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SHORT COMMUNICATION

Lithiation of 1-aminonaphthalene, and preparation of some 8-substituted 1-tritionaphthalenes

Treatment of 1-methoxynaphthalene with n-butyllithium was recently shown to give up to 35% of 8-lithio-1-methoxynaphthalene along with the expected 2-lithio compound[1]. We have found that 8-metallation also occurs (probably exclusively) when 1-aminonaphthalene is treated with n-butyllithium.

Under our conditions, involving 50 hours' refluxing of the ethereal mixture of n-butyllithium and 1-aminonaphthalene in 3 : 1 mole ratio, it seems that less than 20% of C-lithio product is formed. For example, when such lithiation was followed by carbonation, 8-amino-1-naphtholactam was obtained in 10% yield and 80% of the 1-aminonaphthalene was recovered unchanged. Lithiation followed by addition of a known amount and activity of tritiated water gave tritio-1-aminonaphthalene. The amino group was then removed by a method which should cause no significant loss of tritium attached to the 8-carbon atom. 8-Tritio-naphthalene was also prepared by cross-metallation of 1-bromonaphthalene with n-butyllithium followed by similar treatment with tritiated water, and the relative activities of the two tritiated naphthalenes indicated that the efficiency of incorporation of tritium (and thus of lithium) into the 8-position in the first procedure was only 30% of that in the second. The rates of detritiation of the two samples in anhydrous trifluoroacetic acid at 70° were identical, and the absence of any fall-off in the rates during the detritiation indicated that no significant amount of 2-tritionaphthalene was present. This probably means that no 2-lithiation of the 1-aminonaphthalene had occurred, since our experience with related compounds indicates that any 2-tritio-1-aminonaphthalene would not have been detritiated in the acid used for diazotization during the removal of the amino group.

The unlikely possibility that some metallation had occurred in the 4- or 5-position (since tritiation and deamination would still give entirely 1-tritionaphthalene) was ruled out by converting the tritio-1-aminonaphthalene into 8-X-tritionaphthalenes, in which X = F, Cl, or Me, and measuring the rates of detritiation of the products. In all three cases there was no curvature of the first-order plots, and the rate constants were identical with those observed for samples of the 8-X-1-tritio-compounds prepared by unambiguous but more tedious methods.

It is likely that the extent of metallation of 1-aminonaphthalene could be improved, since we made no attempt to find the optimum conditions, but even if this is not the case the 8-metallation could provide a useful route to some 1,8-disubstituted naphthalenes.

Experimental

n-Butyllithium. This was prepared from n-butyl bromide in ether, as described by Gilman and his co-workers[2].

1-*Aminotritionaphthalene.* n-Butyllithium (48 g, 0.75 mole) in anhydrous ether

(250 ml) was added during 0.5 h to a stirred solution of AnalaR 1-aminonaphthalene (35.7 g, 0.25 mole) in anhydrous ether (100 ml) and the mixture was then refluxed under nitrogen for 50 h. Tritiated water (13.5 ml, 29 mc/ml) was added with stirring, followed by an excess of ordinary water. The usual work-up, followed by recrystallisation from aqueous ethanol, gave 1-aminotritionaphthalene, (35 g, 98%), m.p. 49.5° (lit.[3] 50° for 1-aminonaphthalene).

8-*Chloro*-1-*tritionaphthalene*. (*i*) Diazotization of the above amine at 0° with 20% hydrochloric acid and 33% aqueous sodium nitrite solution followed by treatment with mercuric chloride and sodium chloride[4] gave 8-chloro-1-tritionaphthalene (57%), b.p. 119°/9 mm, n_D^{20} 1.6320, (lit.[5,6] 128°/15 mm, n_D^{20} 1.6332, for 1-chloronaphthalene).

(*ii*) 8-Chloro-1-nitronaphthalene (20.8 g, 0.10 mole) was reduced[7] to 8-chloro-1-aminonaphthalene (14.6 g, 82%), m.p. 95°, (lit.[8] 95–6°). This compound (7.1 g, 0.040 mole) was diazotised at 0° with 20% hydrochloric acid and 33% aqueous sodium nitrite solution, and the diazo compound was treated with cuprous bromide in 48% hydrobromic acid. The usual work-up gave 8-chloro-1-bromonaphthalene (2.4 g, 25%), m.p. 96°, (lit.[9] 96.5–97°). The Grignard reagent prepared from this bromide was treated with tritiated water (0.30 ml, 29 mc/ml) followed by an excess of water. Work-up, with addition of 1-chloronaphthalene to facilitate handling, gave 8-chloro-1-tritionaphthalene, b.p. 128°/15 mm, n_D^{20} 1.6322.

8-*Fluoro*-1-*tritionaphthalene*. (*i*) Diazotisation of the 8-aminotritionaphthalene with 6% sulphuric acid and 15% aqueous sodium nitrite solution, followed by treatment with sodium borofluoride[10] gave 8-fluoro-1-tritionaphthalene (25%), b.p. 83°/12 mm, n_D^{20} 1.5938, (lit.[10] 80°/11 mm, $n_D^{19.5}$ 1.5939 for 1-fluoronaphthalene).

(*ii*) 8-Chloro-1-aminonaphthalene (8.9 g, 0.050 mole) was similarly converted into 8-fluoro-1-chloronaphthalene (3.8 g, 21%), m.p. 44° (lit.[11] 44°). The Grignard reagent prepared from this compound (3.6 g, 0.020 mole) in tetrahydrofuran was hydrolysed with tritiated water (0.40 ml, 29 mc/ml) followed by an excess of water. Work-up, with addition of 1-fluoronaphthalene to facilitate handling, gave 8-fluoro-1-tritionaphthalene, b.p. 82°/11 mm.

8-*Methyl*-1-*tritionaphthalene*. (*i*) Diazotisation of the amine at 0° with 20% hydrochloric acid and 33% aqueous sodium nitrite solution followed by treatment with cuprous bromide in 48% hydrobromic acid gave the 8-bromo derivative. The Grignard reagent from this bromide was treated with dimethyl sulphate to give 8-methyl-1-tritionaphthalene (23%), b.p. 98°/7.5 mm, n_D^{25} 1.6147, (lit.[12] 111°/12 mm, n_D^{25} 1.6147 for 1-methylnaphthalene).

(*ii*) The Grignard reagent from 8-chloro-1-tritionaphthalene (3.3 g, 0.020 mole) in tetrahydrofuran was treated with dimethyl sulphate. Work-up, with addition of 1-methylnaphthalene to facilitate handling, gave 8-methyl-1-tritionaphthalene b.p. 105–106°/10 mm, n_D^{25} 1.6145.

8-*Amino*-1-*naphtholactam*. 1-Aminonaphthalene (7.15 g, 0.050 mole) was lithiated as described above. The resulting solution was added to a stirred slurry of solid carbon dioxide (44 g, 1.0 mole) in anhydrous ether (250 ml) at 0°, and stirring was continued for 2 h. The ethereal solution was washed with 2*N* hydrochloric acid (5 × 250 ml) and water, and the ether was then removed. The residue was refluxed for 2 h with 10% aqueous sodium hydroxide (500 ml), the resulting solution was extracted with ether (3 × 250 ml), and the extract was dried (Na_2SO_4). Removal of the solvent left a residue, which was sublimed at 200°/0.5 mm. The crude sublimate (m.p. 110–130°) contained traces of 1-aminonaphthalene, which were removed by washing an ethereal solution with 2 *N* hydrochloric acid (3 × 50 ml). After drying (Na_2SO_4) and evaporation of the solution, the residue was recrystallised (charcoal) from light petroleum (b.p. 60–80°) and then from aqueous ethanol to give 8-amino-1-naphtholactam (0.83 g, 9.8%), m.p. 181° (lit.[13] 181°). 1-Aminonaphthalene (5.72 g, 80%), m.p. 49.5°, was obtained from the combined hydrochloric acid washings.

1-*Tritionaphthalene*. (*i*) From 1-aminonaphthalene. 1-Aminonaphthalene (7.15 g, 0.050 mole) was lithiated as described above, and hydrolysed with tritiated water (2.7 ml, 7 mc/ml) to give 1-tritio-8-aminonaphthalene (7.0 g, 98%). The latter was dissolved in 12% sulphuric acid (100 ml) and diazotised at 0° with aqueous sodium nitrite solution (33%, 15 ml) and an aqueous solution of urea (3 g) was then added. The mixture was added to a stirred suspension of cuprous bromide (12.5 g) in hydrobromic acid (48%, 25 ml) and the mixture was warmed. Ether extraction followed by drying (Na_2SO_4), and fractionation of the extract gave 8-bromo-1-tritionaphthalene (3.8 g, 37%), b.p. 121°/5 mm, n_D^{20} 1.6583, (lit.[6,14], b.p. 144°/15 mm, $n_D^{16.5}$ 1.6601). The Grignard reagent from this compound was hydrolysed to give 1-tritionaphthalene (1.8 g, 81%), m.p. 80° (lit.[15] m.p. 80.3°). The specific activity was found to be 10.2 μc/g.

(*ii*) *From 1-bromonaphthalene*. n-Butyllithium (9.6 g, 0.15 mole) was added to a stirred solution of 1-bromonaphthalene (10.4 g, 0.050 mole) in anhydrous ether (100 ml). After 4 hours' reflux under nitrogen, tritiated water (0.90 ml, 7 mc/ml) was added, followed by an excess of ordinary water. The usual work-up, culminating in recrystallisation from light petroleum and sublimation, gave 1-tritionaphthalene (5.2 g, 81%), m.p. 80.2°. The specific acitvity was found to be 34 μc/g, so incorporation of tritium was 3.3 times as efficient as in preparation (*i*).

Rate measurements. Rates of detritiation in trifluoroacetic acid at 70° were measured in duplicate as previously described[16], except that (*i*) eight samples were withdrawn in each run, and (*ii*) tritium contents were measured on an I.D.L. Type 6012 scintillation counter. The sensitivity of this instrument permitted the use of much smaller quantities of aromatic compound than were previously used, so that correction for the back reaction was unnecessary. The rate constants for the 8-X-1-tritionaphthalenes prepared from the lithio-1-aminonaphthalene (Samples A) or by the alternative routes (Samples B) are shown in Table 1.

TABLE 1

RATE CONSTANTS FOR DETRITIATION, 10^7 *k* (sec^{-1}), IN CF_3COOH AT 70.0°

Sample	*Substituent X*			
	H	*F*	*Cl*	*Me*
A	113	5.92	4.70	166
B	110	5.84	4.70	169

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