

into 400 cc. of water and chilled. The resulting precipitate was filtered, washed and mixed with an amount of alcohol insufficient for complete solution. The residue was recrystallized from alcohol. The yield was 0.5 g. of product, melting at 181–182°, and mix-melting unchanged with (VII).

**C. From the Monobromide (IX).**—Five grams of the monobromide was dissolved in 150 cc. of boiling alcohol. To this solution was added 1 g. of hydroxylamine hydrochloride in 5 cc. of water, and 4.5 g. of potassium hydroxide in 5 cc. of water. The solution turned red as potassium salts separated. After standing for ten minutes, the reaction mixture was cooled and filtered. After recrystallization from alcohol, the material melted and mix-melted with the products from (A) and (B) at 182°.

*Anal.* Calcd. for  $C_{16}H_{12}N_2O_4$ : C, 64.9; H, 4.1. Found: C, 65.3; H, 4.2.

**3-*p*-Methoxyphenyl-5-*m*-nitrophenylisoxazoline (VIII).**—To 11.3 g. of the  $\alpha,\beta$ -unsaturated ketone (I) in 300 cc. of alcohol was added 4.2 g. of hydroxylamine hydrochloride, in 20 cc. of water, and 8 g. of potassium hydroxide in 20 cc. of water. The reaction mixture, which turned dark, was refluxed for two hours. The solution was allowed to stand overnight and the crystals which separated were washed thoroughly with water to take out the potassium chloride formed. Upon recrystallization, 3.5 g. of material melting at 175–179° was obtained. Another recrystallization from alcohol did not change the melting point range.

*Anal.* Calcd. for  $C_{16}H_{14}N_2O_4$ : C, 64.4; H, 4.7. Found: C, 65.0; H, 4.9.

**$\alpha$ -Bromo-*p*-methoxybenzal-*m*-nitroacetophenone (IX).**—A solution of 10 g. of the dibromide in 150 cc. of glacial acetic acid was refluxed for two hours with 20 g. of freshly fused potassium acetate. The solution became slightly colored. It was cooled and poured into a large volume of water. A dark red oil separated. This oil was dissolved in ether, washed with water, freed of the last traces of acetic acid by shaking with sodium bicarbonate solution, washed with water, dried over anhydrous sodium sulfate and evaporated *in vacuo* over solid potassium hydroxide. There resulted a viscous, dark red oil which weighed 6.8 g.

*Anal.* Calcd. for  $C_{16}H_{12}BrNO_4$ : C, 53.1; H, 4.3. Found: C, 53.0; H, 3.6.

### Summary

The authors have prepared 3-nitro-4'-methoxydibenzoylmethane, and have shown that in alcoholic solution it is essentially 100% enolic and behaves as 1-*p*-methoxy-phenyl-3-*m*-nitrophenylpropene-one-3-ol-1 in isoxazole formation, giving rise to 3-*m*-nitrophenyl-5-*p*-methoxyphenylisoxazole (IV).

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

## The Bromination of 4-Phenylphenyl Trimethylacetate

BY LEE C. HENSLEY AND STEWART E. HAZLET

In previous studies of the bromination of 4-phenylphenol esters of various acids, the acetyloxy group has been shown to direct an entering bromine atom to an adjacent position in the biphenyl nucleus,<sup>1</sup> but the presence of a larger benzyloxy<sup>2</sup> or benzenesulfonyloxy group<sup>3</sup> caused bromine to enter the molecules at the remote para position. Similar substitution at the remote end of the biphenyl system was found when the corresponding chloro- and bromoacetates were brominated,<sup>4</sup> although, of necessity, the experimental conditions were modified considerably. In the present report, the trimethylacetyloxy group also has been shown to direct an entering bromine atom to the remote para position under the same experimental conditions as those employed for the haloacetates; difficulties similar to those encountered with the chloro- and bromoacetates were met when acetic acid was used as solvent.

A reason for the selection of the trimethylacetate for study was that in this compound, on the basis of Fisher-Hirshfelder models,<sup>5</sup> effective simple spacial hindering dimensions of the acyloxy group are somewhat comparable to those in the benzoate; *i. e.*, a rather large acyloxy group with

a possible screening effect is present. The results of this investigation corroborate the suggestions advanced previously that steric hindrance may function, in part, in determining the orienting influences of the groups present and force bromination to take place in the ring not bearing the acyloxy group. An alternative view, that the strengths of the acids corresponding to the acyloxy groups involved are factors, is eliminated by the present work with 4-phenylphenyl trimethylacetate. The ionization constant of trimethylacetic acid is lower than that of acetic acid which, in turn, is lower than that of benzoic, bromoacetic, chloroacetic or benzenesulfonic acid.<sup>6</sup> This does not parallel the orienting influences of the acyloxy groups; acetyloxy was the only one which permitted substitution in an adjacent position.

Some related compounds have been prepared; descriptions of these are given in the Experimental Part.

### Experimental Part

**Trimethylacetic Acid.**—This material was obtained by the method of Puntambeker and Zoellner<sup>7</sup> from *t*-butyl chloride or bromide, which had been prepared according to the procedure of Norris and Olmsted<sup>8</sup>; of the two, the chloride gave somewhat better yields.

(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, Vol. VI, p. 262 *et seq.*

(7) Gilman and Blatt, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941, p. 524.

(8) *Ibid.*, p. 144.

(1) Hazlet and Kornberg, *THIS JOURNAL*, **61**, 3037 (1939).

(2) Hazlet, Alliger and Tiede, *ibid.*, **61**, 1447 (1939).

(3) Hazlet, *ibid.*, **59**, 1087 (1937).

(4) (a) Hazlet, Hensley and Jass, *ibid.*, **64**, 2449 (1942); (b) Hensley and Hazlet, *ibid.*, **65**, 987 (1943).

(5) Manufactured and distributed by the Fisher Scientific Co., Pittsburgh, Penna.

TABLE I  
ESTERS OF TRIMETHYLACETIC ACID AND BROMOPHENYLPHENOLS

Phenol used	Yield, % <sup>a</sup>	Solvent, ligroin	Crystal form	M. p., °C.	Formula	Analyses, % Br Calcd.	% Br Found
2-Bromo-4-phenyl <sup>b</sup>	40.2	30-60°	Large prisms	60.5-62	C <sub>17</sub> H <sub>17</sub> O <sub>2</sub> Br	23.95	23.91
4-(4-Bromophenyl)- <sup>c,d</sup>	35.3	70-90°	Plates	119.5-121	C <sub>17</sub> H <sub>17</sub> O <sub>2</sub> Br	23.95	23.99
2,6-Dibromo-4-phenyl <sup>b</sup>	43.6	70-90°	Prisms	86-87	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub> Br <sub>2</sub>	38.78	38.57
2-Bromo-4-(4-bromophenyl)- <sup>c</sup>	36.7	70-90°	Heavy plates	93.5-94	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub> Br <sub>2</sub>	38.78	38.62

<sup>a</sup> Purified products. <sup>b</sup> Ref. 2. <sup>c</sup> Bell and Robinson, *J. Chem. Soc.*, 1127 (1927). <sup>d</sup> Ref. 3.

**Trimethylacetyl Chloride.**—Trimethylacetic acid was treated with thionyl chloride as directed by Helferich and Schaefer<sup>2</sup> for the preparation of *n*-butyryl chloride; yields of between 50 and 60% were obtained.

**4-Phenylphenyl Trimethylacetate.**—Twenty-eight grams of 4-phenylphenol was dissolved in 12 ml. of dry pyridine and 24 ml. of dry 1,4-dioxane. The solution was cooled to 8°, and 18 g. of trimethylacetyl chloride was added in small portions with stirring and cooling. After the reaction mixture had been allowed to stand at room temperature for ninety minutes, it was warmed on a steam-bath for an equal period of time; finally, it was placed in an oil-bath at 100°, gradually heated to 140°, and then permitted to cool slowly. The colorless reaction mixture was extracted three times with 50-ml. portions of hot benzene; the residue was treated with water, and again it was extracted with benzene. The extracts were combined, washed with water, 5% hydrochloric acid, water, 5% sodium hydroxide, and water and dried over sodium sulfate. The residue obtained by filtration and removal of the solvent was crystallized from 30-60° ligroin; large crystals resulted, m. p. 66.5-67.5°, 28.5 g. (75%).

*Anal.* Calcd. for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>: C, 80.28; H, 7.14. Found: C, 80.28; H, 7.23.

**Trimethylacetates of the Bromophenylphenols.**—These esters were prepared by treating the appropriate phenol in the presence of 1,4-dioxane as diluent with 1.1 to 1.2 molecular proportions of trimethylacetyl chloride in an equivalent quantity of dry pyridine. The colorless esters were extracted from the reaction mixtures with boiling benzene and recrystallized from suitable solvents, *cf.* Table I.

**Bromination of 4-Phenylphenyl Trimethylacetate.**—Eight grams of 4-phenylphenyl trimethylacetate was dis-

solved in 60 ml. of carbon tetrachloride, and the solution was warmed to 70° in an oil-bath. At this temperature, 1.7 ml. of bromine in 20 ml. of carbon tetrachloride was added drop by drop with stirring over a period of thirty minutes in the presence of a trace of powdered iron. The stirring was continued for five hours, and the mixture was kept at 80-85°. The red solution was treated with Norite and filtered, and the solvent was distilled off on a steam-bath. The oily residue was dissolved in benzene, and this solution was washed with water, 5% sodium hydroxide solution, and water and set to dry over anhydrous sodium sulfate. (From the alkaline extract, 0.2 g. of unidentified material was isolated.) From the benzene solution an oily residue was obtained; it was dissolved in warm 30-60° ligroin, and colorless crystals appeared upon cooling the solution in a refrigerator. Three recrystallizations from the same solvent raised the melting point to 114-117°, 0.2 g. (1.9%). A mixed melting point determination was made with authentic 4-(4-bromophenyl)-phenyl trimethylacetate; observed, 119-119.5°.

### Summary

1. The bromination of 4-phenylphenyl trimethylacetate in carbon tetrachloride resulted in the formation of 4-(4-bromophenyl)-phenyl trimethylacetate.

2. The results somewhat confirm the suggestion that steric factors may function, in part, in determining the orienting effect of an acyloxy group present in a molecule.

3. Several related compounds were prepared, and some of their properties are reported.

PULLMAN, WASHINGTON

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## The Synthesis of Tri-*t*-butylcarbinol and Other Highly Branched Alcohols by Means of Sodium

BY PAUL D. BARTLETT AND ABRAHAM SCHNEIDER

This is a report of some work, interrupted by the war, which it seems desirable to publish in view of a recent paper by Young and Roberts<sup>1</sup> which extends the list of available highly branched alcohols by the use of organolithium compounds. An unsuccessful attempt was made in this Laboratory in 1941<sup>2</sup> to prepare tri-*t*-butylcarbinol by the reaction of *t*-butyllithium with hexamethylacetone. Thereafter we turned our attention to the possible use of sodium and alkyl halides in the synthesis of highly branched compounds. This

reaction, which has been used many times to achieve results parallel to those of the Grignard reaction,<sup>3</sup> is now found capable of yielding compounds so highly branched as to be inaccessible by other means hitherto reported.

Coarse sodium sand can be stirred for hours with *t*-butyl chloride in ether or pentane without any evidence of reaction. Upon addition of methyl pivalate, however, the sodium and the solution turn black and a vigorous evolution of an unsaturated gas occurs. The products identified

(1) Young and Roberts, *THIS JOURNAL*, **66**, 1444 (1944).

(2) Bartlett, Swain and Woodward, *ibid.*, **63**, 3229 (1941).

(3) Kekulé, *Ann.*, **137**, 181 (1866); Frey, *Ber.*, **26**, 2514 (1895); Schorigin, *ibid.*, **40**, 3111 (1907); **41**, 2711, 2717 (1908); Morton and Stevens, *THIS JOURNAL*, **53**, 2244 (1931).