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.

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(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.

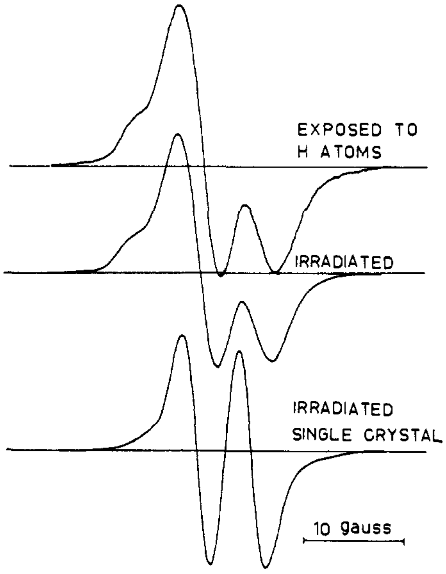
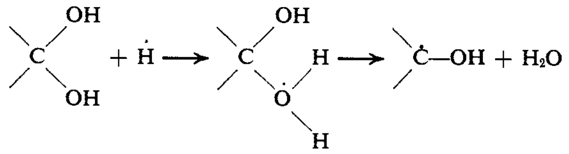


Figure 1. Electron spin resonance spectra (first-derivative curves) of alloxan, exposed to hydrogen atoms (upper curve), irradiated (middle curve), and α-irradiated single crystal (lower curve).

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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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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