rates of Acetolysis of Benzyl Chlorides at 60° [a]

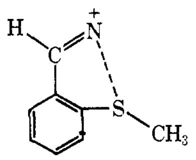
Substituent	k_1, sec^{-1}	*o/p* ratio	Rel *o/p* ratio
o-CH_3O (I)	3.2×10^{-6}	0.0017	1
p-CH_3O (II)	1.9×10^{-3}		
o-CH_3S (III)	3.6×10^{-7}	0.018	11
p-CH_3S (IV)	2.0×10^{-5}		
o-  (V)	3.9×10^{-5}	220	130,000
p-  (VI)	1.8×10^{-7}		

[a] Initial concentration 0.05 *M*; in the presence of 0.06 *M* sodium acetate.

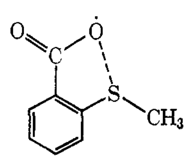
Rates of acetolysis of substituted benzyl chlorides were measured in the presence of a slight excess of sodium acetate at 60°, the reaction being followed titrimetrically by the Volhard method. All reactions obeyed the first-order rate equation up to 40–50% reaction and gave the corresponding acetates as a sole product except in the case of compound V where, besides the acetate, appreciable amounts of polymeric materials were produced beyond 60% reaction.

First-order rate constants, *ortho*:*para* rate ratios, and relative *ortho*:*para* rate ratios are listed in Table I. The *o*-methoxy compound I reacts at about $^1/_{500}$ the rate of the *p*-methoxy compound II, presumably due to steric hindrance to solvation of the transition state. The *o*-methylmercapto III is again considerably less reactive than the corresponding *para* compound IV, but the *ortho*:*para* ratio becomes slightly higher than in the methoxy case. The rate for the *o*-dithiacyclopentyl compound V, however, exceeds that of the corresponding *para* compound VI by a factor of 220. Assuming that the relative *ortho*:*para* rate ratio is a measure of the extent of the participation of the *ortho* substituents, dithiacyclopentyl is 130,000 times more effective in facilitating the solvolytic reaction than methoxy is. Allowing for the relative bulkiness of these two groups, this factor would be still greater.

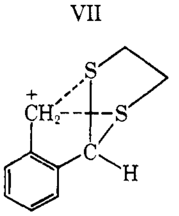
Participation of *o*-methylmercapto is reported in two cases, which results in about 10,000 times rate enhancement: degradation of esters of *syn*-benzaldoximes to the corresponding benzonitriles[3] and thermal decomposition of *t*-butyl perbenzoates.[4] In view of these facts the present result, *i.e.*, much participation in the



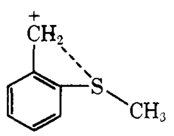
VII



VIII



IX



X

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(2) R. A. Peters and E. Walker, *Biochem. J.*, **17**, 260 (1923); A. G. Ogston, E. R. Holiday, J. St. L. Philpot, and L. A. Stocken, *Trans. Faraday Soc.*, **44**, 45 (1948); P. D. Bartlett and C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1406 (1949).

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(4) W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

dithiacyclopentyl case and little participation in the methylmercapto case, seems quite interesting. Probably, five-membered ring structures at transition states such as VII, VIII, and IX are suited for efficient participation, while four-membered ones, like X, are not.

Acetolysis of the corresponding tosylates gave similar results. The only exception is in the case of *o*-dithiacyclopentyl tosylate[5] which gave no acetate but produced very stable salts[6] on adding potassium iodide or lithium perchlorate to the reaction mixture. Structural determination of this salt is now in progress.

[5] The proton nmr spectrum of this compound exhibits signals at τ 2.46 (m, 4 H, aromatic), 2.75 (m, 4 H, aromatic), 4.33 (s, 1 H, CH), 4.79 (s, 2 H, CH_2), 6.64 (m, 4 H, CH_2CH_2), and 7.58 (s, 3 H, CH_3).

[6] Iodide decomposed at 138°. *Anal.* Calcd for $C_{10}H_{11}S_2I$: C, 37.27; H, 3.45. Found: C, 36.92; H, 3.58. Perchlorate decomposes at 157°. Both salts showed identical proton nmr spectrum.

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Evidence for Hydroxyl-Group Abstraction by Hydrogen Atoms

Sir:

It has been shown[1] that hydrogen atoms of thermal energies are capable of abstracting hydrogen atoms from hydrocarbons in the solid state. Abstraction and replacement of halogen atoms has also been demonstrated.[2] Herak and Gordy[3] showed that various groups, too, can be replaced by thermal hydrogen atoms. However, abstraction of groups has not been observed, except for the amino group in alanine.[4] In this study we present the evidence that hydroxyl groups can also be abstracted by hydrogen atoms. Powdered alloxan, which is known to be in the dihydroxy form,[5] was exposed to the beam of thermal hydrogen atoms at room temperature in a chamber described elsewhere.[6] The produced radicals were studied with electron spin resonance. Figure 1 shows the spectrum of alloxan previously exposed to H atoms (upper curve) in comparison to the resonance of the γ-irradiated specimen (middle line). It is obvious that the same radicals are present in both samples. They have been identified as the $>\dot{C}$–OH radicals.[7] The asymmetry of the resonance line is due to the large anisotropy of the hydroxyl-proton hyperfine splitting. The spectrum of the irradiated single crystal of alloxan (lower curve) clearly demonstrates the presence of the hydroxyl-proton coupling.

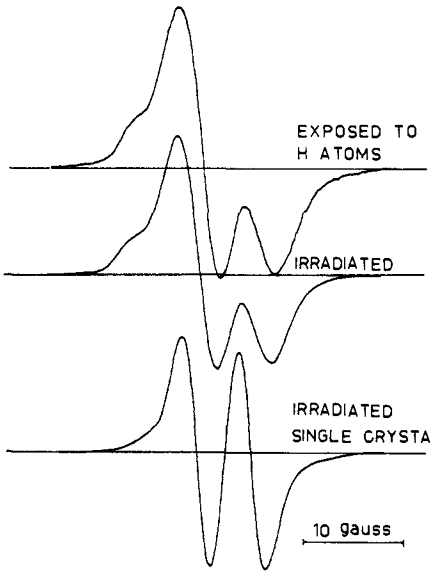
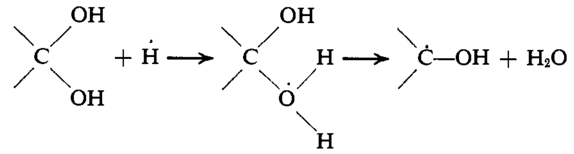


Figure 1. Electron spin resonance spectra (first-derivative curves) of alloxan, exposed to hydrogen atoms (upper curve), irradiated (middle curve), and α-irradiated single crystal (lower curve).

No essential difference in the resonance pattern was observed if deuterium atoms instead of hydrogen were used. This fact demonstrates that addition of hydrogen atoms does not take place. Thus, the observed radicals are formed by abstraction of one of the hydroxyl groups. The reaction with hydrogen atoms probably goes as follows.



First, the unstable complex is formed which then transforms into the radical and a water molecule. The detailed mechanism, however, is not completely understood. It is not known whether n or π electrons of the hydroxyl group participate in the complex formation. In any case, the hydroxyl group must be in the excited state to react with an H atom. Since the first excited state of n electrons is lower than that of π electrons, it is believed that n electrons take part in the complex formation.

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[3] J. N. Herak and W. Gordy, *J. Am. Chem. Soc.*, **89**, 3818 (1967).

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The Alkaline Hydrolysis of 5-Nitrocoumaranone. A Method for Determining the Intermediacy of Carbanions in the Hydrolysis of Esters with Labile α Protons

Sir:

There has recently been a suggestion that certain esters possessing readily ionizable protons adjacent to the carbonyl function might hydrolyze in alkaline solution *via* a pathway with either an isocyanate[1] or a ketene[2] intermediate (eq 1) rather than the well-known tetrahedral intermediate. In these investigations, however, no direct method was proposed to distinguish eq 1

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[1] M. L. Bender and R. B. Homer, *J. Org. Chem.*, 30, 3975 (1965).

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