rate of 2 to 3 bubbles/second. The cyanide accumulated in the alkaline solution in the wash bottle which was removed at the termination of the heating period. Yields in this step were quantitative.

In a series of four runs, using approximately 1 mmole. of barium carbonate, in which the magnesium excess ranged from 14 to 48% over the stoichiometric amount, and the carbon dioxide pressure from 278 to 385 mm., the yields of cyanide obtained were 67, 69, 72 and 59%. The value of 59% was obtained by radioactivity assay, the others by silver nitrate titration.

INSTITUTE OF RADIOBIOLOGY AND BIOPHYSICS
UNIVERSITY OF CHICAGO
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2,4-Dinitrophenylhydrazones of Methoxy- and Methylcyclohexanones

BY HOMER ADKINS AND A. G. ROSSOW

Since the literature record of the melting points of these derivatives is confused and contradictory, we have re-examined the behavior of their ketones in the procedure described by Shriner and Fuson.[1]

2-Methoxycyclohexanone gave in our hands not the 2,4-dinitrophenylhydrazone, m. p. 135°, reported by others[2] but slowly and in low yield a red product, m. p. 218–219° uncor., whose analysis corresponded to cyclohexandione-1,2-bis-(2,4-dinitrophenyl)-osazone. *Anal.* Calcd. for $C_{18}H_{16}N_8O_8$: N, 23.72. Found: N, 23.62. This reaction is analogous to the prior[3] record for 3-methoxy-2-butanone. 3-Methoxycyclohexanone by similar treatment did not yield a 2,4-dinitrophenylhydrazone, m. p. 133.5°,[2] but instead gave rapidly in quantitative yield a product, m. p. 170–170.5° uncor., whose analysis indicated loss of methanol as well as water during the condensation. *Anal.* Calcd. for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.30; H, 4.42; N, 20.54. Our product may therefore be either a ring-closed derivative or cyclohexen-2-one 2,4-dinitrophenylhydrazone; the latter has previously been reported as m. p. 163[4] and 117°.[5] From the 4-methoxy ketone we obtained 4-methoxycyclohexanone 2,4-dinitrophenylhydrazone, orange crystals from ethanol, m. p. 142.5–143.5° uncor. *Anal.* Calcd. for $C_{13}H_{16}N_4O_5$: N, 18.18. Found: N, 18.20. This accords with the m. p. of 141.5–142.5°[6] but disagrees with the values of 150°[2,7] from the prior literature.

The behavior of 2-methylcyclohexanone was not examined, but its position isomers gave conventional results. 3-Methylcyclohexanone gave an orange-yellow 3-methylcyclohexanone 2,4-dinitrophenylhydrazone, m. p. 153.5–155.0° uncor., which appeared to be a mixture of stereoisomers. *Anal.* Calcd. for $C_{13}H_{16}N_4O_4$: N, 19.17. Found: N, 19.22. The same procedure on 4-methylcyclohexanone gave 4-methylcyclohexanone 2,4-dinitrophenylhydrazone, golden yellow crystals from ethanol, m. p. 134.7–135.1° uncor. *Anal.* Found: N, 19.47.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
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[1] Shriner and Fuson, "The Systematic Identification of Organic Compounds," p. 148, John Wiley and Sons, Inc., New York, N. Y., 1935; the preparation and properties of the ketones are given in another paper. Adkins, Elofson, Rossow and Robinson, THIS JOURNAL, **71**, 3622 (1949).

[2] Ferrante and Bloom, *Am. J. Pharm.*, **105**, 381 (1933).

[3] Aston, Clarke, Burgess and Greenburg, THIS JOURNAL, **64**, 300 (1942).

[4] Bartlett and Woods, *ibid.*, **62**, 2933 (1940).

[5] Whitmore and Pedlow, *ibid.*, **63**, 758 (1941).

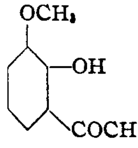
[6] Adamson and Kenner, *J. Chem. Soc.*, 188 (1939).

[7] Marvel and Walton, *J. Org. Chem.*, **7**, 92 (1942).

The Reaction of *o*-Veratronitrile with Methylmagnesium Iodide

BY E. D. AMSTUTZ

In the course of other work to be reported later relatively large quantities of *o*-acetovanillone (I) were required.


I

The usual method of synthesis involves the successive conversion of *o*-veratric aldehyde to the methylcarbinol,[1] acetophenone,[2] and demethylation.[3] It has now been found that several of these steps may be obviated with improvement in yield and facility. Although ether splitting is by no means new, the reaction of *o*-veratronitrile with methylmagnesium iodide has previously been reported[4] to yield the dimethoxyketone. Apparently the phenol formed escaped attention.

The present work has shown that the 2,3-dimethoxyacetophenone may be the main product of the reaction but also that conditions may be so arranged that it appears only as a minor product with 2-demethylated ketone assuming major importance. For example, using double the calculated quantity of Grignard reagent over a total reaction time of sixty hours the yield of *o*-acetovanillone rises to about 75% and the yield of non-phenolic ketone drops to about 18%.

Since the methoxyl group ortho to the acetyl is vinylogous with methyl acetate it is not inconceivable that it could have suffered hydrolysis during the acid treatment to destroy the magnesium complex. A sample of the solid magnesium-containing complex was therefore removed from the reaction mixture and rapidly decomposed with cold ammonium chloride solution. Ether extraction removed a yellow material which exhibited (in alc. soln.) a definitely positive test for the phenolic group with ferric chloride. Since it is hardly likely that the hydrolysis could have occurred under these mild conditions and in such a short interval of time, it appears necessary to suppose that the splitting occurred during the reaction of the Grignard reagent. The same conclusion is indicated by the fact that 2,3-dimethoxyacetophenone (in ether soln.) did not yield phenolic bodies on gentle warming and stirring for three hours with dilute hydrochloric acid, although it was obvious other changes were taking place. Also Fuson and Chadwick[5] have

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[1] Pauly, *et al.*, *Ann.*, **383**, 317 (1911).

[2] Krannichfeldt, *Ber.*, **46**, 4016 (1913).

[3] Reichstein, *Helv. Chim. Acta*, **10**, 392 (1927).

[4] Richtzenhain and Nippus, *Ber.*, **77B**, 566 (1914); Baker and Smith, *J. Chem. Soc.*, 346 (1936).

[5] Fuson and Chadwick, *J. Org. Chem.*, **13**, 484 (1948).