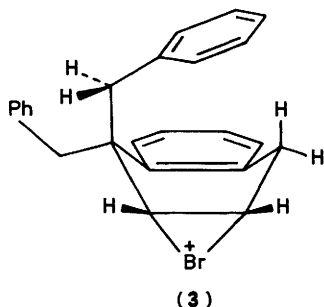


X-Ray crystallographic analysis established the structure of the product as the bicyclo[3.3.1]nonane derivative (2).*

Molecular models of (1) indicate that in the preferred conformation one benzyl group lies over one face of the nonaromatic ring. This assignment is supported by the n.m.r. spectrum of (1), which shows the C-4 methylene signal at δ 2.63 p.p.m., markedly upfield from the corresponding signal which appears at δ 3.35 p.p.m. in the spectrum of 1,1-dimethyl-1,4-dihydronaphthalene. A cyclic bromonium ion derived from (1) would be expected to have a similar conformation (3). In this conformation the 'endo' benzyl group would interfere with nucleophilic attack at C-2 and C-3, and also interfere with the abstraction of those hydrogens *anti* to the bromine atom, thus inhibiting both addition and substitution reactions.



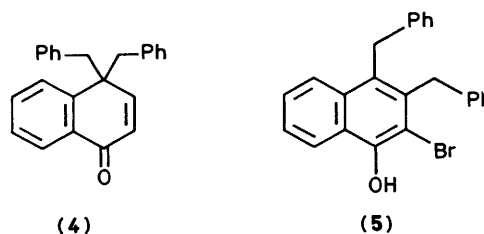
Intermediate (3), however, seems well suited for a rearrangement process, since migration of a benzyl substituent would result in formation of a tertiary, benzylic carbonium ion. A similar migration process *does* occur during reaction of bromine with ketone (4), m.p. 121.5–122 °C, which was prepared by oxidation of (1) with *t*-butyl chromate (1.4 equiv.). Unlike (1), ketone (4) did not react with bromine in carbon tetrachloride solution, but addition of bromine (1.2 equiv.) to a solution of (4) in acetonitrile at room temperature resulted in loss of the bromine colour. Hydrogen bromide was again

* Crystal data: $C_{24}H_{21}Br$, $M = 389.34$. Triclinic space group $P\bar{1}$ (No. 2), $a = 9.566(3)$, $b = 12.097(4)$, $c = 18.341(4)$ Å, $\alpha = 71.41(2)$, $\beta = 75.10(2)$, $\gamma = 66.97(3)$, $V = 1825.6(9)$ Å³, $Z = 4$, $D_c = 1.413$ g cm⁻³, $F(000) = 800$, $\mu(Mo-K\alpha) = 22.3$ cm⁻¹. The crystal used for the study (cut to dimensions of 0.33 × 0.33 × 0.50 mm) was mounted in a thin-walled glass capillary tube which was sealed as a precaution against moisture sensitivity. Preliminary examination and data collection were performed with graphite monochromated $Mo-K\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer at an ambient temperature of 23 ± 2 °C. A total of 4181 unique reflections were measured (+h, ±k, ±l; $\theta = 2\theta$ scan mode, $2\theta_{max} = 43^\circ$). An empirical absorption correction based on psi scans was applied (0.767 to 1.00 on I).

The structure was solved by using Patterson and difference Fourier techniques and was refined by full-matrix least-squares methods [function minimized: $w(|F_o| - |F_c|)^2$, $w^2 = 2F_oL_p/\sigma_1$]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions as fixed isotropic scatterers. The final agreement factors were $R = 0.035$ and $R_w = 0.045$ for the 2964 reflections having $I \geq 3\sigma_I$. All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

Tables of atomic co-ordinates and bond lengths and angles are available on request from the Director of the Cambridge Crystallographic Data Centre, University of Cambridge Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

produced during the reaction. The sole product obtained from the bromination was the dienone-phenol rearrangement product, 3,4-dibenzyl-2-bromo-1-naphthol (5) (m.p. 143.5–145 °C from ethanol). The structure of (5) was established by elemental analysis, spectroscopy, and independent synthesis by bromination of 3,4-dibenzyl-1-naphthol [obtained by rearrangement of (4) in sulphuric acid–acetic acid].



Ketone (4) was recovered unchanged from solution in acetonitrile saturated with hydrogen bromide, demonstrating that rearrangement to (5) must have occurred during reaction with bromine. This is the first reported example of a dienone-phenol rearrangement occurring under such conditions; other α,β -unsaturated ketones either simply add bromine to form dibromides or eliminate HBr to yield 2-bromo-2-en-1-one derivatives. The formation of (5) therefore suggests that the *endo* benzyl group in the reactive intermediate arising from bromination of (4) can inhibit even the normally facile abstraction of a proton α to a carbonyl group.

The 'Friedel–Crafts' process which occurs during bromination of (1) is not observed in the case of (4); this may be due in part to such a reaction requiring the generation of a higher degree of positive charge on the attacking carbon than is compatible with the presence of the carbonyl group at C-1. In addition, previous studies have demonstrated that benzyl is an excellent migrating group in dienone-phenol rearrangements,⁴ but is sometimes less effective in simple Wagner–Meerwein shifts.^{5,6} Nonetheless, it is surprising that migration of a benzyl group during the bromination of (1) should occur so much more slowly than the normally higher energy electrophilic attack on an unactivated aromatic ring.

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