monium bromide dissolved in approximately 50 ml. of liquid ammonia in c were titrated with potassium solutions of known concentration delivered from the calibrated buret a. The first appearance of a permanent blue color (characteristic of solutions of metals in ammonia) was taken as the end-point. Data for two such titrations are given in Table I (Expts. 1 and 2).

TABLE I

REDUCTION OF AMMONIUM BROMIDE AND SILVER(I) BROMIDE

Expt.	Substance	Reactants, g. Measured	Calcd.[a]	Products Measured	Calcd.[a]	Acctd. for, %
	NH_4Br	1.0061				
1	K	0.397[b]	0.402			99
	H_2			109 cc.	115 cc.	95
	NH_4Br	1.0518				
2	K	0.418[b]	.420			100
	H_2			119 cc.	120 cc.	99
	AgBr	.3173				
3	K	.0667[b]	.0660			101
	Ag			0.1818 g.	0.1822 g.	99.8
	AgBr	.2877				
4	K	.0598[b]	.0599			100
	Ag			0.1646 g.	0.1653 g.	99.6

[a] Calcd. on the basis of the weight of ammonium bromide or silver(I) bromide used. [b] Measured as a portion (15–20 ml.) of a known volume (25–30 ml.) of potassium solution containing a weighed quantity of potassium.

Reduction of Silver(I) Bromide with Potassium.—Solutions containing known weights of silver(I) bromide were similarly titrated with potassium solutions. In these cases, however, the end-point could not be detected as indicated above, owing to the presence of the black finely divided precipitate of elemental silver. Consequently, a calculated volume of potassium solution was added, the precipitate allowed to settle, and drops of potassium solution were added to the clear supernatant solution until there was no further evidence of reaction. The combined supernatant solution and washings gave a negative test for silver ion. The resulting data are shown as Expts. 3 and 4, Table I.

Summary

An improved apparatus for the conduct of reactions in liquid ammonia at its boiling point has been described, and its utility demonstrated. This apparatus provides for titrations employing liquid ammonia solutions of metals and permits one to carry out filtration and purification operations at the boiling point of the solvent.

It has been demonstrated that silver(I) bromide is reduced to elemental silver by reaction with solutions of potassium in liquid ammonia.

AUSTIN, TEXAS RECEIVED MARCH 25, 1949

NOTES

Preparation of Radioactive Cyanide from Carbon Dioxide

BY RICHARD ABRAMS

For synthesis of labeled compounds it is often necessary to convert $BaC^{14}O_3$ to $HC^{14}N$. Available methods treat carbon dioxide with ammonia and potassium metal[1] (yield is a sensitive function of experimental conditions[2]), or treat barium carbonate with sodium azide[3] (yields are low in our experience). A method which has been found to be very satisfactory is based upon the reduction of carbon dioxide to carbon with magnesium powder,[4] and the conversion of amorphous carbon to hydrocyanic acid with ammonia gas at 1000°.[2,5,6] Yields are usually between 60 and 70% and not particularly dependent upon carbon dioxide pressure or magnesium excess.

In a typical experiment, carbon dioxide was liberated into a vacuum system from 1.1 mmoles. of barium carbonate by mixing with 1.6 g. of lead chloride and heating with a micro-burner.[7] Traces of water were removed by sublimation at $-80°$. The carbon dioxide was then admitted to a quartz tube containing 2.5 mmoles. of magnesium powder in a thin-walled iron thimble. The tube was heated rapidly with an oxygen flame until the thimble glowed red, and reaction began as noted by the sharp pressure drop. Intermittent heating was continued until the pressure remained constant. The contents of the thimble were washed with 1 *M* hydrochloric acid and with water, transferred as a slurry to a quartz boat, and dried under an infrared lamp. The yield was 0.76 mmole. of carbon which was 89% pure. Based upon the residual pressures of condensable and non-condensable gases and the acetylene liberated upon wetting the reaction mixture, the 30% loss consisted of approximately 5% unreacted carbon dioxide, 10% carbon monoxide, and 15% magnesium carbide.

The boat containing the carbon was placed in a quartz tube surrounded by an electric furnace. Ammonia gas was allowed to flow directly from the tank through the quartz tube and out through a wash bottle containing a 10% excess of 0.1 *M* sodium hydroxide. When all the air had been displaced by ammonia, the furnace was turned on so that the temperature rose to 1000° in thirty minutes, and stayed between 1000° and 1100° for two and one-half hours. All the hydrocyanic acid formed was carried out by the ammonia which flowed through the tube continuously at a

(1) Cramer and Kistiakowsky, *J. Biol. Chem.*, **137**, 549 (1941).

(2) Loftfield, *Nucleonics*, **1**, 54 (1947).

(3) Adamson, THIS JOURNAL, **69**, 2564 (1947).

(4) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, England, 1925, Vol. 6, p. 71.

(5) Mellor, *ibid.*, 1924, vol. 5, p. 827.

(6) Cramer, Thesis, Harvard, 1941.

(7) Zwiebel, Turkevich and Miller, THIS JOURNAL, **71**, 376 (1949).

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.

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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.

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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).

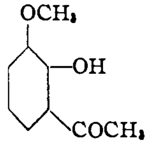
[6] Adamson and Kenner, *J. Chem. Soc.*, 188 (1939).

[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).