Reaction of 1,8-Dehydronaphthalene with Carbon Disulphide

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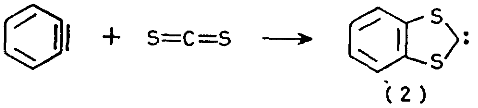
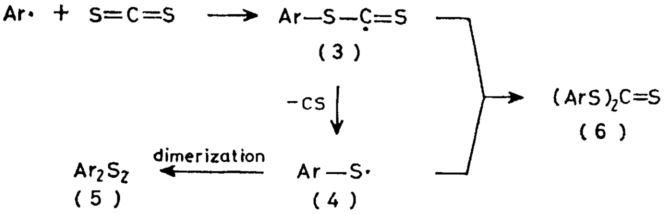
The reaction of carbon disulphide with 1,8-dehydronaphthalene, generated by oxidation of 1-amino-1*H*-naphtho-[1,8-*de*]triazine (7), gave naphtho[1,8-*bc*]thiet (10) (6—8%), naphtho[1,8-*de*]-1,3-dithiin-2-thione (11) (3—5%), naphtho[1,8-*bc*]thiophen-2-thione (12) (4—5%), and naphtho[1,8-*bc*]thiophen-2-one (13) (4—5%). The results can be explained by radical addition of 1,8-dehydronaphthalene to the sulphur atom of carbon disulphide forming a new 1,5-diradical intermediate (8), from which the final products are derived.

1,8-DEHYDRONAPHTHALENE undergoes cycloaddition with simple olefins to give acenaphthenes in a stereospecific manner,[1] although reactions with conjugated dienes are complex.[2] 1,8-Dehydronaphthalene can also undergo radical abstraction and addition reactions.[1] This behaviour, which is significantly different from that of benzyne, can be explained by a singlet diradical structure (1). It is known that benzyne adds to carbon disulphide to yield the carbene (2),[3] and a recent report has also shown that aryl radicals add to carbon disulphide forming the radicals (3), from which the final products (5) and (6) are formed.[4] We now report the first study of the reaction of (1) with carbon disulphide.

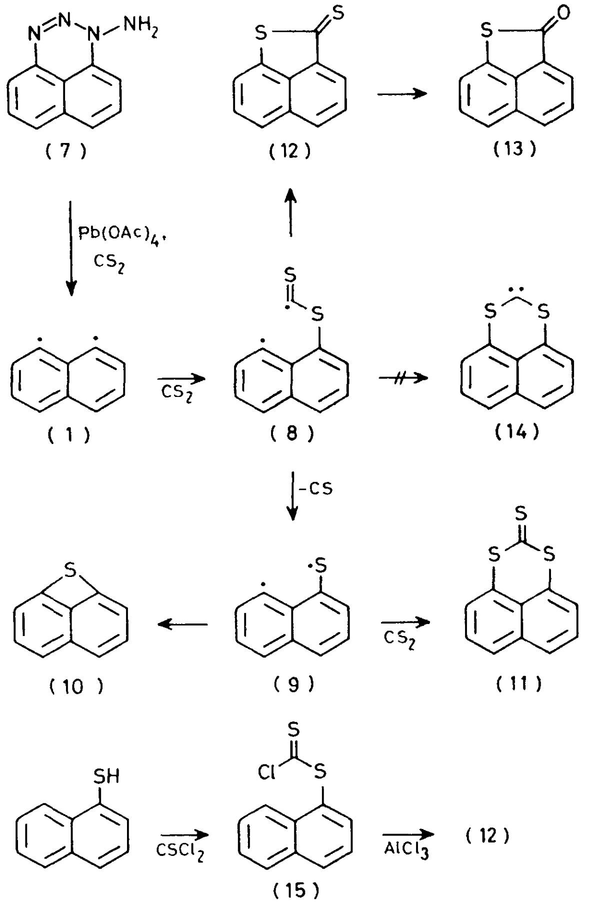


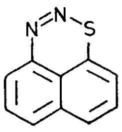


RESULTS AND DISCUSSION

It is well documented that the oxidation of 1-amino-naphtho[1,8-*de*]triazine[1a] (7) by lead tetra-acetate generates 1,8-dehydronaphthalene (1).[1b,c] Compound (7) was oxidised by lead tetra-acetate in a mixture of carbon disulphide and methylene chloride at ambient temperature. Purification of the mixture by silica gel chromatography afforded naphtho[1,8-*bc*]thiet (10) (6—8%), naphtho[1,8-*de*]-1,3-dithiin-2-thione (11) (3—5%), naphtho[1,8-*bc*]thiophen-2-thione (12) (4—5%), and naphtho[1,8-*bc*]thiophen-2-one (13) (4—5%). The low yields of these products is explained by formation of tarry material as is usual in reactions of (1).[1,2] The structures of (10) and (11) were confirmed by direct comparison with authentic samples.[5a] Compound (13) is also known and its properties agreed with those reported.[6] The new compound (12) was identified by spectroscopic and elemental analyses. Furthermore, it was synthesized independently; the reaction of naphthalene-1-thiol with thiophosgene gave a good yield of (15), which was treated with aluminium chloride to give (12) in 19% yield.

The formation of compounds (10)—(13) can be rationalized as below. Addition of (1) to carbon disulphide yields the 1,5-diradical (8) as aryl radicals do.[4] The radical (8) loses carbon monosulphide, like the radical (3), to give another diradical (9), which competitively undergoes 1,4-cyclization to (10), reaction of which with

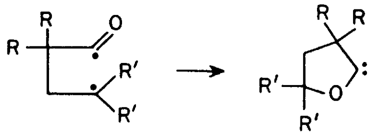




(16)

carbon disulphide produces (11). Supporting evidence for the intermediacy of (8) comes from the fact that the diradical (9), generated by photolysis of the azo-compound (16) in carbon disulphide, gives (10) (52%) and (11) (22%),[5a] in a similar ratio to that observed in the present reaction. Compound (12) must be formed by cyclization of the diradical (8). Its formation by concerted cycloaddition of (1) with carbon disulphide is less probable, since it is not in accordance with the formation of (10) and (11). Compound (13) may be formed from (12) during either the reaction or work-up. The formation of the carbene (14) from (8) seems not to occur, since no products derived from (14) were obtained.*

In conclusion compound (1) behaves towards carbon disulphide like an aryl radical, and adds to the sulphur atom forming a 1,5-diradical intermediate.



(17) (18)

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian A-60D spectrometer using tetramethylsilane as internal standard. I.r. spectra were determined in KBr discs using a JASCO IRA-2 spectrometer. All melting points were determined on a Mel-Temp melting-point apparatus. For silica gel chromatography, Merck Art 7734 (E. Merck, Darmstadt) was employed. 3-Amino-4*H*-naphtho[1,8-*de*]triazine (7) was prepared by a reported method.[1a]

Reaction of 1,8-*Dehydronaphthalene with Carbon Disulphide.*—To a magnetically stirred suspension of lead tetra-acetate (4.73 g, 10.7 mmol) in carbon disulphide (55 ml) was added dropwise (7) (1.48 g, 8 mmol) dissolved in a mixture of carbon disulphide (80 ml) and methylene chloride (40 ml) over a period of 20 min at room temperature. The mixture was stirred for 1 h and the resulting inorganic precipitate was filtered off. The precipitate was washed with methylene chloride, and then the filtrate and washings were combined, washed with water, dried over sodium sulphate, and evaporated. The residue was chromatographed on silica gel (100 g). Elution with hexane gave naphtho[1,8-*bc*]thiet (10) (6—8%), m.p. 39—40 °C (lit., m.p. 40—41,[5a] 40—42 °C [5c]). Further elution with hexane gave a mixture of naphtho[1,8-*de*]-1,3-dithiin-2-thione (11) and *naphtho*[1,8-bc]*thiophen*-2-*thione* (12), which was separated by preparative t.l.c. to give (11) (4—5%), m.p. 199—201 °C (lit.,[5a] m.p. 199—201 °C) and (12) (4—5%). Elution with 20% methylene chloride–hexane afforded naphtho[1,8-*bc*]thiophen-2-one (13), m.p. 145—146 °C (lit.,[6] m.p. 144.5—145.5 °C) (Found: C, 70.75; H, 3.25. Calc. for $C_{11}H_6OS$: C, 70.65; H, 3.35%).

Compound (12), m.p. 96—97 °C (from cyclohexane) was obtained as dark red needles; $\nu_{max.}$ 1 490, 1 450, 1 410, 1 270, 1 190, 1 135, 910, 815, and 758 cm^{-1}; δ 7.45—7.95 (4 H, m) and 8.00—8.45 (2 H, m) (Found: C, 65.15; H, 2.85; S, 31.95%. $C_{11}H_6S_2$ requires C, 65.3; H, 2.65; S, 31.7%).

The reaction was repeated several times and in certain cases, a pale yellow compound, m.p. 208—209.5 °C, was also isolated; $\nu_{max.}$ 1 635, 1 576, 1 500, 1 408, 1 356, 1 045, 1 013, 805, and 750 cm^{-1}.

Naphthalene-1-*thiol.*—A solution of naphthalene-1-sulphonyl chloride (Tokyo Kasei) (18.7 g, 82.7 mmol) in anhydrous ether (150 ml) was added to a stirred suspension of lithium aluminium hydride (7.5 g, 0.1 mol) in anhydrous ether (200 ml) and the mixture was refluxed for 0.5 h. Excess of lithium aluminium hydride was destroyed by careful addition of water (5 ml), and the mixture was then acidified by addition of dilute hydrochloric acid, and extracted with ether (200 ml). The extract was washed with water, dried over sodium sulphate, and evaporated to give the crude product (12.7 g, 97%), which was distilled to afford the pure product (10.6 g, 80%), b.p. 127 °C/3 mmHg (lit.,[7] b.p. 85—88 °C/0.27 mmHg).

1-*Naphthyl Chlorodithioformate* (15).—To a stirred solution of naphthalene-1-thiol (7.8 g, 48.7 mmol) and thiophosgene (5.6 g, 48.7 mmol) in chloroform (60 ml) was added dropwise 10% sodium hydroxide solution (20 ml, 48.7 mmol) over a period of 0.5 h. After completion of the addition, the mixture was stirred for 0.5 h, and then water (50 ml) and chloroform (100 ml) were added. The organic layer was washed with water, dried over sodium sulphate, and evaporated to leave a yellow crystalline solid, which was recrystallized from hexane to give (15) (9.4 g, 80%), m.p. 68—69 °C; $\nu_{max.}$ 1 110 cm^{-1} (C=S); δ 7.2—8.3 (6 H, m) (Found: C, 55.6; H, 2.95; S, 26.55. $C_{11}H_7ClS_2$ requires C, 55.35; H, 2.95; S, 26.85%).

Naphtho[1,8-bc]*thiophen*-2-*thione* (12).—A solution of (15) (2.39 g, 10 mmol) in carbon disulphide (60 ml) was added at room temperature to a stirred suspension of aluminium chloride (1.73 g, 13 mmol) in carbon disulphide (40 ml) over a period of 0.5 h. The mixture was refluxed for 1 h, poured into saturated sodium carbonate solution (300 ml), and extracted with chloroform (300 ml). The extract was washed with water, dried over sodium sulphate, and evaporated. The dark residue was subjected to silica gel chromatography. Elution with carbon tetrachloride first gave a small amount of a yellow solid, and then (13) (0.38 g, 19%), m.p. 96—97 °C (from hexane). The properties of this material agreed in all respects with those obtained from (1) and carbon disulphide. Further elution of the column gave tarry materials.

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* It is well known that diradicals like (17) cyclize to the carbenes (18) (W. Kirmse, 'Carbene Chemistry,' Academic Press, New York and London, 1971, p. 47).