

THE BASE-CATALYSED REGENERATION OF SOME CARBONYL COMPOUNDS FROM THEIR 2,4-DINITROPHENYLHYDRAZONES*

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A number of methods for the regeneration of aldehydes and ketones from their 2,4-dinitrophenylhydrazones have been suggested and their usefulness and limitations discussed.¹⁻¹⁴ In all of these regeneration methods the 2,4-dinitrophenylhydrazone is heated with an acid, usually a keto acid. Little, if any, attention appears to have been given to the possibility of a base-catalysed regeneration.

An investigation made of the stability of the 2,4-dinitrophenylhydrazones of octanal, heptanal, citronellal, and octan-2-one to heating in aqueous ethylene glycol in the presence of potassium bicarbonate has shown that one of the products of the reaction is a steam-volatile oil which appears to consist almost completely of the corresponding carbonyl compound. The yield is about 60% for the aldehydes and 35% for the ketone.

The identifications have been based mainly on gas chromatography on polar and non-polar stationary phases, though thin-layer chromatograms of the derived 2,4-dinitrophenylhydrazones and their mixed melting points have provided confirmation.

Each of the carbonyl compounds distils from the reaction mixture with a small amount of a coloured compound which is not soluble in dilute acid or alkali but can be eliminated by distillation of the oil, either alone or with steam. For octane-2-one and citronellal, thin-layer chromatograms suggest that the coloration is due to the presence of the corresponding 2,4-dinitrophenylhydrazone. Presumably in the other cases also a small amount of the 2,4-dinitrophenylhydrazone distils or is formed from some 2,4-dinitrophenylhydrazine which has distilled.

The regeneration occurs at comparable rates for the three aldehydes studied, but is much slower for the ketone under the same conditions. If the proportion of

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⁴ Djerassi, C., *J. Am. chem. Soc.*, 1949, **71**, 1003.

⁵ Demaecker, J., and Martin, R. H., *Nature*, 1954, **173**, 266.

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⁷ Keeney, M., *Analyt. Chem.*, 1957, **29**, 1489.

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⁹ Ralls, J. W., *Analyt. Chem.*, 1960, **32**, 332.

¹⁰ Elks, J., and Oughton, J. F., *J. chem. Soc.*, 1962, 4729.

¹¹ Ralls, J. W., *Analyt. Chem.*, 1964, **36**, 946.

¹² Mason, M. E., and Johnson, R., *Analyt. Chem.*, 1965, **37**, 760.

¹³ Jones, L. A., and Monroe, R. J., *Analyt. Chem.*, 1965, **37**, 935.

¹⁴ Harrison, H. R., and Eisenbaum, E. J., *J. org. Chem.*, 1966, **31**, 1294.

ethylene glycol to water is increased, the reaction temperature is increased and the ketone is regenerated in a comparable time. The ethylene glycol raises the temperature at which the bicarbonate solution boils and increases the solubility of the dinitrophenylhydrazone, but whether its function is more complex remains uncertain.

Gas chromatograms of the regenerated carbonyl compounds show an additional peak of longer retention time and about 1% of the area of the carbonyl compound. This component is not the corresponding alcohol or acid, but a positive identification has not been made.

The conversion of 2,4-dinitrophenylhydrazine into 1-hydroxy-6-nitro-1,2,3-benzotriazole by the action of bases (hydrazine hydrate, alkali metal hydroxides, and carbonates) has been reported and proceeds also under the conditions described here for the carbonyl regenerations.^{1,15-17} Nevertheless, the presence of this triazole could not be detected in the residue from the regeneration reactions. A simple mechanism involving the displacement of the equilibrium between the 2,4-dinitrophenylhydrazone, the carbonyl compound, and 2,4-dinitrophenylhydrazine seems likely, the carbonyl compound being removed by volatilization and the dinitrophenylhydrazine by conversion into an unidentified resinous product.

While uncertainties of scope and mechanism remain, this method of regeneration possesses some advantages over those previously described. Citronellal, for example, is very sensitive to acid and is largely destroyed under the conditions of acid-catalysed regeneration. Even regeneration from the semicarbazone with aqueous phthalic acid, refluxing under reduced pressure, is unsatisfactory in this respect. It has been reported recently that the optical purity of citronellal semicarbazone, prepared from the citronellal of Java citronella oil, can be increased by recrystallization,¹⁸ but it was not practicable to regenerate the aldehyde because of its instability to acid. However, conversion of the semicarbazone into the 2,4-dinitrophenylhydrazone can be achieved, by refluxing with excess 2,4-dinitrophenylhydrazine in pyridine, for example. Alkaline regeneration can then be used to provide the optically pure aldehyde.

Experimental

(a) Regeneration of Octanal

Octanal 2,4-dinitrophenylhydrazone (m.p. 106–108°, 5.25 g) was refluxed with a solution of potassium bicarbonate (7.5 g) in water (75 ml) and ethylene glycol (75 ml) under an oil trap. After 1½ hr the pot contained a very dark-coloured solution, and in the trap a yellow-coloured oil (1.7 ml) had collected which was redistilled (steam) to give an almost colourless oil (1.38 g, 63%).

Gas chromatographic examination of this oil on ethylene glycol succinate (EGS) revealed the presence of three components—one covering 98% of the total area of the chromatogram, a second (retention relative to octanal 2.9) occupying 1.5%, and the third, 0.5%. The principal peak had a retention identical with that of octanal on 20% EGS and 20% SE-30.

The regenerated oil (1.38 g) was refluxed with 2,4-dinitrophenylhydrazine (3 g) in alcohol (50 ml) for several hours. The solution was diluted with water and the ether-soluble solid which

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¹⁷ Killen Macbeth, A., and Price, J. R., *J. chem. Soc.*, 1934, 1637.

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separated (3.2 g) was recrystallized from ethanol and diethyl ether to provide yellow needles, m.p. 106–108°.

(b) *Regeneration of Heptanal*

Heptanal 2,4-dinitrophenylhydrazone (4.99 g, m.p. 106–107°) yielded 1.22 g of oil or 63%, gas chromatography on EGS showing two peaks, the main peak covering 99% of the total area, the second (retention relative to heptanal 2.86) 1%. The retention time of the main peak coincided with that of heptanal on EGS and on SE-30.

The regenerated oil (1.22 g) on treatment with Brady's reagent gave a 2,4-dinitrophenylhydrazone which recrystallized from ethyl alcohol and diethyl ether as yellow needles, m.p. 106–107° not depressed on admixture with heptanal 2,4-dinitrophenylhydrazone.

(c) *Regeneration of Citronellal*

Citronellal 2,4-dinitrophenylhydrazone (3.036 g, m.p. 76–78°) was treated as in (a), and the oil which collected during 1½ hr was redistilled (steam) to give 0.843 g of oil, a yield of 60%. A gas chromatogram on SE-30 showed several peaks, the main peak having a retention identical with that of citronellal and covering 98% of the total area. A second peak (retention relative to citronellal 3.7) covered 1.5% and the rest 0.5%.

An ethyl acetate extract of the pot residue from the redistillation (steam) of the oil was examined by thin-layer chromatography on alumina with 15% ethyl acetate in light petroleum as the moving phase. Only one spot showed, and this had a mobility identical with that of citronellal 2,4-dinitrophenylhydrazone.

The regenerated oil (0.84 g) was refluxed with excess 2,4-dinitrophenylhydrazine in alcohol for several hours. The alcohol was evaporated and the 2,4-dinitrophenylhydrazone freed of excess 2,4-dinitrophenylhydrazine by chromatography on alumina with diethyl ether as eluent; this provided a 2,4-dinitrophenylhydrazone apparently homogeneous to thin-layer chromatography and identical in mobility with citronellal 2,4-dinitrophenylhydrazone.

Recrystallization from alcohol provided plates, m.p. and mixed m.p. with citronellal 2,4-dinitrophenylhydrazone, 76–78°.

(d) *Regeneration of Octan-2-one*

Octan-2-one 2,4-dinitrophenylhydrazone (2.21 g, m.p. 66–67°) was refluxed with a solution of potassium bicarbonate (3 g), ethylene glycol (60 ml), and water (30 ml) for 1½ hr to give a red-coloured oil which was redistilled (steam) to yield 0.34 g, a yield of 37%. A gas chromatogram on 5% SE-30 showed two peaks: the main peak, identical in retention with octan-2-one, covering 98.5% of the area; the second 1.5% (retention relative to octan-2-one, 2.3).

The regenerated oil (0.34 g) was treated with Brady's reagent and the product recrystallized from ethanol and ether to m.p. 66–67°, not depressed by mixing with octan-2-one 2,4-dinitrophenylhydrazone.

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CORRIGENDA

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Page 2111: Formula (XVIII) should have the OMe group on the bond pointing downwards, not on the bond pointing upwards.

Page 2112, line 2: for 5-O-methylepiinositol read 6-O-methylepiinositol