Diacyl Derivatives of 4,4''-Diamino-o-Terphenyl

ROBERT G. SPLIES and RICHARD R. FISCHER
University of Wisconsin-Milwaukee, Milwaukee, Wis.

RECENTLY during the preparation of 4,4''-diamino-*o*-terphenyl we experienced the same lack of stability as reported by Allen and Pingert (*1*). The diamine could be stored only as the hydrochloride salt. Attempts to purify the amine for a melting point determination were not successful and a literature search indicated that no derivatives had been listed. The preparation of the diacetyl and dibenzoyl derivatives are reported now as an aid to future identification.

EXPERIMENTAL

4,4''-Diamino-*o*-terphenyl dihydrochloride (I). The diamine was prepared by the catalytic reduction of 19.5 grams of 4,4''-dinitro-*o*-terphenyl (*1*) in 275 ml. of dioxane. The reduction was run at room temperature with hydrogen at a cold pressure of 50 p.s.i. and 0.2 gram of platinum oxide catalyst. When reduction was complete the solution was saturated with dry HCl gas. The precipitated salt was washed with ether and stored under vacuum; 20.0 grams (98.5%).

4,4''-Diacetamido-*o*-terphenyl (II). To a solution of 3 ml. of acetic anhydride in 50 ml. of benzene was added 2.0 grams of (I) and 4.0 grams of sodium acetate. After refluxing the suspension for one hour the solid was removed by filtration. Extraction with hot absolute alcohol yielded the diamide as a granular solid, 0.45 gram. The analytical sample, m.p. 323.5–324°, was recrystallized from absolute ethanol. All melting points in this report are uncorrected.

Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.73; H, 5.85. Found: C, 76.80; H, 5.67.

4,4''-Dibenzamido-*o*-terphenyl (III). A suspension of 1.0 grams of (I) 30 ml. of 10% NaOH and 5 ml. of benzoyl chloride was shaken at room temperature for 10 minutes. After washing the amorphous mass with ether, 1.2 grams of (III) was obtained. Solution of the amorphous solid was effected by warming with 75 ml. of methyl cellosolve and adding 20 ml. pyridine until the solid disappeared. The solution on cooling yielded pale yellow needles, m.p. 321–321.5°.

Anal. Calcd. for $C_{32}H_{24}N_2O_2$: C, 82.03; H, 5.16. Found: C, 81.89; H, 5.39.

LITERATURE CITED

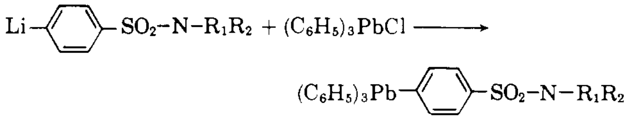
(1) Allen, C.F.H., Pingert, F.P., *J. Am. Chem. Soc.* **64**, 2643 (1942).

RECEIVED for review October 20, 1963. Accepted January 8, 1964.

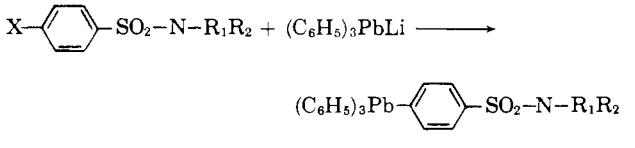
Organolead Compounds Containing the Sulfonamido Group

CHARLES J. FELDHAKE[1] and CHARLES D. STEVENS
College of Medicine, University of Cincinnati, Cincinnati, Ohio.

THIS COMMUNICATION describes the preparation of triphenyllead(*N*,*N*-diethylbenzene) sulfonamide (I) and triphenylleadbenzenesulfonanilide (II), Table I. Synthesis of I was accomplished by two methods. The first method,



was the reaction of *p*-lithio-*N*,*N*-diethylbenzenesulfonamide, prepared by the method of Gilman and Arntzen (*1*) with triphenyllead chloride, which gave I in 45% yield. The second method,



was the reaction of triphenylleadlithium, prepared by the method of Gilman, Summers, and Leeper (*2*), with a halogen-containing compound. With *p*-iodo-*N*,*N*-diethylbenzenesulfonamide, the second method gave I in 30% yield (but, for unknown reasons, the desired reaction did not always occur). The second method never yielded compound II when attempted with *p*-bromobenzenesulfonanilide. The failure may be presumed to result from the reaction of the active hydrogen of *p*-bromobenzenesulfonanilide with the triphenylleadlithium. Compound II was prepared in a yield of 43% by the first method, i.e., by coupling *p*-lithio-*N*-lithio-*N*-phenylbenzenesulfonamide with triphenyllead chloride. Repeated trials of these two methods of coupling suggest that, for the synthesis of organolead compounds containing an active hydrogen, the first method is more dependable.

Because the preparation of *p*-lithio-*N*-lithio-*N*-phenylbenzenesulfonamide has not been reported previously, the halogen-metal interconversions between *p*-bromobenzenesulfonanilide and *n*-butyllithium and between *p*-iodobenzenesulfonanilide and *n*-butyllithium were studied. The yields of *p*-carboxybenzenesulfonanilide (III) obtained under several conditions were determined by carbonation and are reported in Table II. [III melted at 277–279° with slight decomposition. Remsen, Hartman, and Mucken-

---

[1] Present address: College of Mount St. Joseph-on-the-Ohio, Cincinnati, Ohio.

Table I. Properties of Organolead Sulfonamides

			Percentage Composition						Solvent	
			Nitrogen		Lead		Sulfur			
Cpd.	Method of prepn.	Melting point ° C.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Preliminary removal of non-lead anilides	Crystn.
I	First	106–108	2.15	2.10	31.84	29.38	4.93	4.34	70% EtOH	95% EtOH
II	First	156–161	2.09	1.98	30.89	31.09	4.78	4.38	5% aq. NaOH	80% EtOH
I	Second	103–109[a]								70% EtOH

[a] This was prepared from 0.025 mole of the iodosulfonamide and triphenylleadlithium prepared from 0.03 mole of lead chloride; the temperature of the reaction was initially −5° and finally 108°. Mixed melting point with a sample of I made by the first method was 104–106°.

Table II. Reactions of RX Compounds with *n*-Butyllithium

RX in Ether		*n*-BuLi		Interconv. Temp., ° C.	Time of Interconv., Min.	Carbonation Yield, %	Ph_3PbCl Mole	Coupling		Product Yield,[a] %
Mole	Ml.	Mole	Ml.					Temp., ° C.	Time Min.	
				p-Bromobenzenesulfonanilide						
0.03	75	0.06	52	−5	115[b]	36				
0.03	150	0.06	50	0	34	12				
0.03	75	0.06	75	25	145[b]	31				
0.03	75	0.09	78	25	235[c]	46				
0.015	50	0.03	50	26	63	29				
				p-Iodobenzenesulfonanilide						
0.015	75	0.03	30	−70	19	16				
0.015	75	0.03	25	0	14	31				
0.015	50	0.03	50	30	10	27				
				p-Iodo-*N*,*N*-diethylbenzenesulfonamide						
0.03	90	0.03	100	−68	8	..[d]	0.03	−68	8	45
				p-Bromobenzenesulfonanilide						
0.03	100	0.07	75	−10	135[c]	..	0.02	−5	25	0[e]
0.03	100	0.07	78	−10	140[c]	..	0.03	−5	30	0[e]
0.03	100	0.06	38	−10[g]	120[b]	..	0.03	21	25[f]	43
0.03	100	0.06	50	−10[g]	105[b]	..	0.015	21	25	28
0.06	150	0.12	100	25	100	..	0.06	25	5	11

[a] Based on Ph_3PbCl used. [b] Color Test II negative. [c] Color Test II positive. [d] Gilman and Arntzen (*1*) reported a yield of 78%. [e] Obtained 2 grams of triphenylbutyllead. [f] Color Test I negative. [g] Allowed to warm to 21° C. after addition of butyllithium.

fuss (*3*) reported 252–253° decomp.] *p*-Iodobenzenesulfonanilide was found to have no advantage over *p*-bromobenzenesulfonanilide, which is more readily obtained. Because the yields of III did not vary appreciably with temperature, the interconversions could be carried out at room temperature. The yields of III were increased by lengthening the time of interconversion and by using an excess of *n*-butyllithium. However, the use of an excess of *n*-butyllithium resulted in the formation of butyltriphenyllead when triphenyllead chloride was added (Table II); under these conditions, none of the desired product, II, was obtained. Although only half of the *p*-bromobenzenesulfonanilide was converted to *p*-lithio-*N*-lithio-*N*-phenylbenzenesulfonamide, a much better yield of II resulted from doubling the quantity of triphenyllead chloride instead of using a single equivalent of triphenyllead chloride per mole of *p*-lithio-*N*-lithio-*N*-phenylbenzenesulfonamide (Table II).

ACKNOWLEDGMENT

We are grateful to John F. Nobis of the Formica Corporation, Cincinnati, Ohio, for his encouragement and advice. Analyses were made by the Clark Microanalytical Laboratory, Urbana, Ill.

LITERATURE CITED

(1) Gilman, H., Arntzen, C., *J. Am. Chem. Soc.* **69**, 1537 (1947).
(2) Gilman, H., Summers, L., Leeper, R.W., *J. Org. Chem.* **17**, 630 (1952).
(3) Remsen, I., Hartman, R.N., Muckenfuss, A.M., *Am. Chem. J.* **18**, 161 (1896).

RECEIVED for review October 23, 1963. Accepted January 20, 1964.