

A few drops of the deuterium oxide is run from the funnel into the flask containing a two to three mole excess of benzoyl chloride (reagent grade). The flask is gently heated until deuterium chloride is evolved at a satisfactory rate, and the temperature is maintained at this level until all of the deuterium oxide has been added and the evolution of gas has noticeably slackened. The temperature is then slowly raised to the boiling point of the benzoyl chloride and maintained there until gas is no longer produced.

At the end of the reaction, a slow stream of dry air is passed into the system through the dropping funnel (the refluxing of the reaction mixture is not interrupted) to force the last traces of deuterium chloride to the outlet. At all times the evolution of deuterium chloride is smooth, easily controlled (the addition of a few chips of porous plate to the reaction flask is advisable), and may be halted simply by removing the source of heat.

The details of one test preparation will be given to illustrate the yields and degree of purity which may be expected.

Five ml. (0.550 equiv.) of deuterium oxide (99.6%) were treated with an excess (*ca.* 1.5 moles) of benzoyl chloride. The deuterium chloride obtained was dissolved in distilled water (contained in a 250-ml. volumetric flask), the solution in the flask diluted to the mark, and samples removed for analysis. Total acidity found was 0.528 equiv. (average of three deter-

minations: 0.526, 0.527, 0.531), representing a yield of 96% of the theoretical. The solution was analyzed volumetrically for chloride ion by the Volhard method; found: 0.529 equiv. (average of three determinations: 0.528, 0.530, 0.530). The deuterium content was determined by the temperature float method on a portion of the solution after the acid had been carefully neutralized with barium oxide and the water distilled; found: 0.528 equiv. of deuterium (average of two determinations: 0.530, 0.526). It is evident that, within the accuracy of the experiment, a nearly quantitative yield⁷ of pure deuterium chloride had been obtained.

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Summary

Deuterium chloride may be prepared conveniently by the action of benzoyl chloride on deuterium oxide at elevated temperatures. The product is analytically pure and the yields (based on the available deuterium) are practically quantitative.

(7) In three preliminary experiments in which 9 to 18 g. of water (1.0 to 2.0 equiv.) were transformed into hydrogen chloride by this method, the yields obtained were 98.5, 100, 99%.

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NOTES

Physical Constants of Methyl Isopropenyl Ketone

BY JOSEPH H. BRANT

The literature dealing with methyl isopropenyl ketone¹⁻⁸ shows a considerable variance with respect to the physical constants of this ketone.

(1) Beilstein IV, Vol. I, p. 733, Supp., 381.

(2) Morgan, Megson and Pepper, *Chemistry and Industry*, **57**, 390 (1938).

(3) Morgan, Megson and Pepper, *ibid.*, **57**, 885 (1938).

(4) Rutovskii and Jakobson, *J. Applied Chem.*, (U. S. S. R.), **14**, 528 (1941).

(5) Rutovskii and Dmitrieva, *ibid.*, **14**, 535 (1941).

(6) Rutovskii and Goncharov, *ibid.*, **14**, 542 (1941).

(7) Brant and Hasche, U. S. Patent 2,245,567.

(8) Marvel, Riddle and Corner, *THIS JOURNAL*, **64**, 92 (1942).

Two methods of preparation have been described in the recent literature. The liquid phase synthesis from methyl ethyl ketone and formalin has been studied extensively by Morgan and co-workers^{2,3} and also by Rutovskii and co-workers.^{4,5,6} A vapor phase synthesis has been described by Brant and Hasche⁷ in which the ketone is produced in one step starting with methyl ethyl ketone and formalin or paraformaldehyde.

More recently Marvel, Riddle and Corner⁸ reported the boiling point of methyl isopropenyl ketone as 45–46° at 40 mm. It would appear that this value is considerably too high.

In order to help clarify this situation regarding the physical constants the following table is presented which shows the effect of time on the physical constants of methyl isopropenyl ketone. The first determinations listed were made within a few minutes after the completion of a careful vacuum distillation. The fraction studied was the middle 75 cc. from an 800-cc. batch and collected in a brine cooled receiver at about -10° . The material used in these tests was stored in a clear glass bottle without an inhibitor present and at room temperature. This sample contained less than 0.01% H_2O .

TABLE I

Age, days	n_{20}^D	d_{20}^{20}	Age, days	n_{20}^D	d_{20}^{20}
	1.4163	0.8459	12	1.4242	0.8710
1	1.4162	.8458	13	1.4260	.8758
2	1.4163	.8465	14	1.4280	.8809
3	1.4166	..	15	1.4293	.8862
4	1.4168	..	16	1.4310	.8884
5	1.4170	.8485	17	1.4328	.8954
6	1.4174	..	18	1.4360	..
7	1.4183	..	19	1.4380	..
8	1.4190	.8566	20	1.4400	..
9	1.4208	.8604	21	1.4424	..
10	1.4214	.8632	22	Too viscous to examine	
11	1.4230	.8670	30	Glass-like solid	

Other samples have shown comparable behavior except that the change has set in more quickly. One other sample on record was as much polymerized after thirteen hours as the one above was in seven days based on the density and refractive index values. No doubt some catalyzing impurities present in very small amounts account for this variation in rate of polymerization.

It appears necessary that physical constants of pure methyl isopropenyl ketone be determined as soon after distillation as possible even when inhibitors have been added.

The following are constants obtained for pure freshly vacuum distilled methyl isopropenyl ketone made by the vapor phase process.⁷

n_{20}^D	1.4163
d_{20}^{20}	0.8459
Molecular refraction, calculated	24.84
Molecular refraction, observed	25.05
Boiling point (735 mm.), $^{\circ}C$.	98.5
Boiling point (100 mm.), $^{\circ}C$.	45-46
Boiling point (75 mm.), $^{\circ}C$.	37-38
Boiling point of the water azeotrope (735 mm.)	82
(100 mm.)	34-35

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The Further Nitration of Certain Dinitrophenyls

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2,3',4,4'-Tetranitrobiphenyl has been obtained by Blakey and Scarborough¹ by the nitration of either 2,3'- or 3,4'-dinitrobiphenyl. These authors were, however, unable to obtain the corresponding trinitro derivatives. In this Laboratory, 2,3',4-trinitrobiphenyl (m. p. 137-138 $^{\circ}$, from alcohol) was the sole product isolated after heating 2,3'-dinitrobiphenyl with nitric acid (sp. gr. 1.5) for three minutes.

Anal. Calcd. for $C_{12}H_7N_3O_6$: N, 14.54. Found: N, 14.77.

When 3,4'-dinitrobiphenyl (6 g.) was heated for one hour with nitric acid (50 cc., sp. gr., 1.5), the reaction mixture poured into water, and the precipitate crystallized from benzene, 3,4,4'-trinitrobiphenyl (1.1 g., m. p. 205-206 $^{\circ}$) was first obtained.

Anal. Calcd. for $C_{12}H_7N_3O_6$: N, 14.54. Found: N, 14.70.

On evaporation of the benzene mother liquors and crystallization from alcohol, 2,3',4-trinitrobiphenyl (1.5 g., m. p. 136-137 $^{\circ}$) separated. This product melted unchanged when mixed with the trinitro isomer from 2,3'-dinitrobiphenyl. The structure of the isomer melting at 137-138 $^{\circ}$ follows from its dual method of synthesis; that of the isomer (m. p. 205-206 $^{\circ}$) depends on the fact that it is different from II, and yet yields the known 2,3',4,4'-tetranitrobiphenyl on further nitration.

When 3,3'-dinitrobiphenyl (5 g.) was nitrated under the conditions described above for the 3,4'-compound, and the product was crystallized from a mixture of acetone and alcohol, 3,3',4-trinitrobiphenyl (2.4 g., m. p. 179-180 $^{\circ}$) was obtained.

Anal. Calcd. for $C_{12}H_7N_3O_6$: N, 14.54. Found: N, 14.53.

The structure of this compound was evident from the fact that on further nitration with mixed acids (1:1) at 100 $^{\circ}$, 3,3',4,4'-tetranitrobiphenyl, m. p. 203-204 $^{\circ}$ (from alcohol-acetone), identical (mixed m. p. undepressed) with a sample prepared by Ullmann's method² from 3,4-dinitroiodobenzene, was obtained.

Anal. Calcd. for $C_{12}H_5N_4O_8$: N, 16.77. Found: N, 16.90.

(1) Blakey and Scarborough, *J. Chem. Soc.*, 3000 (1927).

(2) Cf. Ullmann and Bielecki, *Ber.*, **34**, 2179 (1901). These authors, apparently through an error, record the m. p. of this compound as 186 $^{\circ}$.

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Preparation of *p*-Aminobenzenesulfonyl Urea

BY EDWARD H. COX

The procedure for the preparation of the aryl-sulfonyl ureas¹ has now been applied in making

(1) Cox and Raymond, *This Journal*, **63**, 300 (1941).