Studies on Amine Oxide Rearrangement: An Unusual Product from the Reaction of 1-Phenoxy-4-tetrahydroquinolylbut-2-yne with *m*-Chloroperbenzoic Acid

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1-Phenoxy-4-tetrahydroquinolylbut-2-yne on treatment with *m*-chloroperbenzoic acid rearranges to give 5,5',6,6'-tetrahydro-2,2'-diphenoxymethyl-1,1'-methylenebis(4*H*-pyrrolo[3,2,1-*ij*]quinoline).

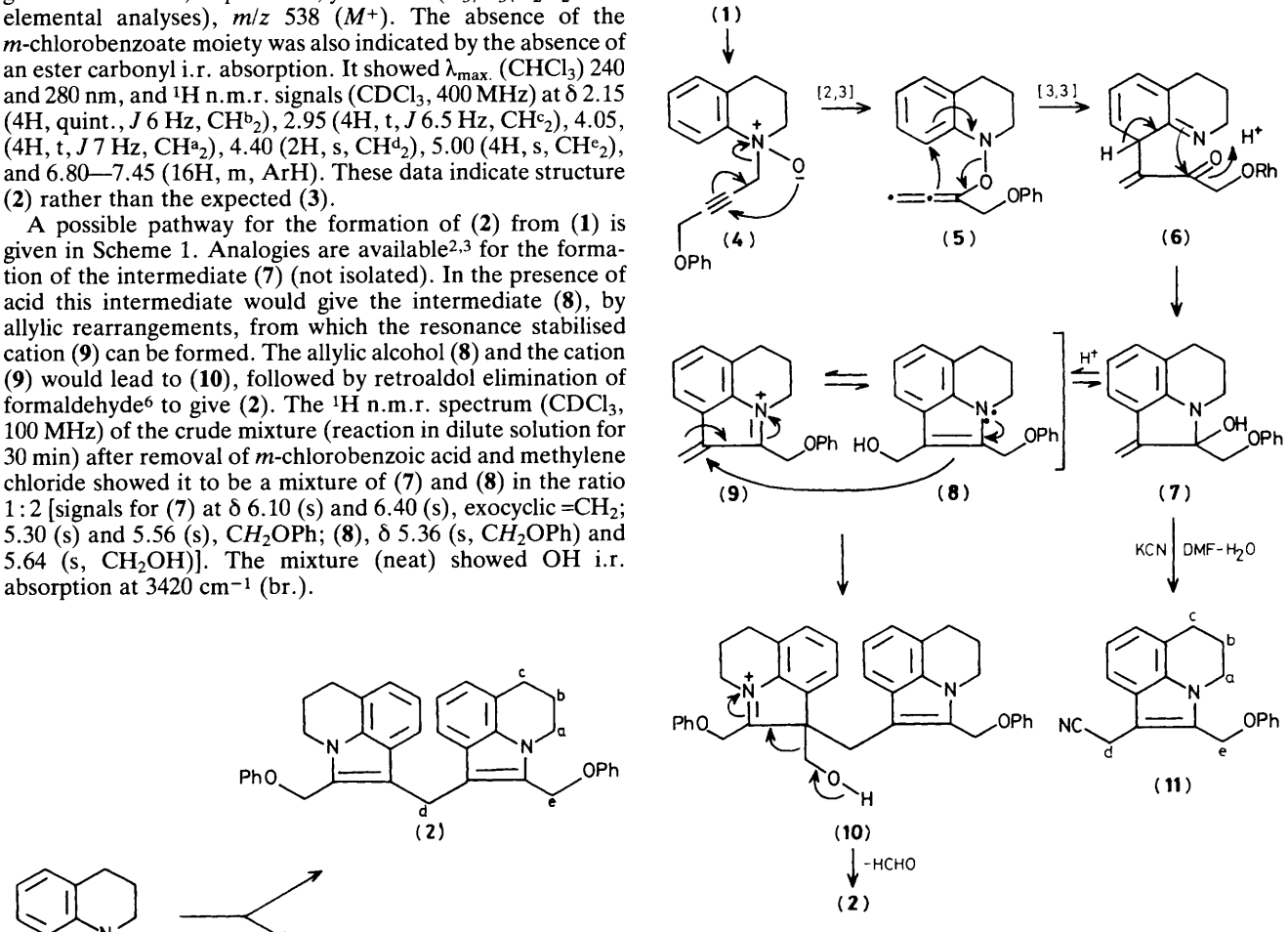
Some years ago we reported the unusual molecular rearrangement of aryl propynyl sulphoxides[1] and its use for the synthesis of substituted benzo[*b*]thiophenes.[2] In an extension to nitrogen analogues we synthesised substituted indoles.[3—5] We now report the formation of the unusual product (**2**) during the amine oxide rearrangement of 1-(4-phenoxybut-2-ynyl)tetrahydroquinoline *N*-oxide.

Compound (**1**), a white solid, m.p. 58 °C, was synthesised in 70% yield by refluxing (12 h) 1-chloro-4-phenoxybut-2-yne and tetrahydroquinoline with anhydrous potassium carbonate in acetone. Treatment of (**1**) with *m*-chloroperbenzoic acid (1 equiv.) in methylene chloride at room temperature for 12 h gave a white solid, m.p. 158 °C, yield 30% ($C_{37}H_{34}N_2O_2$ from elemental analyses), *m/z* 538 (M^+). The absence of the *m*-chlorobenzoate moiety was also indicated by the absence of an ester carbonyl i.r. absorption. It showed $\lambda_{max.}$ ($CHCl_3$) 240 and 280 nm, and ^{1}H n.m.r. signals ($CDCl_3$, 400 MHz) at δ 2.15 (4H, quint., *J* 6 Hz, CH^b_2), 2.95 (4H, t, *J* 6.5 Hz, CH^c_2), 4.05, (4H, t, *J* 7 Hz, CH^a_2), 4.40 (2H, s, CH^d_2), 5.00 (4H, s, CH^e_2), and 6.80—7.45 (16H, m, ArH). These data indicate structure (**2**) rather than the expected (**3**).

A possible pathway for the formation of (**2**) from (**1**) is given in Scheme 1. Analogies are available[2,3] for the formation of the intermediate (**7**) (not isolated). In the presence of acid this intermediate would give the intermediate (**8**), by allylic rearrangements, from which the resonance stabilised cation (**9**) can be formed. The allylic alcohol (**8**) and the cation (**9**) would lead to (**10**), followed by retroaldol elimination of formaldehyde[6] to give (**2**). The ^{1}H n.m.r. spectrum ($CDCl_3$, 100 MHz) of the crude mixture (reaction in dilute solution for 30 min) after removal of *m*-chlorobenzoic acid and methylene chloride showed it to be a mixture of (**7**) and (**8**) in the ratio 1:2 [signals for (**7**) at δ 6.10 (s) and 6.40 (s), exocyclic $=CH_2$; 5.30 (s) and 5.56 (s), CH_2OPh; (**8**), δ 5.36 (s, CH_2OPh) and 5.64 (s, CH_2OH)]. The mixture (neat) showed OH i.r. absorption at 3420 cm^{-1} (br.).

We failed to obtain the expected product (**3**) in various attempts. Attempted trapping of the allyl alcohol (**7**) with ethanol did not give any well defined product; however, (**7**) was successfully trapped by addition of a stronger nucleophile (CN^-), to furnish (**11**) as a white crystalline solid, m.p. 144 °C, yield 60%.†

The formation of (**2**) by the sequence in Scheme 1 is not totally unexpected; it is interesting that (**2**) is obtained in one step under such mild conditions.



Scheme 1. DMF = dimethylformamide.

† Satisfactory elemental analyses for $C_{20}H_{18}N_2O$; *m/z* 302 (M^+), 276 (M^+ − CN), and 209 (M^+ − OPh, 100%); $\lambda_{max.}$ ($CHCl_3$) 240 and 278 nm; ^{1}H n.m.r. ($CDCl_3$, 400 MHz) δ 2.20 (2H, quint., CH^b_2), 3.00 (2H, t, CH^c_2), 3.85 (2H, s, CH^d_2), 4.15 (2H, t, CH^a_2), 5.25 (2H, s, CH^e_2), and 6.90—7.70 (8H, m, ArH).

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