

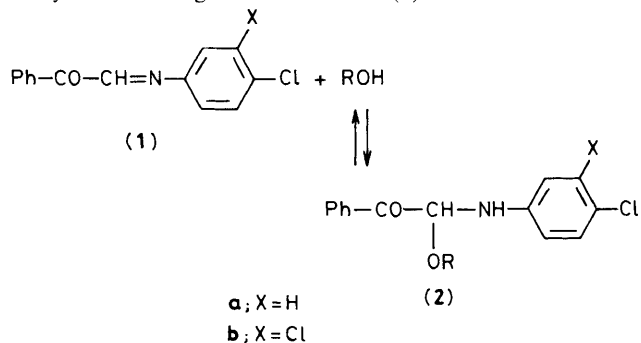
The Reaction of Anils with Conjugated Dienes

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2-(4-Chlorophenylimino)-1-phenylethanone (**1**) or its adducts with alcohols (**2**) react with butadiene, cyclopentadiene, cyclohexa-1,3-diene, or cycloheptatriene under BF_3 catalysis to give the tetrahydroquinoline derivatives (**11**), (**8a**), (**12**), and (**13**), respectively.

The anils of phenylglyoxal (**1**) have been reported to give Diels–Alder adducts with conjugated dienes under Lewis acid catalysis.¹ Although in our hands (**1**) or its adducts with



alcohols (**2**) do form Diels–Alder adducts with 2,3-dimethylbuta-1,3-diene,² the analogous reaction of (**1a**) or (**2a**) with cyclopentadiene (**3**) gives a 1 : 1 adduct [from mass spectroscopy; m.p. 178–179 °C (decomp.)], which is not the Diels–Alder adduct (**5**), but the tetrahydroquinoline (**8**) (see Scheme 1).

From the reaction conditions used,³ we can reasonably postulate the zwitterionic intermediate (**4**), from which six primary or secondary cycloadducts (**5**)–(**10**) can form, as illustrated in Scheme 1.†

† A similar reaction scheme was proposed for the reaction between enamines and other Schiff bases (ref. 4). There is no firm evidence for the intervention of the zwitterionic intermediate shown in Scheme 1. A concerted reaction involving one aromatic double bond could equally explain the present results.

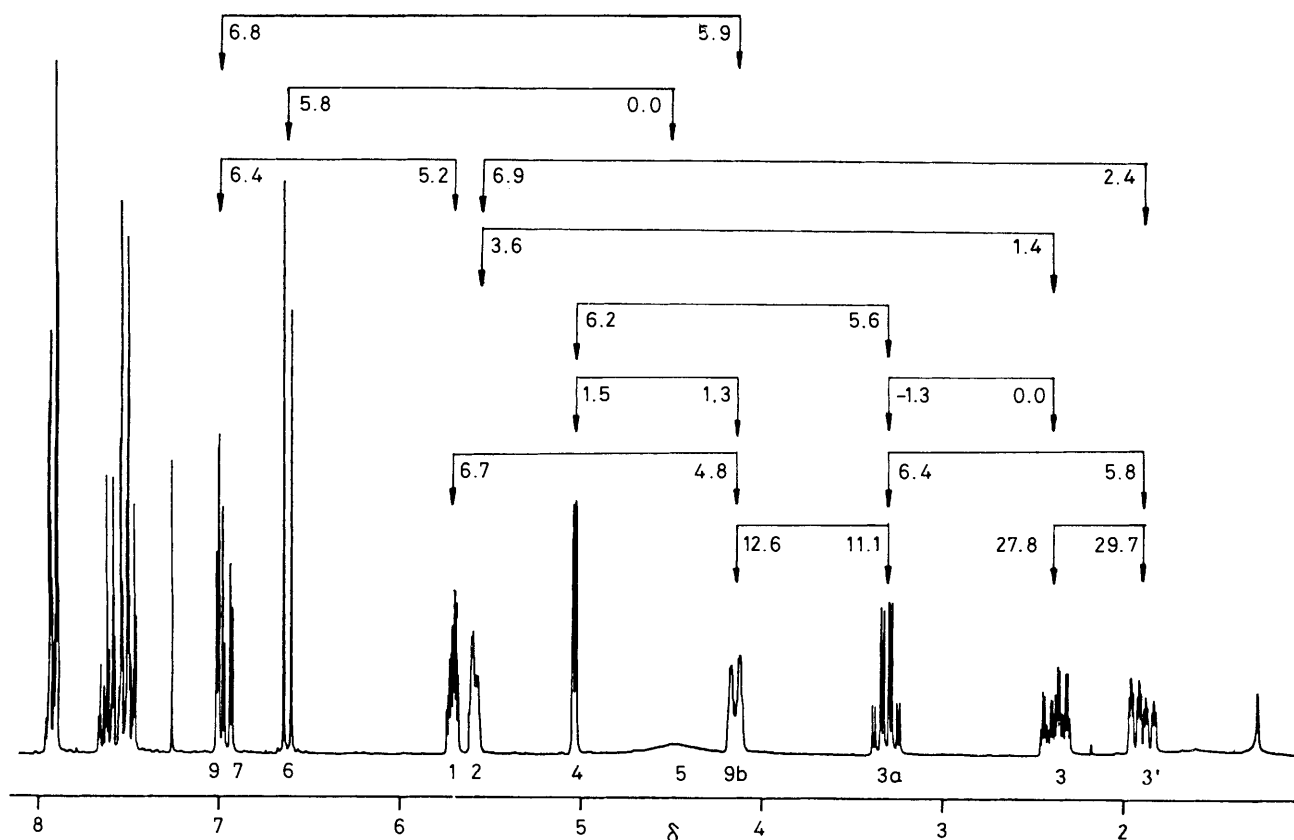
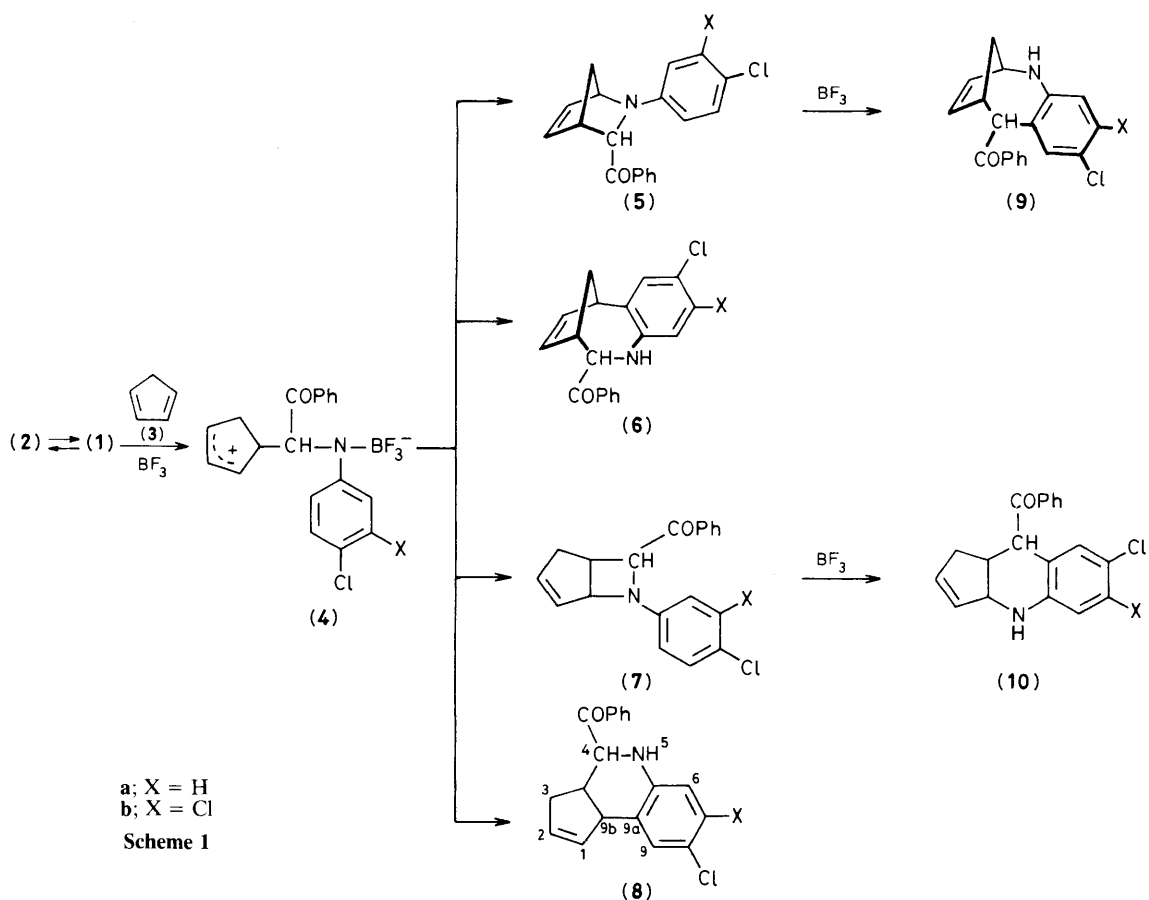
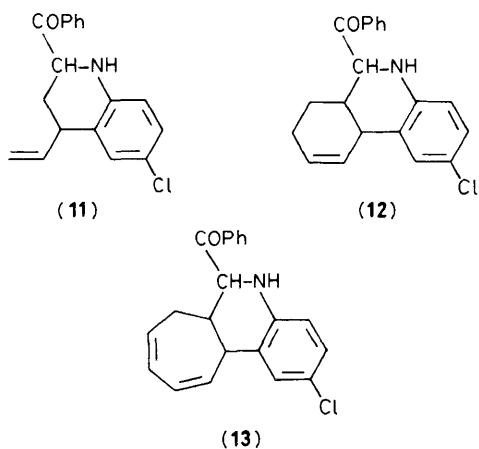


Figure 1. 200 MHz ^1H N.m.r. spectrum (CDCl_3) of (8a). Numbers give percentage n.o.e. enhancements upon perturbation of the connected nucleus (error ca. 1%).



In the ^1H n.m.r. spectrum of the actual adduct formed (Figure 1), the doublet at δ 5.02 attributable to the $-\text{CH}-\text{CO}-$ proton, couples (J 3.4 Hz) with the bridgehead proton at δ 3.30. Decoupling experiments show that the latter couples (J 8.8 Hz) with the two methylenic protons at δ 1.89 and 2.37, and, with the same constant, with the other bridgehead proton at δ 4.14. This coupling scheme is consistent with the 1,2 adducts (7), (8), or (10) only. This is confirmed by nuclear Overhauser effect (n.O.e.) experiments (Figure 1).

The aromatic section of the spectrum shows the five protons of the phenone ring resonating at δ 7.92 and 7.4–7.6, but three protons only for the aniline ring, thus excluding (7). The missing proton can be found as a broad band, the position of

which depends on the experimental conditions. In the adduct \ddagger from (1b) or (2b), two aniline resonances appear as a singlet at δ 6.77 and a doublet at δ 7.06 (J 1.2 Hz). From decoupling experiments, the coupled nucleus is the bridgehead proton at δ 4.14 and not the $-\text{CH}-\text{CO}-$ proton at δ 5.02, thus suggesting (8), rather than (10), as the actual structure. This is confirmed by n.O.e. experiments, which show the proximity of the 6 and 9 aromatic protons to the NH proton and to the bridgehead proton at δ 4.14 and the vinylic proton at δ 5.70, respectively.

The reactions of (1a) or (2a) with buta-1,3-diene, cyclohexa-1,3-diene, and cycloheptatriene give similarly the products of substitution at the aniline ring, (11) [m.p. 115–116°C (decomp.)], (12) [m.p. 170°C (decomp.)], and (13) [m.p. 167°C (decomp.)], as is evident from inspection of the aromatic section of the ^1H n.m.r. spectrum.

The unusual behaviour of 2,3-dimethylbuta-1,3-diene² will be the subject of further investigation.

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References

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\ddagger This is the isomer [m.p. 170–172°C (decomp.)] arising from substitution at the 6 position in the aniline ring of (4); a second isomer can be isolated [m.p. 176–178°C (decomp.)], arising from substitution at the 2 position.