

## HALOGEN—METAL INTERCONVERSION IN 2,7-DIBROMONAPHTHALENE AND 2,7-DIBROMOANTHRACENE

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### Summary

The halogen—metal exchange between 2,7-dibromonaphthalene or 2,7-dibromoanthracene and  $n\text{-C}_4\text{H}_9\text{Li}$  has been investigated. For exchange of only one bromine atom the best yields are achieved in diethyl ether at  $20^\circ\text{C}$ , while the exchange of both bromine atoms gives satisfactory yields in tetrahydrofuran at  $-35^\circ\text{C}$ .

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During our work, we needed to exchange one or both bromine atoms of 2,7-dibromonaphthalene and 2,7-dibromoanthracene with Li and the results obtained may be of interest.

Exchanges were carried out with  $n\text{-C}_4\text{H}_9\text{Li}$  in diethylether (DEE), di-*n*-butylether (DBE) and tetrahydrofuran (THF) at various temperatures. At fixed time intervals, samples were removed with a hypodermic syringe, hydrolyzed, and submitted to gas chromatographic analysis.

The results for 2,7-dibromonaphthalene are shown in Table 1. The exchange of one bromine atom is fast, as already reported for 2-bromonaphthalene [1], and best yields are observed in DEE at  $20^\circ\text{C}$ . In THF at  $-35^\circ\text{C}$  during 15 min, concurrent formation of 2-brom-7-butylnaphthalene takes place.

The exchange of the second bromine atom occurs at a significantly lower rate, satisfactory yields being obtained only in THF at  $-35^\circ\text{C}$ . In this solvent however, rapid alkylation of the naphthalene nucleus also occurs at  $-70^\circ\text{C}$  and at  $-35^\circ\text{C}$  dialkylation takes place as shown by the appearance of 2,7-dibutylnaphthalene after 15 min. The alkylnaphthalenes were identified by mass spectrometry. It is well known that the alkylation of organolithium compounds is particularly favoured in THF [2,3,4].

Considering the progressive increase in products which are not detected by the gas chromatographic analysis, it may be inferred that some dinaphthyl derivatives are also formed as a result of side reactions [5].

It has not proved possible to carry out a similar investigation on 2,7-dibromoanthracene which is weakly soluble (<0.5%) in the solvents used previously.

TABLE 1  
 YIELDS (%) IN THE HALOGEN-METAL EXCHANGE REACTIONS OF 2,7-DIBROMONAPHTHALENE<sup>a</sup> (A = 2,7-dibromonaphthalene, B = 2-bromonaphthalene, C = naphthalene)

Time (min)	Mono-exchange									Double-exchange															
	DEE			DBE			THF			DEE				DBE				THF							
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	
0.5	85	91	3	28	63	23	65	57	42	11	72	85	7	88	9	81 <sup>c</sup>	80	8	38	54	10	70			
2	77	83	4	18	68	20	68	61	50	7	74	78	11	60	18	88	82	8	32	59	6	72			
5	4	76	80	6	14	64	10	59	50	51	77	60	16	42	36	80	4	72	12	26	63	4	57		
15	—	69	75	7	13	63	18	60	50	52	66	60	24	21	50	77	7	50	22	24	62	—	38		
30	—	67	68	6	13	63	17	59	45	54	68	55	29	15	60	68	10	38	31	24	60	—	23		
60	—	47	30	—	13	65	15	55	49	50	61	48	42	6	48	58	21	25	35	24	56	—	13		

<sup>a</sup> The yields were determined by GLC by use of appropriate correction factors with respect to the n-tridecane used as internal standard, *b* 2-brom-7-butyl-naphthalene is present; its GLC peak appears after that of A, *c* 2-butyl-naphthalene is present; its GLC peak appears after that of B, *d* 2-butyl-naphthalene and 2,7-dibutyl-naphthalene are present; the peak of the latter appears after that of 2-brom-7-butyl-naphthalene, *e* 7% of A is also present.

Even 2-bromoanthracene, employed as a reference standard in gas chromatographic analysis, is barely soluble. The reaction was performed therefore in a heterogeneous phase and observation was limited to the exchange of both bromine atoms (which was of major interest for our purposes). The determination of anthracene has shown that the formation of 2,7-dilithioanthracene in DEE and in DBE at 20°C is maximal (50%) after 30 min and then decreases to 35% after 60 min.

## Experimental

### Exchange reaction

A 20% solution of  $n\text{-C}_4\text{H}_9\text{Li}$  in *n*-hexane was added under an inert gas to about 20 ml of  $5 \times 10^{-2} M$  solution of the halogeno-compound in DEE, DBE or THF containing *n*-tridecane as internal standard. At fixed time intervals, samples were removed with a hypodermic syringe, added to aqueous acid and extracted with DEE. The ether phase was then analysed by GLC on a 10% GAL CWLA 60-80 column. Naphthalene, halogenonaphthalenes and anthracene were identified by comparison with authentic samples and the yields were calculated by reference to the *n*-tridecane.

### 2,7-Dibromonaphthalene

Naphthalene-2,7-diol was brominated with dibromotriphenylphosphine in acetonitrile as reported for 2-bromonaphthalene [6]. After evaporation of the solvent, the residue was heated for 1 h at 250°C, then cooled and extracted with boiling ligroin to give the crude 2,7-dibromonaphthalene. After two crystallizations from ethanol, the product had m.p. 140–141°C (yield 60%). The procedure is better than that starting from 2-naphthylamine [7,8].

### 2,7-Dibromoanthracene

The following sequence was used:

$2.5 \times 10^{-2}$  mol of 5-bromo-*o*-phthalaldehydic acid, dissolved in 200 ml of DEE/THF 50% were added to  $6 \times 10^{-2}$  mol of *p*-bromophenylmagnesiumbromide in 150 ml of DEE. When the reaction was complete, diluted HCl was added and the organic solution separated and quickly extracted with 5%  $\text{NaHCO}_3$ . Acidification of the aqueous layer gave an oil which slowly crystallized. The crude phthalide I was recrystallized from ethanol: m.p. 151–152°C (yields 35–40%). IR:  $\nu(\text{CO})$  1770  $\text{cm}^{-1}$ . NMR ( $\text{CDCl}_3$ ):  $\delta$  6.35(s, —CH aliph.), 7.1–8.2 (m, —CH arom.). Found: C, 45.42; H, 2.35; Br, 43.08.  $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}_2$  calcd.: C, 45.69; H, 2.19; Br, 43.47%.

The corresponding acid, II, was obtained by refluxing a mixture of  $10^{-2}$  mol of I, 20 ml of propionic acid, 2.5 ml of water,  $8 \times 10^{-2}$  mol of red phosphorus and 2 g of iodine for 15 h. The phosphorus was filtered off then DEE and 2 N NaOH were added. The aqueous layer was acidified, to precipitate the acid II which, after recrystallization from ligroin had a m.p. of 159–160°C (yield 75–80%): acidimeter titre 99%. IR:  $\nu(\text{CO})$  1690  $\text{cm}^{-1}$ . NMR ( $\text{CDCl}_3$ ):  $\delta$  4.35 (s, —CH<sub>2</sub> aliph.), 7–8.3 (m, —CH arom.), 10.8 (—COOH). The dibromoanthrone, III, was obtained in nearly quantitative yield by keeping 3 g of the acid II overnight in 15 ml of 96% sulfuric acid at 0–5°C. Addition of water gave a yellow

precipitate of III (m.p. 200°C, with decomposition). IR:  $\nu(\text{CO})$  1660  $\text{cm}^{-1}$ . Found: C, 47.48; H, 2.29; Br, 45.8.  $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}$  calcd.: C, 47.76; H, 2.29; Br, 45.45%.

2,7-Dibromoanthracene was obtained, as reported for similar compounds [9], by refluxing  $2 \times 10^{-3}$  mol of dibromoanthrone III for about 40 h with  $2 \times 10^{-2}$  mol of  $\text{NaBH}_4$  in 100 ml of isopropanol. The cooled solution was acidified with 4 *N* HCl, boiled for a few minutes and cooled. The solid was filtered off and eluted on a silica gel column with n-hexane to give 2,7-dibromoanthracene, m.p. 268–270°C (yield 40%). Found: C, 50.13; H, 2.58; Br, 47.34.  $\text{C}_{14}\text{H}_8\text{Br}_2$  calcd.: C, 50.04; H, 2.40; Br, 47.61%. A similar yield was obtained by reducing the anthrone(III) in heterogeneous phase with an equimolar quantity of  $\text{LiAlH}_4$  in DEE/THF 50% at room temperature for about 40 min.

By the same procedure reported above, starting from phthalaldehydic acid, we prepared the previously described 2-brom-9-anthrone [10], from which 2-bromoanthracene, m.p. 211–212°C was obtained (yield 50%). Found: C, 65.21; H, 3.89; Br, 30.95.  $\text{C}_{14}\text{H}_9\text{Br}$  calcd.: C, 65.40; H, 3.53; Br, 31.08%.

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