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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-C_4H_9Li has been investigated. For exchange of only one bromine atom the best yields are achieved in diethyl ether at 20° C, while the exchange of both bromine atoms gives satisfactory yields in tetrahydrofuran at −35° C.

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-C_4H_9Li 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° C. In THF at −35° 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° C. In this solvent however, rapid alkylation of the naphthalene nucleus also occurs at −70° C and at −35° 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 [a] (A = 2,7-dibromonaphthalene, B = 2-bromonaphthalene, C = naphthalene)

Time (min)	Mono-exchange												Double-exchange											
	DEE				DBE				THF				DEE				DBE				THF			
	0°C		20°C		0°C		20°C		−70°C		−35°C [b]		0°C		20°C		0°C		20°C		−70°C [c]		−35°C [d]	
	A	B	B	C	A	B	A	B	A	B	A	B	B	C	B	C	B	C	B	C	B	C	B	C
0.5	5	85	91	3	26	63	23	65	57	42	11	72	85	7	88	9	81 [e]	—	80	8	38	54	10	70
2	5	77	83	4	18	68	20	68	51	50	7	74	78	11	69	18	88	—	82	8	32	59	6	72
5	4	76	80	6	14	64	19	59	50	51	—	77	69	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

[a] 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-butylnaphthalene is present; its GLC peak appears after that of A. [c] 2-butylnaphthalene is present; its GLC peak appears after that of B. [d] 2-butylnaphthalene and 2,7-dibutylnaphthalene are present; the peak of the latter appears after that of 2-brom-7-butylnaphthalene. [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-C_4H_9Li in n-hexane was added under an inert gas to about 20 ml of 5×10^{-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:
2.5×10^{-2} mol of 5-bromo-*o*-phtalaldeidic acid, dissolved in 200 ml of DEE/THF 50% were added to 6×10^{-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% $NaHCO_3$. 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: ν(CO) 1770 cm^{-1}. NMR ($CDCl_3$): δ 6.35(s,—CH aliph.), 7.1—8.2 (m,—CH arom.). Found: C, 45.42; H, 2.35; Br, 43.08. $C_{14}H_8Br_2O_2$ 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, 8×10^{-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: ν(CO) 1690 cm^{-1}. NMR ($CDCl_3$): δ 4.35 (s,—CH_2 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: ν(CO) 1660 cm^{-1}. Found: C, 47.48; H, 2.29; Br, 45.8. $C_{14}H_8Br_2O$ calcd.: C, 47.76; H, 2.29; Br, 45.45%.

2,7-Dibromoanthracene was obtained, as reported for similar compounds [9], by refluxing 2×10^{-3} mol of dibromoanthrone III for about 40 h with 2×10^{-2} mol of $NaBH_4$ 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. $C_{14}H_8Br_2$ 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 $LiAlH_4$ in DEE/THF 50% at room temperature for about 40 min.

By the same procedure reported above, starting from phtalaldeidic acid, we prepared the previously described 2-brom-9-anthrone [10], from wich 2-bromanthracene, m.p. 211—212°C was obtained (yield 50%). Found: C, 65.21; H, 3.89; Br, 30.95. $C_{14}H_9Br$ calcd.: C, 65.40; H, 3.53; Br, 31.08%.

References

1 H. Gilman and F.W. Moore, J. Amer. Chem. Soc., 62 (1940) 1843.
2 H. Heaney Organometal. Chem. Rev., 1(1) (1966) 27.
3 V.S. Petrosyan and O.A. Reutov J. Organometal. Chem., 52 (1973) 307.
4 L.I. Zakharkin et al., Tetrahedron, 21 (1965) 881.
5 H.J.S. Wilker and G. Wittig J. Org. Chem., 28 (1963) 1733.
6 J.P. Schaefer et al., Org. Synth., 49 (1969) 6.
7 H. Franzen and A. Eidis J. Prakt. Chem., (2)88 (1913) 755.
8 H. Franzen and G. Stäuble J. Prakt. Chem., (2)101 (1921) 58.
9 T.R. Griswell and B.H. Klanderman J. Org. Chem., 39 (1974) 770.
10 E.D. Bergmann and E. Loewenthal Bull. Soc. Chim. Fr., (1952) 66.