One-Step Synthesis of Dinitropolymethylbiphenyls from Polymethylbenzenes

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Coupling of selected methylbenzenes or methylbenzene mixtures with nitric acid, followed by addition of sulfuric acid, results in the formation of dinitropolymethylbiphenyls. Seven of these compounds were readily isolated and characterized.

ADDITION OF NITRIC ACID at −46° to −20° C to 1,2-dialkylbenzenes or 1,2,3-trialkylbenzenes alone or to their mixture with a more basic polymethylbenzene gave polyalkylbiphenyls in addition to the expected nitration products (*3*); at somewhat higher temperatures, mononitropolyalkylbiphenyls were formed (*1, 2*). The reaction conditions can be adjusted to form dinitrated polyalkylbiphenyls (*1*). This note describes improved procedures for the preparation of the dinitrated products and their identification.

In the improved process the selected alkylbenzenes are coupled with nitric acid under conditions that give mononitropolyalkylbiphenyls (*1, 2*), and then sulfuric acid is added to the reaction mixture to introduce the second nitro group. This sequence is more easily controlled than the one previously described (*1*); the reaction of alkylbenzenes with nitric acid alone can be violent.

Although the coupling usually gives only one major biphenyl isomer (*3*), the introduction of nitro groups in most cases leads to an increased number of isomers. Nevertheless, in several cases the major isomers were readily isolated, even though in low yields.

2,2′-Dinitro-4,4′,5,5′-tetramethylbiphenyl (compound 1), 2,3′-dinitro-4,4′,5,5′-tetramethylbiphenyl (2), and 2,2′-dinitro-3,3′,4,4′,5,5′-hexamethylbiphenyl (3) have been described (*1*). The four additional dinitropolymethylbiphenyls that have been isolated are listed in Table I. Compound 4 was obtained from hemimellitene, 5 and 6 from an *o*- and *m*-xylene mixture, and 7 from an *o*-xylene–mesitylene mixture. Their structural assignment is based on the known pattern of alkylbenzene coupling (*2, 3*) and on spectroscopic data [Experimental Section and (*1, 2, 4*)].

In a previous discussion of the spectroscopic criteria useful in the identification of nitrated polymethylbiphenyls we attributed the NMR shielding of the methyl groups in methyl-*o*′-nitrobiphenyls to the nitro group (*1*). Because similar shielding of the *o*-methyl protons was also observed in unnitrated sterically hindered biphenyls [(Table III of (*3*)], the origin of the shielding must be predominantly, if not entirely, the ring current, and not the nitro group as suggested.

The dinitropolymethylbiphenyls and the previously described nitropolymethylbiphenyls (*1, 2*) exhibit a pale but distinct yellow color in the solid state, if at least one nitro group is not flanked by a methyl. By contrast, the compounds having nitro and methyl substituents ortho to each other are white or off-white. Low intensity $n \rightarrow \pi^*$ transitions may be responsible for the yellow color; ultraviolet and visible spectroscopic studies of extremely pure samples would be required to prove this assumption.

EXPERIMENTAL

The NMR spectra were recorded on a Varian Associates HR-60 spectrometer with tetramethylsilane as internal standard in deuteriochloroform solution. Absorptions are given in τ values, numbers in brackets indicating the number of protons. The ultraviolet absorptions are shown in millimicrons for methylene chloride solution.

Dinitropolymethylbiphenyls. GENERAL PROCEDURE. All reactions were carried out in a fume hood behind closed windows. If for some reason (failure in the cooling system, etc.) temperature control is lost, the hot acid might shoot out several feet.

Table I. Physical Constants and Elemental Analyses of the New Dinitropolymethylbiphenyls

	Substituents on Biphenyl					Elemental Analyses, %		
Compound	NO_2 groups	CH_3 groups	M.P., °C[a]	Formula[b]		C	H	N
4[c]	2,3′	3,4,4′,5,5′,6′	156–58	$C_{18}H_{20}N_2O_4$	Calcd.	65.84	6.14	8.53
					Found	65.96	6.16	8.68
5	3,3′	4,4′,5,6′	158.5–59.5	$C_{16}H_{16}N_2O_4$	Calcd.	63.99	5.37	9.33
					Found	63.70	5.30	9.13
6	2,3′	4,4′,5,6′	130–31	$C_{16}H_{16}N_2O_4$	Calcd.	63.99	5.37	9.33
					Found	63.80	5.26	9.12
7	3,3′	2′,4,4′,5,6′	160–61	$C_{17}H_{18}N_2O_4$	Calcd.	64.96	5.77	8.91
					Found	64.73	5.56	9.05

[a] Corrected. [b] Confirmed by mass spectrometry. [c] Compound only 94% pure according to GLPC analysis; isomeric impurity could not be removed.

A 1000-ml round-bottomed, three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel and containing 2 moles of a single hydrocarbon (*o*-xylene or hemimellitene) or, in crosscoupling reactions, one mole of each hydrocarbon (*o*-xylene–*m*-xylene or *o*-xylene–mesitylene) was immersed in an efficient cooling bath. The cooling rate was regulated by the temperature of the coolant, the stirring rate, and the degree of immersion. At −14° ± 2° C, 280 ml of 90% nitric acid (about 6 moles) and 150 ml of concentrated sulfuric acid were added in sequence dropwise, slowly enough to control the exothermic reaction. After the sulfuric acid addition, the flask was gradually lifted from the bath, so that the mixture warmed very slowly to room temperature. Lastly, the mixture was poured onto ethanol-free ether (2 liters) and ice and extracted. The workup procedures for the individual cases are given below.

PRODUCTS FROM *o*-XYLENE. The ether extract was immediately seeded with pure crystals of compound 1. After 15 to 30 minutes, the crystals were filtered and recrystallized from DMF to give pure 2,2′-dinitro-4,4′,5,5′-tetramethylbiphenyl (*1*) (compound 1) (m.p. 250–52°). The ether filtrate was washed with 10% sodium hydroxide and seeded with crystals of compound 2. After 18 hours, the resultant crystals were recrystallized from dimethylformamide or dimethyl sulfoxide to give 2,3′-dinitro-4,4′,5,5′-tetramethylbiphenyl (*1*) (2) (m.p. 173–74°). The ether filtrate at 0° C slowly deposited another crop of crystals, mostly of compound 1. In this way, 1 was isolated in about 2.0% and 2 in about 1.3% yield. Further workup gave crystalline mixtures of isomeric dinitrobixylyls which could not be separated.

PRODUCTS FROM HEMIMELLITENE. A white solid that precipitated in the ether layer was filtered after 1 hour and recrystallized from dimethylformamide to give white crystals of 2,2′-dinitro-3,3′,4,4′,5,5′-hexamethylbiphenyl (*1*) (3) (m.p. 284–86°) in 1.0% yield. The ether filtrate was washed free of acid with 10% sodium hydroxide and with water and then was fractionated up to 170° still-head temperature at 0.8 torr. 4,5-Dinitrohemimellitene and 4,6-dinitrohemimellitene (*1*) were isolated from the higher boiling fractions. The distillation residue, after two recrystallizations from acetic acid and one carbon treatment in ethyl acetate, gave a 2.2% yield of 94% pure crystals of 2,3′-dinitro-3,4,4′,5,5′,6′-hexamethylbiphenyl (4). This was the highest purity obtained. NMR: 2.59 (1), 3.10 (1), 7.60 (3), 7.65 (3), 7.72 (6), 7.77 (3), 7.89 (3). Ultraviolet: λ_{max} 232, ϵ_{max} 13.000 with inflection at 275 mμ.

PRODUCTS FROM *o*-XYLENE-*m*-XYLENE CROSSCOUPLING. The ether extract was washed with 10% sodium hydroxide and with water and then vacuum-distilled to remove volatile products up to 170° (1.0 torr). The distillation residue was crystallized from small amounts of acetic acid at 5°. The first crop of crystals was carbon-treated (Darco G-60) in ethyl acetate and recrystallized from acetic acid to give white 3,3′-dinitro- 4,4′,5,6′-tetramethylbiphenyl (5). NMR: 2.15 (1), 2.48 (center of doublet, J = 1.7 cps) (1), 2.69 (center of doublet, J = 1.7 cps) (1), 2.75 (1), 7.38 (3), 7.57 (6), 7.68 (3). Ultraviolet: λ_{max} 241 mμ; ϵ_{max} 27.000. Methanol was added to the mother liquors. The separated solids were purified as compound 5 to give pale yellow crystals of 2,3′-dinitro-4,4′,5,6′-tetramethylbiphenyl (6). NMR: 2.13 (1), 2.25 (1), 2.79 (1), 2.95 (1), 7.41 (3), 7.64 (6), 7.91 (3). Ultraviolet: λ_{max} 278 mμ, ϵ_{max} 14.000, end absorption with ϵ = 17.000 at 2.40 mμ. Fractional crystallization of the mother liquors produced further crops of 5 and 6, raising the total yields to 0.7 and 1.4%, respectively.

PRODUCTS FROM *o*-XYLENE–MESITYLENE CROSSCOUPLING. The ether layer was washed with 10% sodium hydroxide and with water. Low boiling components were removed by vacuum distillation up to 170° (1.0 torr), and the residue was crystallized from acetic acid. Two recrystallizations from acetic acid–methylene dichloride (9 to 1) gave 23.5 grams (7.5% yield) of 3,3′-dinitro-2′,4,4′,5,6′-pentamethylbiphenyl (7). NMR: 2.60 (1), 2.83 (1), 2.93 (1), 7.55 (6), 7.68 (3), 7.95 (3), 8.08 (3). Ultraviolet showed end absorption only, ϵ = 14.300 at 240 mμ.

LITERATURE CITED

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Preparation of 3- and 4-(4-Nitrophenyl)phthalic Acid

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2,3-Dimethyl-4′-nitrobiphenyl and the 3,4-dimethyl isomer were prepared in low yields by modified Gomberg reactions. Oxidation gave the previously unreported 3-(4-nitrophenyl)phthalic acid and the incorrectly described 4-(4-nitrophenyl)phthalic acid.

DURING A STUDY of substituted nitrophthalic acids, a sample of 4-(4-nitrophenyl)phthalic acid was desired. This acid had been prepared (*3*) by nitration of 4-phenylphthalic anhydride, which was prepared from diazotized methyl 4-aminophthalate and benzene. In an attempt to simplify this procedure, diazotized 3,4-dimethylaniline was made to react with nitrobenzene and alkali (*6*) to give a 21.0% yield of distilled dimethylnitrobiphenyls, shown by VPC to contain 62% 3,4,2′-, 8% 3,4,3′-, and 30% 3,4,4′-isomer. This crude mixture was oxidized with potassium permanganate in pyridine to give a low yield of 4-(4-nitrophenyl)phthalic acid (m.p. 195–96°), which was characterized by infrared and NMR spectra. Vacuum sublimation of the acid gave the anhydride (m.p. 195–98°).

Since Butterworth *et al.* (*3*) report melting points of 178–79° and 136–37° for the acid and anhydride, respectively, it was of interest to repeat their nitration. Employing the modified Gomberg procedure of Hellwinkel (*8*), the