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ON THE CONDENSATION OF PHENYL ETHYNYL KETONE WITH CYCLOPENTADIENE—A REINVESTIGATION

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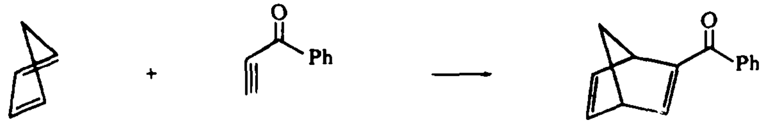
Abstract—The earlier structural assignment as **1** for the product obtained by the condensation of phenyl ethynyl ketone with cyclopentadiene is now revised to the dimeric structure **5d**.

IN CONNECTION with some other work on norbornadienyl systems we required a sample of 2-benzoylnorbornadiene (**1**). This was reported to have been made by Bowden and Jones[1] by the most obvious approach—*viz.* the condensation of phenyl ethynyl ketone with cyclopentadiene. Condensation of phenyl ethynyl ketone with freshly distilled cyclopentadiene under Jones' condition (20°, neat) yielded a pale yellow crystalline solid, m.p. 158–59° (reported m.p. 159°). However, in our hands, at no time we could get a quantitative yield of the adduct as claimed by Bowden and Jones. The best yields (60%) were obtained by refluxing a solution of phenyl ethynyl ketone in excess cyclopentadiene on a water bath for 15 min.



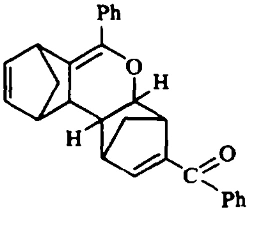
1

The solid was homogeneous to TLC and a routine spectral examination revealed the adduct to be more complex in nature than the simple 2-benzoylnorbornadiene structure (**1**) suggested by Bowden and Jones. In this paper we present both spectral and chemical evidence to show that the adduct (m.p. 158–59°) has the dimeric structure (**5d**).

The relative abundance of the isotope peaks related to the molecular ion (*m/e* 392) in the mass spectrum indicated the adduct to be a dimer of 2-benzoylnorbornadiene with a $C_{28}H_{24}O_2$ composition. The dimer had absorptions at 6·0 and 6·3μ in the IR and at 225mμ (ε, 9738) and 250mμ (ε, 16,740) in the UV. (Reported UV: 225 (ε, 6000), 250 (ε, 9000), 280 (ε, 5500) and 288mμ (ε, 4500).)

There are at least three different pathways by which 2-benzoylnorbornadiene can dimerise; (i) by a 2 + 2 + 2 addition, (ii) by a 2 + 2 addition and (iii) by a 4 + 2 addition. This predicts that 18 different isomeric structures are possible for the dimer, not to mention stereochemistry.

The 2 + 2 + 2 addition pathway was ruled out by a cursory glance of the NMR spectrum of the dimer in which the cyclopropyl protons are conspicuously absent. The 2 + 2 addition pathway was also ruled out by a careful examination of the NMR spectrum which indicated the presence of two dissimilar aromatic rings. Thus the 2:3 ratio of multiplets centered at δ8·2 and δ7·4 and a sharp singlet at δ7·1 whose integral intensity is the total of the multiplets at δ8·2 and δ7·4 strongly suggested the presence of a —CO—Ph group and a Ph group not bound to a carbonyl function. This inference was further substantiated by the fact that the reduction of the dimer with excess LAH yielded a monohydroxy compound (6) devoid of any carbonyl absorption in the IR spectrum. (M^+ 394; IR: 2·8μ; NMR: (δ)7·2–7·6, m, 5H; 7·0–7·2, s, 5H: 6·0–6·3, m, 4H; 4·5, s, 1H; 1·2–3·5, m, 11H). The dimers (2–5) arising out of a 4 + 2 addition of two 2-benzoylnorbornadiene molecules can explain the absorption pattern in the aromatic region of the NMR.



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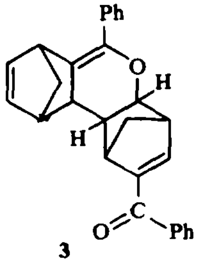

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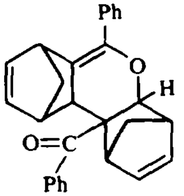

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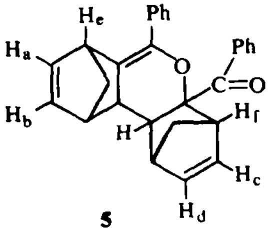
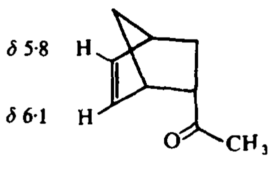
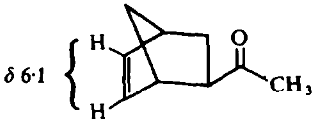


5

The broad three proton multiplet centered at δ6·3 and an one proton quartet centered at δ5·5 can be reasonably assigned to the isomeric dimers **2**, **3** and **5**. The dimeric structure **4** can thus be ruled out as this must account for a five proton absorption in the region δ6·3–5·5. However, that the one proton quartet centered at δ5·5 is not due to O—C—H was borne out by the fact that it disappears in the tetrahydro derivative (7), obtained by the catalytic hydrogenation of the dimer (M^+ 396; IR: 6·0 and 6·3μ; NMR: (δ)8·0–8·3, m, 2H; 7·3–7·5, m, 3H; 7·0–7·1, s, 5H; 1·3–3·2, m, 18H. It is significant that there is no absorption in the region δ3·1–6·9 where one expects to find O—C—H.) and coalesces with the absorption centered at δ6·15 to form a four proton multiplet in the LAH reduction product (6) of the dimer. This observation thus categorically ruled out the isomeric structures **2** and **3** also for the dimer.

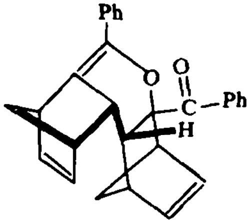
The two olefinic protons of endo-5-acetylnorbornene are known to be nonequivalent, apparently caused by the proximity of one of the olefinic protons to the carbonyl of the endo acetyl group, and have absorptions at δ5·8 and 6·1 respectively in the NMR.[2] In the *exo* isomer the acetyl group is too far removed from the olefinic protons to exert any influence and the two olefinic protons appear equivalent and have a single absorption at δ6·1. The following are the assignments made for the olefinic protons in the endo-5-acetylnorbornene.



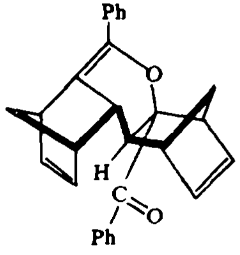


The 3:1 ratio of absorptions at δ6·2 and 5·5 can thus be reasonably explained by structure **5** if one assumes the benzoyl group to be *endo* with respect to the norbornene ring to which it is bonded. This would result in proton H_c, due to the deshielding effect of the carbonyl of the *endo* benzoyl group, absorbing downfield along with protons H_a and H_b at δ6·2 and proton H_d absorbing at δ5·5. The *endo* orientation of the benzoyl group is also indicated by a broad two proton singlet at δ3·6. This absorption can be reasonably assigned to protons H_e and H_f in structure **5**, for the methine protons in norbornadiene which are *bis* allylic and the C_4 methine proton in *endo*-5-acetylnorbornene absorb downfield at δ3·5 and 3·12 respectively.[3]

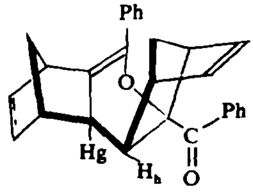
An inspection of the models of the eight possible stereoisomers showed that the benzoyl group is *endo* to the norbornene ring to which it is bonded in four of the stereomers (**5a**–**5d**).



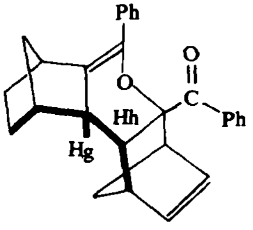
5a



5b

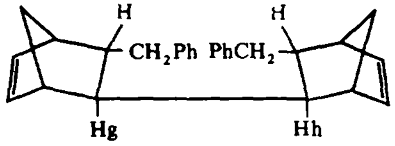


5c



5d

From the data presented above a choice among the four possible stereoisomers could not be made. The Li/NH_3 reduction product of the dimer provided further evidence for the α-alkoxyketone structure (**5**) and also some clue as to its probable stereochemistry. Thus the reduction of the dimer by a solution of Li in liquid NH_3 in the presence of a proton source like NH_4Cl[4] at $-30°$ yielded a white crystalline solid. (M^+ 366; IR: 6.2μ; NMR: (δ): 7·2, s, 10H; 6·0–6·3, m, 4H; 2·0–3·0, m, 10H; 1·3, s, 4H; 0·9, s, 2H). The hydrocarbon nature of the solid was indicated by combustion analysis. The ten proton singlet at δ7·2 and the four proton multiplet centered at δ6·2 indicated that the Ph groups and the four olefinic protons are under identical environments respectively. The two proton singlet at δ0·9 seemed significant and indicated the presence of two *endo* hydrogens.[3] The peaks at *m/e* 300 and 234 in the mass spectrum indicated the sequential loss of two cyclopentadiene units and the peaks at *m/e* 275, 209, 143, 117, 91 and 77 all were consistent with the *bis* benzylnorbornene (**8** or **9**) for the reduction product.



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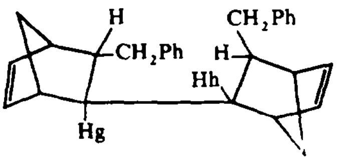

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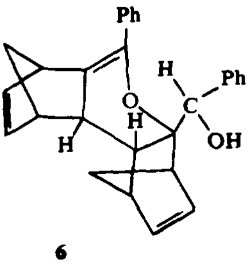
Formation of **8** or **9** can be easily explained in terms of stereomers **5c** or **5d** both of which have two *endo* hydrogens H_g and H_h, by the pathway shown in Scheme 1, assuming, however, that the kinetic protonation of the intermediate *bis* enolate (**10**) takes place from the *exo* side. The stereoisomers **5a** and **5b**, each of which possesses only one *endo* hydrogen, are incapable of giving rise to the reduction product with two *endo* hydrogens. Since the transition state leading to the formation of **5d** allows the maximum accumulation of negative charges as per Alder's rule and is sterically more favourable than the one for **5c**, we believe the dimer can be best represented by stereomeric structure **5d**.* Thus the product obtained by the Li/NH_3 reduction of the dimer can be represented by structure **9**.

The LAH and catalytic reduction products of the dimer can be accordingly formulated as follows:



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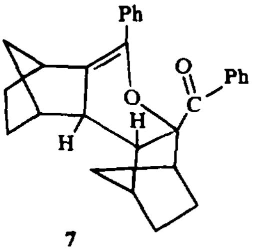

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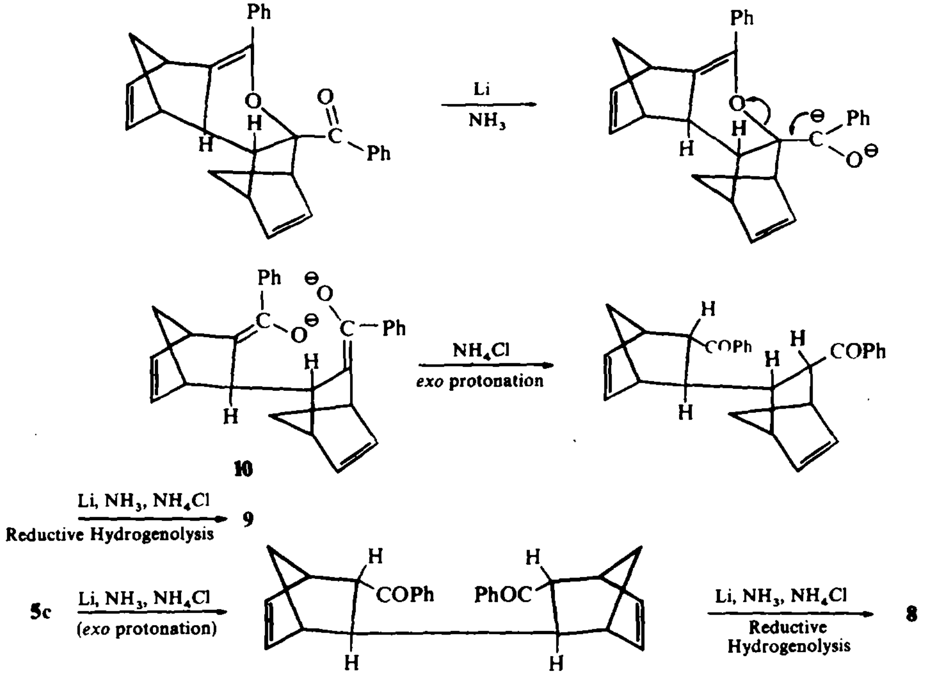
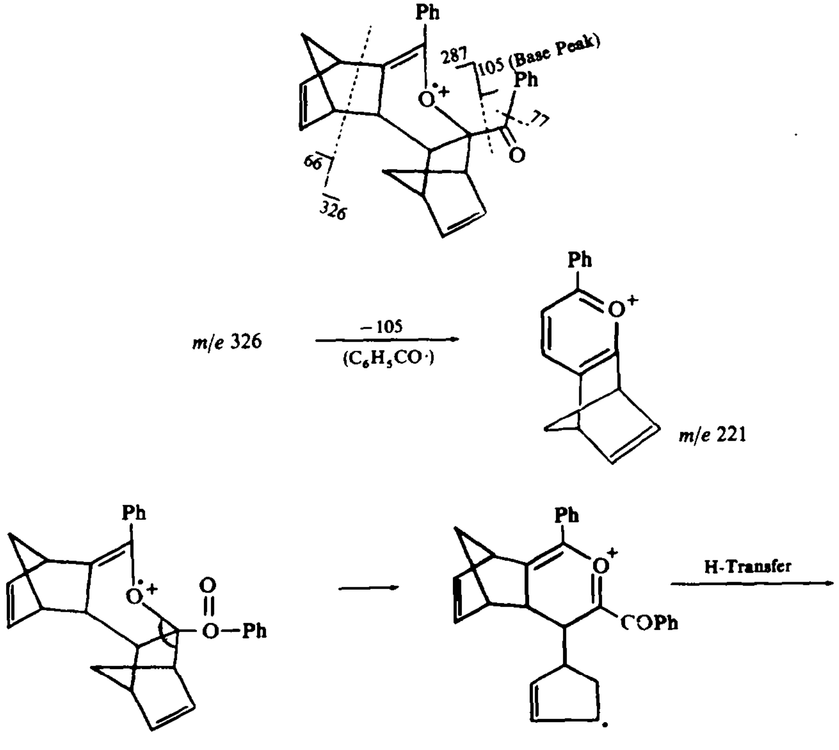
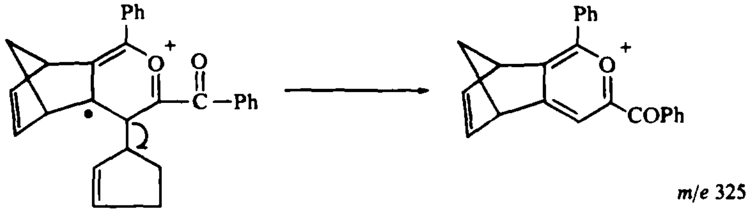
* At our request, the stereochemical assignment (**5d**) for the dimer is independently being examined by X-ray studies on the bromoacetyl derivative of the alcohol (**6**) by workers in the Department of Physics, University of Madras.

SCHEME 1



SCHEME 2

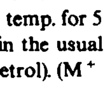
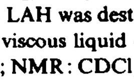
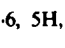
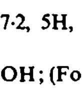
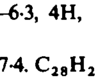


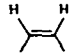


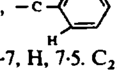
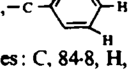
The mass spectral fragmentations also supported the gross structure 5 for the dimer. (Scheme 2.)

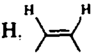
Dimerisations of α,β-unsaturated aldehydes and ketones to form 2-substituted—2,3-dihydropyrans have been well documented in the literature.[5] However, such dimerisations are effected at temperatures greater than 150°, and the ease with which 2-benzoylnorbornadiene dimerises to form **5d** can be ascribed to the strain and consequent reactivity of the norbornadienyl double bond. Condensation of cyclopentadiene with propiolaldehyde is reported to have yielded an equivalent dimeric compound.[6] The structural assignment, however, lacks spectral evidence. This seems to be the only other example in the literature of a facile dimerisation of a 2-acylnorbornadiene. In our hands the condensation of cyclopentadiene with various aryl ethynyl ketones has yielded equivalent dimeric compounds. Details of this will be published in a forthcoming paper.

EXPERIMENTAL

Condensation of phenyl ethynyl ketone with cyclopentadiene. A solution of phenyl ethynyl ketone[7] (1g) in freshly distilled cyclopentadiene (750 mg) was refluxed over a water-bath for 15 min. The excess cyclopentadiene was removed under vacuum and the residual liquid refrigerated overnight. The solid formed was triturated with a little cold EtOH and collected by filtration. Yield 500 mg (60%), m.p. 142–48°. After three crystallisations from EtOH it had m.p. 158–59° (reported m.p. 159°). M$^+$ 392; λ_{max}^{KBr} 6·0 and 6·3μ; λ_{max}^{EtOH} 225 mμ, ε 9738, 250mμ, ε 16,740; NMR: CDCl$_3$: (δ)8·1–8·3, 2H, ; 7·3–7·5, 3H, ; 7·0–7·2, 5H, ; 6·2–6·4, 3H, ; 5·4–5·6, 1H, ; 3·6, 2H, $-\overset{|}{\underset{|}{C}}H$; 1·7–3·0, 8H, $-\underset{|}{C}H_2$ and $-\overset{|}{\underset{|}{C}}H$; (Found: C, 85·4, H, 6·2. $C_{28}H_{24}O_2$ requires: C, 85·7, H, 6·2%).

Lithium aluminium hydride reduction of the dimer. To a solution of the dimer (200 mg) in dry ether (50 ml) was added LAH (25 mg) and the mixture stirred at room temp. for 5 hr. The excess LAH was destroyed by careful addition of EtOAc and the mixture worked up in the usual manner. The viscous liquid obtained solidified on refrigeration. Yield 140 mg, m.p. 150–51° (petrol). (M$^+$ 394; λ_{max}^{KBr} 2·8μ; NMR: CDCl$_3$: (δ)7·2–7·6, 5H, Ar protons; 7·0–7·2, 5H, Ar protons; 6·0–6·3, 4H, ; 4·5, 1H. $Ph-\underset{|}{C}H-O-$; 1·2–3·5, 11H, $-\overset{|}{C}H_2$ and —OH; (Found: C, 84·5, H, 7·4. $C_{28}H_{26}O_2$ requires: C, 84.8, H, 7·1%).

Catalytic reduction of the dimer. A solution of the dimer (200 mg) in EtOAc (25 ml) was hydrogenated in the presence of 10% Pd/C catalyst in a Parr apparatus at 50 psi for 1 hr. After usual work-up a white crystalline solid was obtained. Yield 170 mg, m.p. 134–35° (petrol). M$^+$ 396; λ_{max}^{KBr} 6·0 and 6·3μ; NMR: CDCl$_3$: (δ)8·0–8·3, 2H, ; 7·3–7·5, 3H, ; 7·0–7·1, 5H, Ar protons; 1·3–3·2, 18H, $-\overset{|}{C}H_2$; (Found: C, 84·7, H, 7·5. $C_{28}H_{28}O_2$ requires: C, 84·8, H, 7·1%).

Lithium-ammonia reduction of the dimer. To a stirred solution of Li (90 mg) in liquid NH_3 (300 ml) containing a pinch of NH_4Cl was added a solution of the dimer (500 mg) in dry ether (30 ml). The blue solution was stirred for 1 hr and decomposed with solid NH_4Cl. The NH_3 was evaporated, water was added to the residue and extracted with ether. The ether extract was washed with water, dried ($MgSO_4$) and solvent removed. The pasty solid obtained was cooled and triturated with a little ether and collected by filtration. Yield 340 mg, m.p. 100–100·5° (EtOH). M^+ 366; λ_{max}^{KBr} 6·27μ; NMR: $CDCl_3$: (δ)7·2, 10H, Ar protons; 6·0–6·3, 4H,  ; 2·0–3·0, 10H, $-\overset{|}{C}H_2$ and $-CH$; 1·3, 4H, $-\overset{|}{C}H_2$ and 0·9, 2H, endo $-\overset{|}{C}H$; (Found: C, 91·4, H, 8·5. $C_{28}H_{30}$ requires: C, 91·7, H, 8·2%).

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