

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

BY FRANCIS H. CASE

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).

p-aminobenzenesulfonyl urea. The therapeutic properties of this compound and some of its salts are under investigation.

***p*-Acetaminobenzenesulfonyl Ethyl-isourea.**—In a five-liter flask provided with a mechanical stirrer was placed 600 g. of anhydrous potassium carbonate, 2 liters of acetone and 100 cc. of water. The suspension of carbonate-acetone-water was stirred and cooled in an ice-bath. To this suspension 272 g. (2.2 moles) of ethyl-isourea hydrochloride was added gradually over a period of one-half hour. With each addition some water was added until the total amount was 400 cc. The ice-bath was removed after the addition and the reaction mixture stirred at room temperature for four hours.

The reaction material was then poured into five liters of water, and the crude product filtered and washed. The weight of the crude dried product was 458 g. (87% yield). It crystallized from 50% acetic acid as white needles and melted at 223–224°.

Anal. Calcd. for $C_{11}H_{15}O_4N_3S$: N, 14.71. Found: N, 14.76, 14.79.

***p*-Aminobenzenesulfonyl Urea.**—One mole (285 g.) of *p*-acetaminobenzenesulfonyl ethyl-isourea (crystallized once from dilute acetic acid) was placed in a two liter flask and covered with 700 cc. of concentrated hydrochloric acid. The isourea first dissolved and then reprecipitated as the hydrochloride. The flask was immersed in a boiling water-bath and the reaction mixture stirred until solution took place (fifteen to twenty minutes). Decolorizing charcoal was added while still hot and the solution was filtered. After the addition of an equal volume of alcohol the filtrate was set aside to crystallize. The dried crystalline product weighed 200 g. (80% yield). White needles were produced when the product was recrystallized from dilute acetic acid. The compound melted with gas formation (ammonia) at 140–146°. ^{2,3}

Anal. Calcd. for $C_7H_9O_3N_3S$: N, 19.54. Found: N, 19.53, 19.59.

Salts of *p*-Aminobenzenesulfonyl Urea.—The ammonium, potassium and sodium salts were prepared by treating slightly more than one equivalent of the *p*-aminobenzenesulfonyl urea with one equivalent of the metallic carbonate in 50% alcohol. After the addition of the carbonate, ether was added to produce the maximum yield of the salt.

Ammonium Salt. *Anal.* Calcd. for $C_7H_{12}O_3N_4S$: N, 24.12. Found: N, 24.09, 24.19.

Potassium Salt. *Anal.* Calcd. for $C_7H_9O_3N_3SK$: N, 16.59. Found: N, 16.54, 16.56.

Sodium Salt. *Anal.* Calcd. for $C_7H_9O_3N_3SNa$: N, 17.71. Found: N, 17.59, 17.64.

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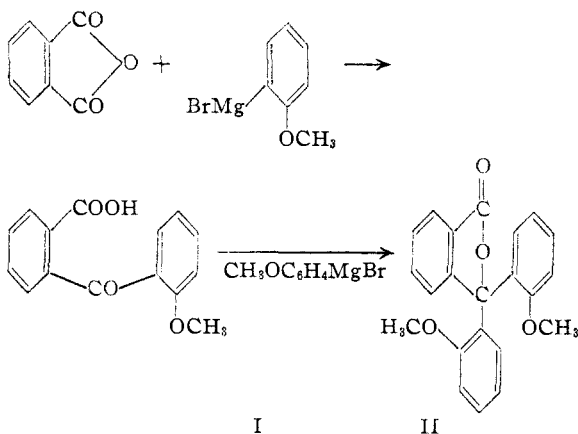
(2) The properties of this compound as given by Geigy, British Patent 538,884, are not in agreement with those recorded here.

(3) Since the completion of this work, *p*-aminobenzenesulfonyl urea has been reported by Roblin and his co-workers, *THIS JOURNAL*, **64**, 1683 (1942).

A Synthesis of 2-(2'-Methoxybenzoyl)-benzoic Acid

BY BRADFORD P. GEYER¹

In the course of a projected synthesis of 1-hydroxyfluorenone it became necessary to prepare a quantity of 2-(2'-methoxybenzoyl)-benzoic acid (I). This keto acid was prepared previously by Sieglitz² by methylation of 2-salicylylbenzoic acid. The synthesis of I has now been accomplished, using phthalic anhydride and *o*-bromoanisole as starting materials.



A by-product formed in the Grignard reaction of *o*-anisylmagnesium bromide with phthalic anhydride is 2,2-di-*o*-anisylphthalide (II), reported earlier by Ferrario³ and by Blicke and Weinkauff.⁴

Experimental

Before preparing the Grignard reagent, *o*-anisylmagnesium bromide, the flask containing 9.6 g. (0.4 mole) of magnesium was heated with a low, free flame to expel traces of moisture. A 20-ml. portion of anhydrous diethyl ether, freshly distilled from an ethereal ethylmagnesium bromide solution and containing 10 drops of ethyl bromide, was placed in the flask with the magnesium. To this mixture, agitated by means of a mercury-seal stirrer, 63 g. (0.34 mole) of *o*-bromoanisole in 100 ml. of diethyl ether, the latter likewise freshly distilled from the same ethylmagnesium bromide solution, was added dropwise. After complete addition of the *o*-bromoanisole, the solution of the arylmagnesium halide was heated under reflux for one-half hour. This Grignard reagent was then introduced slowly, dropwise, to a vigorously stirred, hot solution of 37 g. (0.25 mole) of phthalic anhydride in 600 ml. of thiophene-free benzene, ether being removed simultaneously by distillation. Pale yellowish-white solid formed immediately. After the addition of all of the re-

(1) Present address: Shell Development Company, Emeryville, California.

(2) Sieglitz, *Ber.*, **57**, 316 (1924).

(3) Ferrario, *Gazz. chim. ital.*, **41**, I, 1 (1911).

(4) Blicke and Weinkauff, *THIS JOURNAL*, **54**, 1452 (1932).