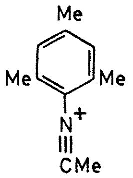
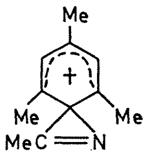
The Beckmann Rearrangement of 2,4,6-Trimethylacetophenone Oxime in Sulphuric and Perchloric Acids

By B. J. GREGORY, R. B. MOODIE, and K. SCHOFIELD*

(*Department of Chemistry, The University, Exeter*)

2,4,6-TRIMETHYLACETOPHENONE OXIME undergoes the Beckmann rearrangement extremely readily.[1] In sulphuric acid it reacts about 3000 times as fast as *p*-methylacetophenone oxime. This high reactivity in rearrangement, coupled with its inertness towards hydrolysis, has permitted the measurement of the rate of rearrangement of 2,4,6-trimethylacetophenone oxime over a wide range of acidity in both sulphuric and perchloric acids.


(I)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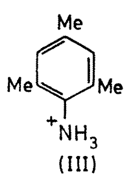
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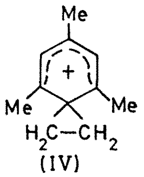
(IV)

The Beckmann rearrangement of acetophenone oximes in sulphuric acid[2] is accompanied by a change in the u.v. absorption spectrum of the reaction solution. For *m*- and *p*-substituted acetophenone oximes the spectral change observed is that to be expected for the conversion of the oxime into the corresponding acetanilide, no intermediate stage being detectable. However, study of the rearrangement of 2,4,6-trimethylacetophenone oxime indicates that the reaction proceeds through the intermediate formation of an *N*-arylnitrilium ion (I). The rate of formation of (I) (λ_{max} 258 nm., ϵ 14,000 in 95% sulphuric acid) has been measured in 55—98% sulphuric acid and in 52—72% perchloric acid, and the rate of hydration of (I) has been measured in 77—92% sulphuric acid and in 72% perchloric acid. The variation of the observed first-order rate constants with acidity is shown in the Figure. The rate constants show that where the formation of an intermediate is not observed, as with *m*- and *p*-substituted acetophenone

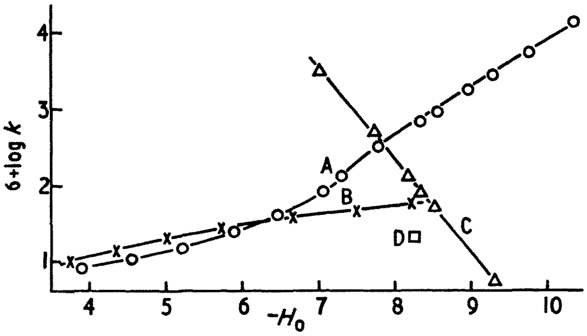

FIGURE. *The Beckmann rearrangement of* 2,4,6-*trimethylacetophenone oxime in sulphuric and perchloric acids at* 25°. (A) *Formation of intermediate in sulphuric acid*; (B) *formation of intermediate in perchloric acid*; (C) *hydration of intermediate in sulphuric acid*; (D) *hydration of intermediate in perchloric acid.*

oximes, the rate being measured is the rate of formation of the intermediate which is, however, not "seen" because of its rapid hydration to give the amide.

That the observed intermediate in the rearrangement of 2,4,6-trimethylacetophenone oxime is the *N*-arylnitrilium ion (I) and not the phenonium ion (II) is made probable by its ^{1}H n.m.r. spectrum [τ 2·42 (2H), 6·24 (3H, methyl group not attached to ring), 7·06 (6H), and 7·18 (3H), in 94·8% sulphuric acid. Very similar spectra were observed using 85% sulphuric acid and 72% perchloric acid]. By comparison the ^{1}H n.m.r. spectrum in 94·8% sulphuric acid of the 2,4,6-trimethylanilinium ion (III) shows signals at τ 2·00 (3H, NH_3^+), 2·56 (2H), 7·18 (6H), and 7·30 (3H), whilst Olah *et al.*[3] have reported the spectrum of the phenonium ion (IV) to consist of singlets at τ 2·34 (2H), 6·23 (4H), 7·40 (3H), and 7·62 (6H). The structure of the observed intermediate must therefore be similar to (III) and rather different from (IV). We conclude that the intermediate is the *N*-arylnitrilium ion (I). A similar intermediate has been observed in the rearrangement of *o*-methylacetophenone oxime in 90—98% sulphuric acid.

The divergence of the curves (Figure) for reaction in sulphuric acid and in perchloric acid at high acidity indicates that the reactive species in concentrated sulphuric acid is the oxime *O*-sulphonic acid, rather than the protonated oxime.

(*Received, April* 24*th*, 1969; *Com.* 560.)

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[2] B. J. Gregory, R. B. Moodie, and K. Schofield, *Chem. Comm.*, 1968, 1380.

[3] G. A. Olah, E. Namanworth, M. B. Comisarow, and B. Ramsey, *J. Amer. Chem. Soc.*, 1967, **89**, 711.