formation of $PbBr_3^-$ rather than $PbBr_4^{-2}$ ions in solution. Under these conditions 13 of the resulting compounds were tribromo salts. The formation of the tetrabromo complex compounds in the solid state was not due to concentration differences, since they were practically constant in every preparation. The geometry of the crystal of a particular compound may be a critical factor in determining the final solid product.

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Synthesis of Some Nitrocyanomethyl Biphenyls, Diphenylmethanes, and Diphenyl Ethers

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2- and 3-Nitro-4′ cyanomethylbiphenyl, 2- and 3-nitrophenyl 4′-cyanomethylphenyl ether, and 2- and 3-nitrophenyl-4′-cyanomethylphenylmethane, as well as certain of their chloromethyl precursors, have been prepared. Improved synthetic routes to o-nitrobenzyl cyanide and 2- and 3-nitrodiphenylmethane are also described.

IN CONNECTION with other work in this laboratory, the need for a series of aromatic nitrocyanomethyl compounds arose for use as intermediates in the synthesis program. The present paper describes a general route to these new aromatic nitrocyanomethyl compounds involving chloromethylation of the aromatic nitro compound and subsequent conversion of the chloride to the nitrile. The intermediate chloromethyl compounds were not isolated but converted directly with sodium cyanide to the cyanomethyl compounds. Isolation was, in fact, not attempted because of their apparent heat sensitivity. Several readily decomposed upon attempted fractional distillation under reduced pressure or gas-liquid chromatography. Pertinent data for the cyanomethyl compounds are listed in Table I.

Nuclear magnetic resonance was particularly valuable in optimizing chloromethylation conditions. Optimum reaction conditions (especially temperature) were indicated when the experimentally determined methylene to aromatic proton ratio closely approached the theoretical value. In addition, the closeness of the methylene proton chemical

Table I. Nitrocyanomethyl Biphenyls, Diphenylmethanes, and Diphenyl Ethers

		Analysis[a]									
		Carbon, %		Hydrogen, %		Nitrogen, %		N.M.R., τ[b]		I.R., $\lambda_{\text{Max.},\mu}^{\text{KBr}}$	
Compound	M.P., ° C.[c]	Calcd.	Found	Calcd.	Found	Calcd.	Found	$—CH_2—$	$—CH_2CN$	NO_2	CN
2-Nitro-4′-cyanomethylbiphenyl	112.5–113.0[d]	70.51	70.58	4.49	4.23	11.46	11.76	. . .	6.26	6.53, 7.40	4.42
3-Nitro-4′ cyanomethylbiphenyl	116.0–117.5[e]	70.51	70.37	4.49	4.32	11.46	11.66	. . .	6.18	6.50, 7.40	4.42
2-Nitrophenyl-4′-cyanomethylphenylmethane	55.0– 56.0[d]	71.41	71.58	4.79	4.92	. . .	. . .	5.73	6.34	6.58, 7.52	4.42
3-Nitrophenyl-4′-cyanomethylphenylmethane	104.8–105.5[f]	71.41	71.66	4.79	5.03	11.11	11.06	5.95	6.31	6.59, 7.35	4.41
2-Nitrophenyl 4′-cyanomethylphenyl ether	. . .[g]	66.14	65.91	3.96	4.14	11.02	11.16	. . .	6.30	6.55, 7.42	4.41[h]
3-Nitrophenyl 4′-cyanomethylphenyl ether	71.0– 71.8[d, i]	66.14	65.92	3.96	4.08	11.02	10.95	. . .	6.21	6.53, 7.40	4.40

[a] Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] N.M.R. spectra were determined in deuterochloroform on a Varian A-60 spectrophotometer by Nuclear Magnetic Resonance Specialties, Inc., New Kensington, Pa. Tau values are in p.p.m. down field from tetramethylsilane (=10). The aromatic protons appeared as poorly resolved multiplets in the range 1.6–3.2. [c] Melting points were taken in a Mel-Temp melting point apparatus; they are uncorrected. [d] From ethanol. [e] From acetonitrile. [f] From carbon tetrachloride. [g] B.p. 211° at 0.1 mm. [h] Smear. [i] B.p. 207–208° at 0.22 mm.

Table II. N.M.R. Chemical Shift Values for the Crude Nitro Chloromethyl Biphenyls, Diphenylmethanes, and Diphenyl Ethers

	τ^a	
Compound	—CH_2—	—CH_2—Cl
2-Nitro-4′-chloromethylbiphenyl[b]	. . .	5.44
3-Nitro-4′-chloromethylbiphenyl	. . .	5.40
2-Nitrophenyl-4′-chloromethylphenyl-methane	5.73	5.48
3-Nitrophenyl-4′-chloromethylphenyl-	5.95	5.47
3-Nitrophenyl 4′-chloromethylphenyl-ether	. . .	5.46
3-Nitrophenyl 4′-chloromethylphenyl ether	. . .	5.40

[a] The aromatic protons appeared as poorly resolved multiplets in the range 1.6–3.2. Spectra were determined under the same conditions as in Table I. [b] Pure material, m.p. 88–89° C.; lit. (*2*) m.p. 89° C.

shift values for the crude chloromethyl compounds (Table II) gave an early indication of the success of the reaction. In contrast, infrared spectra of the crude chloromethyl compound were extremely similar, if not identical, to the aromatic starting materials and provided no indication of reaction.

The synthesis of *o*-nitrobenzyl cyanide by the dehydration of *o*-nitrophenylacetamide using thionyl chloride with benzene as solvent was first reported by Pschorr and Hoppe (*5*). Repetition of their procedure gave, not only a low yield (although Pschorr and Hoppe reported a 75% yield, the authors could not obtain a yield greater than 21% using their procedure), but an extremely toxic by-product. Handling of the crude product, probably contaminated by the isonitrile (*4*), in the open air caused dizziness and heart palpitations. In this study, changing the dehydration solvent to *N,N*-dimethylformamide not only eliminated the toxic side-product, but also increased the yield threefold (62%).

The preparation of 2-nitrodiphenylmethane as described by Geigy and Konigs (*3*) and Tanasescu (*6*) involves the reaction of *o*-nitrobenzyl chloride with benzene using aluminum chloride as the catalyst. Although the diphenylmethane (b.p. 116–118° C. at 0.06 mm.) is reported as nondistillable, fractional distillation was, in fact, the best mode of purification. Similarly, the purification of 3-nitrodiphenylmethane (b.p. 114–117° C. at 0.04 mm.) by direct fractional distillation of the crude product was much simpler than the repeated concentrated sulfuric acid washings indicated in the literature (*1*).

EXPERIMENTAL

The procedure of Cambell (*2*) for the chloromethylation of 2-nitrobiphenyl using paraformaldehyde, gaseous hydrogen chloride, and zinc chloride was equally effective in chloromethylating 3-nitrobiphenyl. Preliminary attempts to chloromethylate 2-nitrophenyl phenyl ether using these same conditions or methyl chloromethyl ether and zinc chloride at reflux gave a thick mass of polymeric material. Methyl chloromethyl ether and acetic acid (no zinc chloride catalyst) gave a trace of the chloromethyl compound after 42 hours at 80° C. (as indicated by N.M.R.). Zinc chloride and methyl chloromethyl ether (10 mole excess) at 0° C. for 2-½ hours gave the best yields for the chloromethylation of both 2- and 3-nitrophenyl phenyl ether. Similarly, the chloromethylation of 2- and 3-nitrodiphenylmethane proceeded most satisfactorily using methyl chloromethyl ether and zinc chloride at room or somewhat higher temperatures. Since the chloromethyl compounds could not be distilled, yields could not be determined. The one exception was the known 2-nitro-4′-chloromethylbiphenyl which could be distilled to give a 24% yield.

Conversion of the crude chloromethyl compounds to nitriles was accomplished in every case by means of sodium cyanide in a dioxane-ethanol-water reaction medium. Accurate yields could not be calculated since the chloromethyl compounds could not be purified. Based on the crude chloromethyl compounds, the yields were 20 to 30%. In the case of 2-nitro-4′-chloromethylbiphenyl which could be purified, the yield was 90%. Recent results have indicated a potentially cleaner reaction with increased yields using an anhydrous system with acetone as the reaction medium.

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