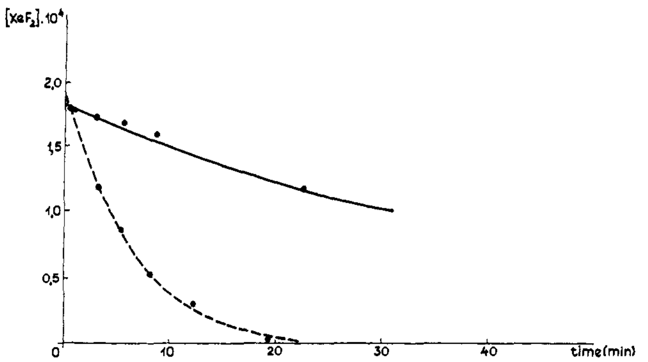

Figure 2. Effect of potassium nitrate and potassium fluoride on the decomposition of xenon difluoride: ———, 1 *M* KNO_3, 0.06 *M* $KHCO_3$, pH 8.4; - - - -, 1 *M* KF, 0.06 *M* $KHCO_3$, pH 8.4.

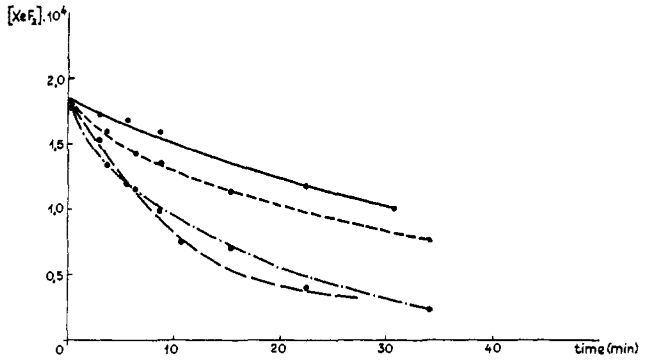

Figure 3. Effect of ionic strength on the decomposition of xenon difluoride at pH 8.4: ———, 1 *M* KNO_3, 0.06 *M* $KHCO_3$; - - - -, 0.2 *M* KNO_3, 0.06 *M* $KHCO_3$; - - - - -, 2 *M* $NaClO_4$, 0.06 *M* $NaHCO_3$; - · - ·, 0.2 *M* $NaClO_4$, 0.06 *M* $NaHCO_3$.

hydrogen carbonate as well as phosphate and hydrogen phosphate ions is even much greater.[5] Besides these specific ionic effects it was observed that when the ionic strength is increased the reaction is retarded (Figure 3).

The accelerating effect of the different anions can be formally interpreted by the formation of reactive complex ions; however, more detailed investigation is necessary to give a satisfactory explanation. These and analogous experiments with other xenon fluorides are in progress in collaboration with the Central Research Institute of Physics of the Hungarian Academy of Sciences.

[5] The catalytic effect of these ions was also observed by Dr. E. H. Appelman (personal communication, Aug 11, 1967).

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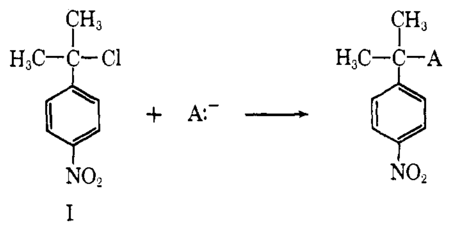
New and Facile Substitution Reactions at Tertiary Carbon. The Displacement of a Nitro Group from a Saturated Carbon Atom

Sir:

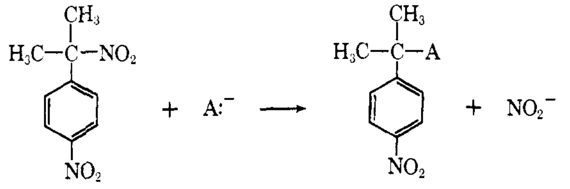
We have recently reported a new type of substitution process at tertiary carbon in which the chlorine of *p*-nitrocumyl chloride (I) is replaced by a variety of anions (eq 1).[1] We now wish to describe an even more



(1)

I

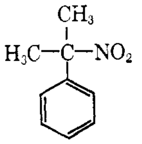
striking set of reactions in which the aliphatic nitro group of α,p-dinitrocumene (II) is displaced (eq 2). The reaction of eq 2 is noteworthy not only because it involves substitution at a tertiary carbon atom but also because it is a reaction without precedent—the displacement of a nitro group from a saturated carbon atom.



(2)

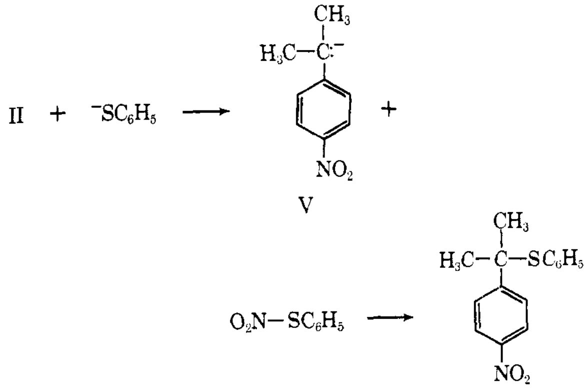
II III

For example, the reaction of II with sodium thiophenoxide in DMF (or in DMSO) solution at 25° is complete in 20 min and produces the pure tertiary sulfide III (A = SC_6H_5) in 96% yield. In contrast, α-nitrocumene (IV) is not attacked by sodium thiophenoxide under these conditions.



IV

Since substitution at the tertiary carbon is facilitated by a *p*-nitro group, the possibility that the thiophenoxide ion displaces on the aliphatic nitro group to give carbanion V, and that this in turn gives the tertiary sulfide (eq 3), must be considered. If carbanion V is indeed an intermediate, it would be anticipated that, on conducting the reaction in DMSO containing 20 moles of methanol for each mole of II, a significant fraction of the carbanions would be scavenged by the methanol.[2] This is not what is observed; in methanolic DMSO a



V

(3)

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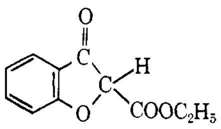
[1] N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Am. Chem. Soc.*, **89**, 725 (1967).

[2] I. J. Borowitz and R. Virkhaus, *ibid.*, **85**, 2183 (1963).

97% yield of the pure tertiary sulfide (III, A = SC_6H_5) is obtained. An even more compelling argument against the carbanion mechanism is the fact that the pure tertiary sulfide is isolated in 97% yield when the reaction is conducted in absolute ethanol.

The reaction of II with sodiomalonic ester is also extraordinarily clean; in DMF, at 25°, after 1 day a 95% yield of the alkylated malonic ester III, A = $CH(COOC_2H_5)_2$, is produced. Treatment of II with the lithium salt of 2-nitropropane at 25° in DMSO gives the carbon alkylate III, A = $C(CH_3)_2NO_2$, in 71% yield. Furthermore, the reaction of II with the sodium salt of β-keto ester VI also follows eq 2, the yield of carbon alkylate being about 70%.

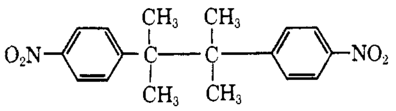


VI

Sodium phenoxide in DMSO at 25° displaces the nitro group of II according to eq 2, giving the tertiary ether III, A = OC_6H_5, in 66% yield; the sodium salt of 1-methyl-2-naphthol reacts with II in a strictly analogous way, giving the tertiary ether (64% yield). Finally, treatment of II with methanolic sodium methoxide at 60° results in the formation of the methyl ether III, A = OCH_3, in 56% yield.

In no instance does α-nitrocumene (IV) undergo any significant amount of reaction when exposed to the various anions under conditions which result in complete reaction according to eq 2 when α,*p*-dinitrocumene (II) is employed.

It seems very likely that the reactions of eq 2 are radical anion processes.[1,3] This view is supported by a number of observations, including the fact that various of these reactions show some of the following characteristics: light speeds up the reaction whereas oxygen retards it, and small amounts of the dimer VII are isolated.[4]



VII

Acknowledgment. We thank the Petroleum Research Fund and the Explosives Department of Du Pont for generous support.

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[3] G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966).

[4] All reactions were conducted under nitrogen or argon.

[5] X-R Fellow of the Purdue Research Foundation, 1965–1967.

[6] National Science Foundation Cooperative Fellow, 1965–1967.

[7] National Science Foundation Cooperative Fellow, 1964–1966; Standard Oil of Ohio Fellow, 1966–1967.

[8] Union Carbide Fellow, 1965–1966.

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Nearest Neighbor Triplet Quenching at High Quencher Concentrations[1]

Sir:

The purpose of this communication is to point out a feature of triplet energy transfer which has not, to my knowledge, been elaborated previously. It is widely assumed that *exothermic* triplet energy transfer is intrinsically so efficient that the rate at which it occurs in solution is limited by and equals the rate at which the excited donor and the quenching acceptor can diffuse together.

In the absence of transient effects,[2] the ability of low concentrations of a particular compound to quench excited-state photoreactions of another compound is adequately expressed by the Stern–Volmer expression

$$\phi_0/\phi_q = 1 + k_q[Q]\tau_0 \qquad (1)$$

where k_q is the bimolecular rate constant for quenching, [Q] is the concentration of quencher, and τ_0 is the lifetime of the excited state being quenched. However, if quenching is so efficient that it occurs at the diffusion-limited rate, the simple Stern–Volmer expression above is no longer accurate at high quencher concentrations.

Let us consider as a typical case the quenching of some triplet-state photoreaction of a ketone. At quencher concentrations greater than 0.1 *M*, a significant percentage of the ketone molecules will have a quencher molecule as nearest neighbor at the moment of excitation. This percentage increases rapidly with quencher concentration. If exothermic energy transfer from the ketone triplet to the quencher is 100% efficient, that portion of the excited ketone molecules "born" with quencher molecules as nearest neighbors will be quenched immediately and will never be able to enter into the normal competition between photoreaction and diffusional quenching. Consequently, high concentrations of quenchers should be much more efficient at quenching a photoreaction than might be extrapolated from Stern–Volmer plots at low quencher concentrations. Such behavior is conceptually similar to the "static" fluorescence quenching postulated long ago by Bowen and Metcalf,[3] except that no special interactions between ground-state ketone and quencher need be invoked. Weller has developed and applied the kinetics of static quenching to fluorescence studies.[4]

Simple statistical considerations yield the following expression for the quantum yield of triplet-state reaction, where *u* is the fraction of ketone molecules which have at least one quencher molecule as a nearest neighbor, k_r is the unimolecular rate constant for reaction of the ketone triplet, and k_{et} is the rate at which energy transfer occurs once excited ketone and quencher molecules are nearest neighbors.

$$\Phi = \frac{(1-u)k_r}{1/\tau_0 + k_q[Q]} + \frac{uk_r}{1/\tau_0 + k_{et}} \qquad (2)$$

Division of the above equation into $k_r\tau_0$ yields the following modification of the Stern–Volmer equation,

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[1] Triplet Energy Transfer. II. Part I is P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2820 (1967). This work was supported by the Office of Naval Research and the National Science Foundation.

[2] R. M. Noyes, *Progr. Reaction Kinetics*, **1**, 131 (1961).

[3] E. J. Bowen and W. S. Metcalf, *Proc. Roy Soc.* (London), **A206**, 437 (1951).

[4] A. Weller, *Discussions Faraday Soc.*, 27, **28** (1959); *Progr. Reaction Kinetics*, **1**, 187 (1961).