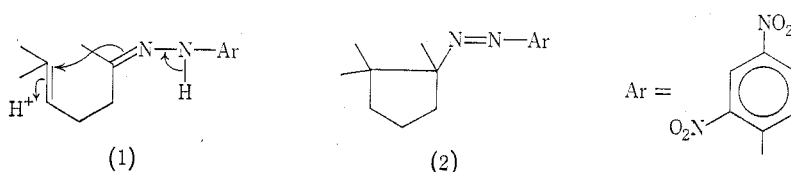


HYDRATION OF THE $>C=N-$ GROUP BY *p*-TOLUENESULPHONIC ACID HYDRATE. READY REGENERATION OF KETONES FROM THEIR 2,4-DINITROPHENYLHYDRAZONES

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While investigating the possibility of an acid-catalysed ring closure (intramolecular C-C bond formation, see¹ for an analogous intermolecular reaction) of the 2,4-dinitrophenylhydrazone (DNP) of 6-methylhept-5-en-2-one (1) to a five-membered ring of type (2)[†] we refluxed (1) with an equimolar proportion of *p*-toluenesulphonic acid hydrate in chloroform for 15 hr.



A solid formed in the reaction mixture proved to be the *p*-toluenesulphonate of 2,4-dinitrophenylhydrazine (m.p. 201–202° from dry methanol). The chloroform solution, after removal of the solvent, gave a residue which was identified as 6-methylhept-5-en-2-one by i.r. and t.l.c. The yield of the pure ketone after steam distillation was 75%.

Table I gives some additional examples of the cleavage of ketone 2,4-dinitrophenylhydrazones by *p*-toluenesulphonic acid hydrate. Harrison and Eisenbraun⁴ recommended the use of α -ketoglutaric acid or γ -ketopimelic acid in the place of pyruvic acid or laevulinic acid used conventionally as “acceptors” in this cleavage. Demaecker and Martin⁵ employed acetone for exchange and the acetone 2,4-dinitrophenylhydrazone was eliminated by reduction with stannous chloride, followed by extraction with mineral acid. The regeneration of ketones, now reported by us,

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[†] In justification of this attempt, two instances of what may be regarded as electrophilic attack on the carbon of $R-NH-N=C<$ can be cited from the literature.^{2,3}

¹ Saucy, G., and Marbet, R., *Helv. chim. Acta*, 1967, **50**, 1158.

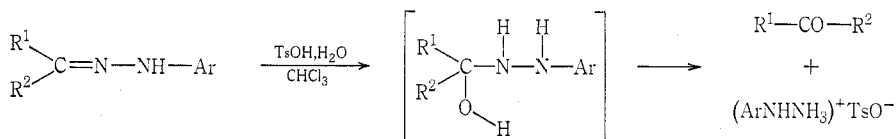
² Akhrem, A. A., Dubrovsky, V. A., Kamernitzky, A. V., and Skorova, A. V., *Tetrahedron*, 1969, **25**, 4737.

³ Berry, D. W., Bryant, R. W., Smith, J. K., and Landolt, R. G., *J. org. Chem.*, 1970, **35**, 845.

⁴ Harrison, H. R., and Eisenbraun, E. J., *J. org. Chem.*, 1966, **31**, 1294.

⁵ Demaecker, J., and Martin, R. H., *Nature*, 1954, **173**, 266; *Bull. Soc. chim. Belg.*, 1959, **68**, 365.

embodies a novel principle, viz., the ready stoichiometric transfer of water of hydration from *p*-toluenesulphonic acid hydrate to the $>\text{C}=\text{N}-$ double bond of the dinitrophenylhydrazone and the concomitant fragmentation of the hydrazino alcohol to the ketone and the base, the base being effectively immobilized as the sparingly soluble *p*-toluenesulphonium salt, according to the Scheme 1.



Scheme 1

The present procedure appears to be unsuitable for conjugated ketones (for example, pulegone) because of extensive retro-aldol reaction. Harrison and Eisenbraun⁴ had a similar experience with pulegone. However, in contrast to their maximum recovery of 61%, the present technique gives 90% yield of indanone.

TABLE I
p-TOLUENESULPHONIC ACID CLEAVAGE OF KETONE 2,4-DINITROPHENYL-HYDRAZONES

Starting Material	Reflux (hr)	Ketone Recovered (%)
Acetone DNP	20	63 ^a
6-Methylhept-5-en-2-one DNP	15	75
Acetophenone DNP	20	91
	2.5	86
3-Methylindan-1-one DNP	20	90
Pulegone DNP	24	<2 ^b

^a Calculated on the basis of recovered 2,4-dinitrophenylhydrazine.

^b 3-Methylcyclohexanone (c. 31%) was also obtained (yields by g.l.c.).

In order to check whether a $-\text{C}\equiv\text{N}$ group could be similarly hydrated to an amide (with 1 equiv. of *p*-toluenesulphonic acid hydrate) or to an acid (with excess of the reagent), benzonitrile was refluxed in chloroform with various quantities of acid hydrate for 24 hr. Only traces of benzoic acid and benzamide were detected.

Solid phase hydration of nitriles to amides,⁶ using hydrated manganese dioxide is known. *p*-Toluenesulphonic acid catalysed alcoholysis of a nitrile to an ester is also recorded in literature.⁷ In our literature survey we have also encountered an unusual case of hydration of a C-N single bond of the type $>\text{N}-\text{CHR}-\text{N}<$ followed by fragmentation to an aldehyde⁸ by *p*-toluenesulphonic acid hydrate which parallels our own observation reported here.

⁶ Cook, M. J., Forbes, E. J., and Khan, G. M., *Chem. Commun.*, 1966, 21.

⁷ James, F. L., and Bryan, W. H., *J. org. Chem.*, 1958, **23**, 1225.

⁸ Gottstein, W. J., Bocian, G. E., Crast, L. B., Dadabo, K., Essery, J. M., Godfrey, J. C., and Cheney, L. C., *J. org. Chem.*, 1966, **31**, 1922.

Our original objective of attempting to effect an intramolecular ring closure of (1) to (2) or its derived products is still under study with other reagents, including anhydrous *p*-toluenesulphonic acid.

Experimental

The following experiment outlines a typical procedure for the cleavage of ketone 2,4-dinitrophenylhydrazones.

To a suspension of acetophenone 2,4-dinitrophenylhydrazone (m.p. 238–240°) (3.19 g, 0.01064 mol) in chloroform (75 ml) was added *p*-toluenesulphonic acid monohydrate (2.02 g, 0.01064 mol) and the mixture was refluxed (2.5 hr). The red solid rapidly turned yellow. It was filtered off, and the residue was washed with chloroform (3 × 7 ml). The yellow solid (m.p. 201–202° from dry MeOH) was characterized as *p*-toluenesulphonate of 2,4-dinitrophenylhydrazine. From the filtrate and the combined washings, chloroform was removed and the residue was steam-distilled using a cyclic constant-volume steam-distillation set-up. The recovered acetophenone was trapped in hexane. Drying of the hexane extract over Na₂SO₄, removal of solvent, and short-path sublimation furnished pure acetophenone (1.1 g, 86%), identified by i.r. and t.l.c. comparison with an authentic sample.