First Successful Substitution of 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-one

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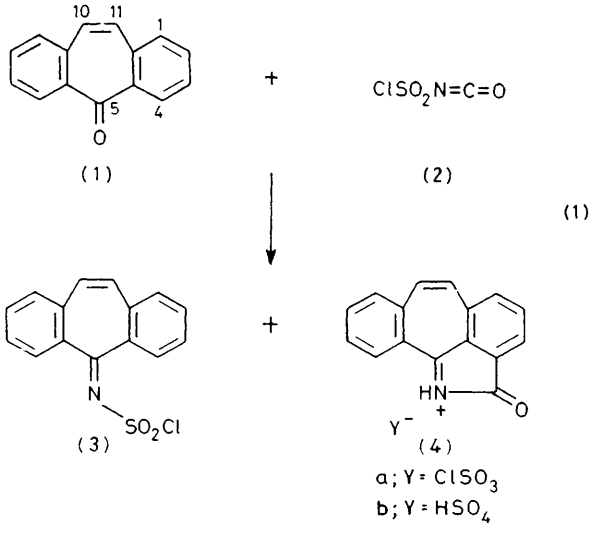
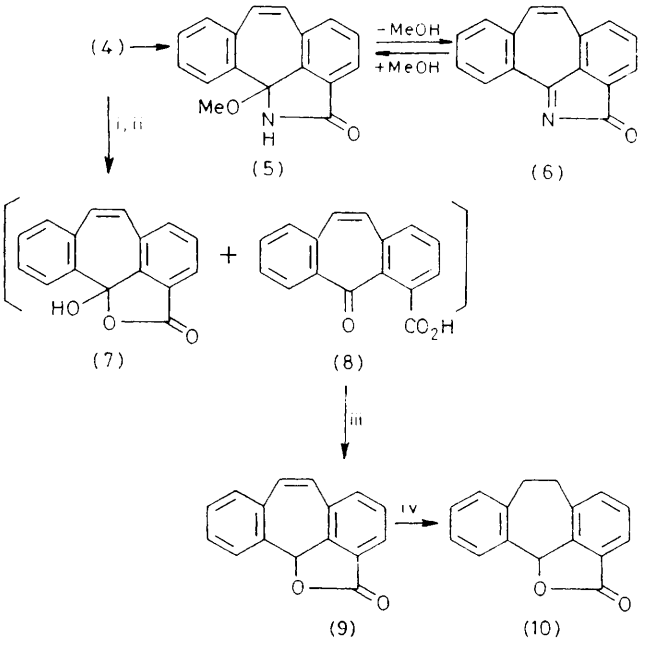
Summary Reaction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**1**) with chlorosulphonyl isocyanate (**2**) results in the unexpected introduction of a carbon substituent at the 4-position of (**1**), through an assisted electrophilic substitution.

THE direct introduction of substituents in the benzene rings of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one, (**1**), has not yet to our knowledge been successfully accomplished. It has previously been carried out by the total synthesis of substituted 10,11-dihydro compounds, followed by introduction of the double bond,[1] or by electrophilic substitution on 10,11-dihydro-(**1**), with subsequent introduction of the double bond in the 10,11-position.[2] Even in the latter case, substitution in general, when successful, is not selective, *e.g.* nitration gives a mixture of disubstituted products.[3]

We report here a novel method for the direct introduction of a carbon substituent into the 4-position of (**1**). The reaction of (**1**) and chlorosulphonyl isocyanate (**2**) in refluxing benzene afforded along with (**3**) (51% yield), the structure normally expected from the reaction of (**2**) with ketones,[4] a new compound in 48% yield to which we have ascribed the structure (**4a**), based on evidence presented below (equation 1). These were separated quantitatively by decanting the benzene solution, (**3**) being in the benzene layer, while (**4a**) was deposited as an insoluble, red, granular residue.



Compound (**4a**) is a very unstable, bright red solid, which fumes copiously when exposed to air, liberating an acidic gas, presumably HCl. The i.r. spectrum shows a band at ν(KBr) 1760 cm^{-1} and the mass spectrum shows a molecular ion at *m/e* 231 (M^+). Elemental analysis of a sample of (**4a**) exposed to air for complete liberation of HCl corresponded to the hydrogen sulphate (**4b**).† On treatment with methanol the red colour of (**4**) was instantaneously discharged and a white solid, m.p. 175—192 °C (decomp.), was formed in quantitative yield to which we have assigned the structure (**5**)‡ (Scheme 1) on the basis of



SCHEME 1. i, NaOH–EtOH–H_2O; ii, HCl; iii, NaOH, $NaBH_4$; iv, H_2, Pd/C–MeOH.

its spectral data. The i.r. spectrum shows secondary amide absorptions at ν(KBr) 1710 and 3220 cm^{-1}; the ^1H n.m.r. spectrum ($CDCl_3$) shows δ 2·65 (s, Me), 7·14 and 7·18 (2d, AB system, 10- and 11-H $J_{10,11}$ 12 Hz), 7·35—8·0 (m, ArH), and 9·7 (br s, NH) [numbering as in (**1**)]; the mass spectrum shows the expected molecular ion at *m/e* 263, and the fragmentation pattern (263 — MeOH, 231), (231 — CN, 205), (231 — CO, 203), and (205 — CO = 203 — CN, 177), is consistent with the proposed structure.

When heated at 125 °C under high vacuum, (**5**) eliminates 1 mol methanol to yield (**6**), m.p. 198—199 °C. The i.r. spectrum of (**6**) lacks the NH absorption and shows a carbonyl band at ν(KBr) 1720 cm^{-1}; the ^1H n.m.r. spectrum ($CDCl_3$) shows δ 7·05 (s, 10- and 11-H), 7·2—8·1 (m, ArH), and 9·3 (m, 6-H); the mass spectrum *m/e* 231 (M^+) and the fragmentation pattern (231 — CN, 205), (231 — CO, 203), (205 — CO = 203 — CN, 177) confirm the identity of the compound. Compound (**6**) is very reactive and reacts readily with MeOH, for example, to regenerate (**5**).

† All new compounds gave satisfactory elemental analyses.

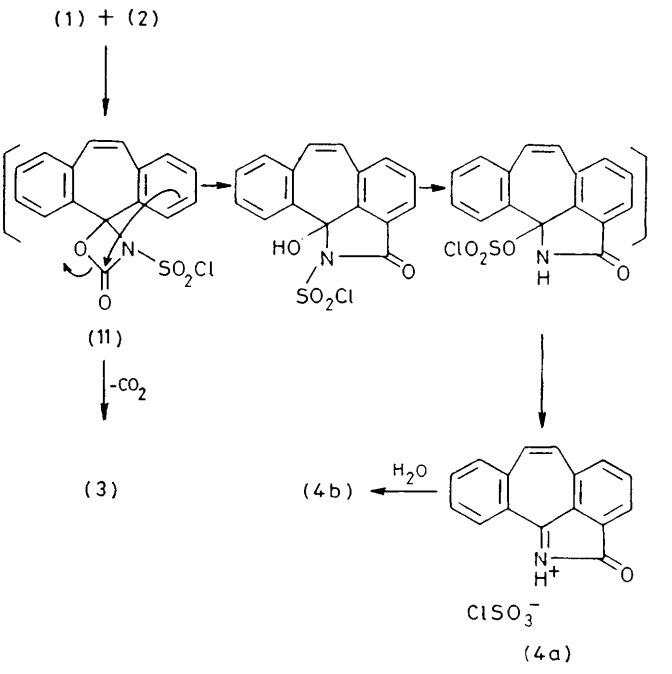
‡ The m.p.s of (**5**) and related compounds are rather broad owing to the concomitant elimination to form (**6**).

That the compound isolated in the reaction mixture (**4a**), and the somewhat more stable sulphate, (**4b**), are in fact salts of (**6**) is based on the following evidence: (a) the red colour is readily explained considering that (**4**) is in effect a tropylium ion;[5] (b) the methanol treatment described above leading to (**5**); (c) the mass spectrum of (**4**) (M^+ 231) is identical with that of (**6**); (d) compounds (**5**) and (**6**), when shaken for a few minutes with 1 equiv. sulphuric acid in benzene–ethyl acetate solution, gave a bright red precipitate which analysed correctly for the sulphate salt of (**6**) and whose i.r., n.m.r., and mass spectra are identical with those of (**4b**); and (e) through the sequence shown in Scheme 1, we have prepared the known lactone (**10**), m.p. 122 °C; i.r. $\nu_{C=O}$ (KBr) 1760 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ2·6—3·7 (m, $-CH_2-CH_2-$), 6·75 (s, 5-H) 7·0—7·8 (m, ArH) [lit.,[6] m.p. 122 °C, i.r. $\nu_{C=O}$ (KBr) 1760 cm^{-1}].

The formation of (**4**) in the reaction between (**1**) and (**2**) was quite unexpected. Electrophilic substitution on the tricyclic ketone was not predicted, since this aromatic ketone is not particularly reactive and does not, for example, react under normal Friedel–Crafts conditions. If a normal electrophilic substitution had occurred in the reaction between (**1**) and (**2**), a 10(11)-substituted product would have been expected, as this is the site of bromine addition for example.[7]

The formation of (**4**) is best explained by the reactive intermediate (**11**)[4] as shown in Scheme 2. Such intermediates are normally postulated for the formation of chlorosulphonylimines from aldehydes or ketones. Here, nucleophilic attack of the adjacent ring competes with the loss of CO_2. It follows from our proposed mechanism that the red material (**4a**) as initially formed in the reaction mixture is probably the chlorosulphonic acid salt of (**6**), atmospheric moisture accounting for the formation of the sulphate (**4b**).

The generality of direct introduction by an electrophilic reaction of a carbon substituent at the *ortho*-position of



SCHEME 2

aromatic carbonyl compounds, as described for (**1**), is unusual, and is under further investigation. Simple modifications of (**4**) should provide an easy method for the introduction of various functional groups at the 4-position of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**1**). Such compounds are largely unknown and can only be synthesized at present by total synthesis.

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