

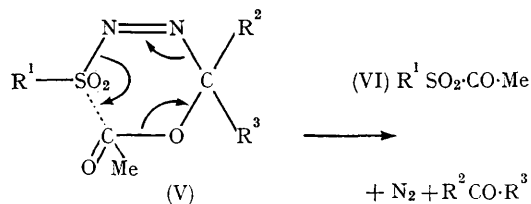
Regeneration of Ketones from their Toluene-*p*-sulphonylhydrazones by Reaction with Lead Tetra-acetate

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LEAD TETRA-ACETATE reacts with the toluene-*p*- and benzene-sulphonylhydrazone of benzaldehyde to form monoacetoxy-derivatives¹ [(I), *p*-Me.C₆H₄.SO₂.NH.N:C(OAc)C₆H₅ and (II), C₆H₅.SO₂.NH.N:C(OAc)C₆H₅ respectively. With a view to finding out if this acetoxylation results by a direct or an indirect substitution at the benzylic carbon atom, the toluene-*p*-sulphonylhydrazone of acetophenone was treated with lead tetra-acetate in glacial acetic acid at 20°. Besides the usual by-products, namely acetic acid and lead diacetate, compound (I) and methyl acetate from direct substitution, and compound (III), *p*-Me.C₆H₄.SO₂.N:N.C(Me)(OAc)C₆H₅ or (IV), *p*-Me.C₆H₄.SO₂.N(Me).N:C(OAc)C₆H₅ from indirect substitution were expected. Actually acetophenone, nitrogen, and an unidentified product which contained sulphur but no nitrogen were obtained. That this was not an ordinary regeneration of a ketone from its toluene-*p*-sulphonylhydrazone by acid was confirmed firstly by the fact that the sulphonylhydrazone is unaffected by acetic acid alone, and secondly the use of dry benzene or dichloromethane instead of acetic acid as solvent affords the same products. The reaction rate was studied both by quantitative estimation of the nitrogen evolved, and by iodometric estimation of the amount of lead tetra-acetate consumed. Using 102.5 mg. and 35.2 mg. respectively for these determinations it was found that one molar equivalent of nitrogen

was evolved in 8 min., and two molar equivalents of lead tetra-acetate were consumed in 15 min. The toluene-*p*-sulphonylhydrazones of acetone, cyclohexanone, (+)-camphor, (-)-piperitone, and benzophenone reacted similarly. The regenerated ketones could be isolated easily, and were identified by their infrared spectra and m.p. of their semi-carbazones. The optical rotation of the regenerated camphor was identical with that of the camphor used in the preparation of toluene-*p*-sulphonylhydrazone. It appears that the intermediate (V, where R¹ denotes *p*-Me.C₆H₄ and R² and R³ either alkyl, aryl, or alicyclic ring-residue) collapses due to steric reasons, presumably *via* a six-membered cyclic transition state as shown.



Attempts to isolate the acetyl *p*-tolyl sulphone (VI, R¹ = *p*-Me.C₆H₄) have so far failed.

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¹ A. Bhati, *J. Chem. Soc.*, 1965, 1020.