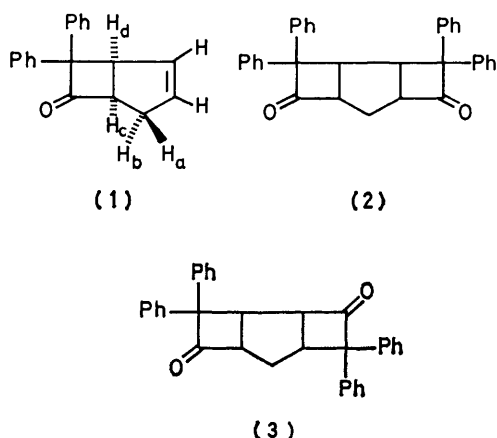# Keten. Part 18.[1] The 2 : 1 Adducts of Diphenylketen with Cyclopentadiene

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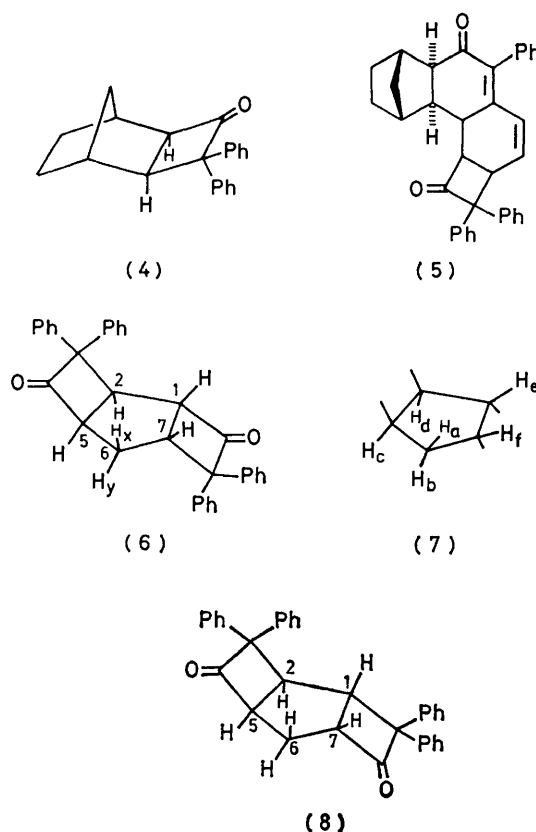**Süleyman Yildirir,** Department of Chemistry, Hacettepe University, Ankara, Turkey

The two 2 : 1 adducts of diphenylketen with cyclopentadiene are shown to have the tricyclononane structures (6) and (8).

THE addition of diphenylketen to cyclopentadiene to give a 1 : 1 adduct was reported by Staudinger in 1920,[2] and the structure of this compound was established as the bicycloheptenone (1) by two independent groups.[3,4] Smith and his co-workers [4] also reported that prolonged heating of (1) with diphenylketen gave a compound, $C_{33}H_{26}O_2$, whose molecular formula corresponded to addition of a second molecule of diphenylketen to (1). Structures (2) and (3) were suggested for this compound, but no conclusive evidence for either was adduced. The conditions employed for formation of the 2 : 1 adduct (110 °C for 9 days) were such as might cause dissociation of (1) into diphenylketen and cyclopentadiene,[2] and recently Huisgen *et al.* have reported [5] that prolonged heating of diphenylketen with norbornene gives, in addition to the first formed cyclobutanone (4), a 2 : 1 adduct (5) apparently arising by a process involving initial rearrangement of (4). Even if one of the structures (2), (3) proposed by Smith were to be correct it seemed surprising that only one regioisomer is formed. The stereochemistry of the tricyclononane skeleton was also uncertain. We have therefore repeated Smith's work.

agreed with the previous report.[4] The n.m.r. spectra were consistent with the constitution (3), the ^{13}C spectrum showing two carbonyl resonances and six other signals due to aliphatic carbon atoms. The signals due to the two diphenyl-substituted carbon atoms are superimposed. A single carbonyl absorption in the i.r. spectrum at 1 766 cm^{-1} is consistent with the presence of the cyclobutanone rings.

(4)   (5)

(6)   (7)

(1)   (2)

(3)

(8)

The bicycloheptenone (1) was prepared and spin decoupling permitted assignment of the non-aromatic proton signals in the n.m.r. spectrum. Reaction of this compound with diphenylketen in approximately equimolar proportions at 130 °C for 11 days gave a gummy product which solidified to an amorphous powder on treatment with methanol. Recrystallisation of this solid gave a compound whose molecular formula and m.p.

The ^1H n.m.r. spectrum is also fully consistent with structure (3) and establishes the *transoid* stereochemistry of the three rings (6). The spectrum shows multiplets due to six aliphatic protons in a cyclic array with one CH_2 group as in (7). Spin decoupling permits assignment of the resonances to proton positions around the ring with reference to the methylene group. The very low coupling (0.5 Hz) between H_d and H_e clearly indicates a *trans*-arrangement of the C–H bonds and hence the *transoid* stereochemistry shown in (6). It is noticeable

that the couplings between the magnetically non-equivalent protons of the methylene group and the adjacent hydrogen atoms [H_c, H_f in (7)] are quite different. Whilst one of the adjacent atoms, say H_f, is coupled equally to H_a, H_b, and H_e, giving a signal which is a symmetrical quartet, the other adjacent hydrogen atom, H_c, is only weakly coupled (1 Hz) to one of the methylene protons. Molecular models show that if torsional flexing of structure (6) occurs so as to reduce the steric compression of the *endo*-phenyl groups, the five-membered ring adopts an envelope-like conformation in which the C–H bond flanked by carbonyl and methylene groups is almost perpendicular to one of the methylene C–H bonds, whilst the C–H bond flanked by diphenyl-methyl and methylene groups is roughly antiperiplanar and synclinal to the methylene C–H bonds.

T.l.c. examination of the mother liquor from the recrystallisation of (6) showed the presence of another compound with similar chromatographic behaviour. A tiny sample of this compound was separated by high-performance liquid chromatography and was shown by the n.m.r. and mass spectra to be (8). The molecular formula was established by high-resolution mass spectrometry. The ^{13}C spectrum showed one carbonyl resonance and three aliphatic carbon signals; the signal due to the diphenyl substituted carbon atoms in this case lay underneath the solvent resonance. The ^{1}H n.m.r. spectrum showed three two-proton multiplets due to aliphatic protons. A high-field absorption assigned to the CH_2 group in (8) is a double doublet which is very nearly a symmetrical triplet. A multiplet attributed to the two protons adjacent to the methylene group is almost a regular quartet consistent with interaction with three adjacent protons with slightly different coupling constants. The third signal is a simple doublet. The overall pattern and, in particular, the magnetic identity of the methylene protons is wholly consistent with the axial symmetry of (8) and the *transoid* stereochemistry of the tricyclic system. The i.r. spectrum shows an absorption at 1774 cm^{-1}, a slightly higher frequency than for (6).

Although compound (6) was isolated in relatively large quantities and was clearly the compound originally reported by Smith,[4] compound (8) was obtained in only tiny quantities for experimental reasons. The ratio of these adducts in the crude, amorphous, solid reaction product was measured by comparing the integrated intensity of absorption of the multiplets at δ 1.55 and δ 2.32 in the ^{1}H n.m.r. spectrum, and was found to be approximately 5 : 1 with (6) predominating. H.p.l.c. examination of the methanol-soluble material extracted in the first treatment of the crude reaction product showed that only traces of the adducts were lost at that stage. The 5 : 1 ratio of (6) to (8) is therefore the ratio in which they are formed in the reaction, and there is clearly a marked regioselectivity in the addition of diphenyl-keten to (1). That both the adducts have *transoid* fusion of the three rings is not surprising. The cycloaddition of ketens to alkenes is known to involve an antarafacial

process[6] and formation of a *cisoid* fused system in (2) or (3) would require approach of diphenylketen to the very hindered *endo*-face of the C=C group in (1). Regioselectivity has been reported for the addition of dichloro-keten to cholest-2-ene[7] and 4-t-butylcyclohexene[8] and explained in these cases in terms of the principle of least motion, which does not seem to be applicable in the formation of (6) and (8). It is clear from the ^{1}H n.m.r. spectrum of (6) that the conformation adopted by the five-membered ring is such as to relieve the steric crowding arising from the *endo*-phenyl groups. It may be that in (8) the strain is less easily relieved by flexing of the five-membered ring and that this difference, partly present in the transition states of the reactions, is responsible for the preferential formation of (6). Enhanced strain in (8) may be responsible for the higher frequency of carbonyl absorption in the i.r. spectrum.

EXPERIMENTAL

N.m.r. spectrometers used in this work were: Perkin-Elmer R34 (^{1}H, 220 MHz), JEOL PFT-100 (^{13}C, 25 MHz), and Bruker WH400 (^{1}H, 400 MHz; ^{13}C, 100 MHz). I.r. spectra were measured with a Perkin-Elmer PE180 spectrometer and mass spectra with a Kratos (AEI) MS8 mass spectrometer. M.p.s were measured with a Koffler apparatus. Diphenylketen was prepared by pyrolysis of benzoylphenyldiazomethane.[9]

6,6-Diphenylbicyclo[3.2.0]*hept-3-en-7-one* (1).[4]—Spectral properties for the compounds were as follows: $\nu_{max.}$ (KBr) 1 770 cm^{-1}; δ_H (CDCl$_3$, 220 MHz) 2.44 (1 H, ddd, J 17, 8, 2 Hz, H_b), 2.75 (1 H, d, J 17 Hz, H_a), 3.90 (1 H, t, J 8 Hz, H_c), 4.35 (1 H, m, H_d), 5.51 (1 H, m), 5.75 (1 H, m), 7.0—7.4 (8 H, m), and 7.4—7.6 (2 H, m); δ_C (CDCl$_3$, 25 MHz) 34.5 (t), 49.4 (d), 58.5 (d), 126.4, 126.9, 128.1, 128.7, 131.0 (d), 133.9 (d), 140.6 (s), 140.8 (s), and 212.1 (s).

Reaction of (1) *with Diphenylketen.*—A mixture of diphenylketen (from 10 g of diazoketone) and compound (1) (10 g) was heated in a sealed tube at 130—140 °C for 11 days. The gummy product was stirred with hot methanol (100 ml) until solidification was complete and after cooling to 0 °C the granular solid (13 g) was collected. Repeated recrystallisation of a sample (4 g) from ethyl acetate gave 3,3,8,8-*tetraphenyl-cis-transoid-cis-tricyclo*[5.2.0.0^{2,5}]*nonane-4,9-dione* (6) as needles (0.3 g), m.p. 251 °C (lit.,[4] 249—250 °C) (mass spectrum, M^+ 454.1945. Calc. for C$_{33}$H$_{26}$O$_2$: 454.1933), $\nu_{max.}$ (KBr) 1 766 cm^{-1}, δ_H (CDCl$_3$, 400 MHz) 1.55 (1 H, dt, J 15, 8.5 Hz 6-H$_y$), 2.51 (1 H, ddd, J 15, 8.5, 1 Hz, 6-H$_x$), 3.50 (1 H, dd, J 8.5, 0.5 Hz, 1-H), 3.74 (1 H, q, J 8.5 Hz, 7-H), 3.82 (1 H, dt, J 1, 8 Hz, 5-H), 4.08 (1 H, dd, J 8, 0.5 Hz, 2-H), and 7.0—7.5 (20 H, m); δ_C (CDCl$_3$, 25 MHz) 31.5, 42.5, 43.4, 65.4, 65.9, 77.2, 126.4, 126.5, 126.7, 127.1, 127.3, 128.6, 128.7, 128.9, 140.0, 141.1, 141.9, 208.6, and 210.6.

T.l.c. examination (silica gel–CH$_2$Cl$_2$–CCl$_4$) of the mother liquor showed the presence of another compound which was isolated by h.p.l.c. giving 3,3,9,9-*tetraphenyl-cis-transoid-cis-tricyclo*[5.2.0.0^{2,5}]-*nonane-4,8-dione* (8), m.p. 254—255 °C (mass spectrum, M^+ 454.1917. C$_{33}$H$_{26}$O$_2$ requires 454.1933), $\nu_{max.}$ (KBr) 1 774 cm^{-1}, δ_H (CDCl$_3$, 400 MHz) 2.32 (2 H, dd, J 8, 7 Hz, 6-H), 3.59 (2 H, d, J 8.5 Hz, 1-, 2-H), 3.71 (2 H, m, 5-, 7-H), and 7.0—7.5 (20 H, m); δ_C (CDCl$_3$, 100 MHz), 29.1, 45.7, 65.1, 126.9, 127.17, 127.25, 127.5, 128.7, 128.8, 128.9, 129.1, 141.0, 141.1, and 210.0.

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