

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

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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).