SECTION C

Organic Chemistry

Overcrowded Molecules. Part V.[1] Stereochemistry and Stereospecific Photochemical Rearrangement Reaction of 1,2-Bisdiphenylmethylene-3-methylindane

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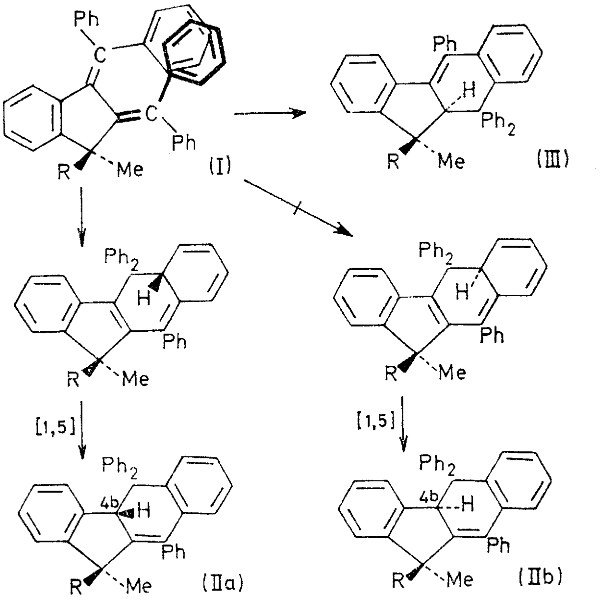
The stereochemistry of 1,2-bisdiphenylmethylene-3-methylindane is discussed, and evidence is presented that this severely overcrowded molecule undergoes photochemical ring closure by only one of the possible conrotatory modes, followed by a [1,5] hydrogen shift, to give 4b,5-dihydro-11-methyl-5,5,10-triphenylbenzo[*b*]fluorene having the methyl group *anti* to the 4b-hydrogen.

THE n.m.r. spectra of 1,2-bisdiphenylmethylene-3,3-dimethylindane (I; R = Me) and one of its photochemical rearrangement products, 4b,5-dihydro-11,11-dimethyl-5,5,10-triphenylbenzo[*b*]fluorene (II; R = Me)[2] suggested a method not only of investigating the stereochemistry of 1,2-bisdiphenylmethylene-3-methylindane (I; R = H), but also of determining whether its photochemical ring closure is concerted, and, if so, of ascertaining the influence of steric effects on the mode of cyclisation.

We have suggested[2] that molecular overcrowding in diene (I; R = Me) is relieved by out-of-plane bending and twisting of the exocyclic double bonds, as well as by in-plane bending of these bonds away from each other, since the strong steric interaction between phenyl groups B and C cannot be relieved to any appreciable extent by their rotation or by puckering of the rigid indane ring. When phenyl group B overlaps phenyl group C, bond distortions cause phenyl group A to shield the methyl group projecting forward from the plane of the system [see (I; R = Me)] and to deshield the other, as demonstrated by n.m.r. studies which show methyl group absorptions at τ 9·0 and 8·3.

1,2-Bisdiphenylmethylene-3-methylindane (I; R = H) was synthesised in the same manner as the dimethyl diene (I; R = Me).[2] Its n.m.r. spectrum shows the methyl group absorption as a doublet centred at τ 8·4, indicating that phenyl group A projects towards the 3-hydrogen and deshields the methyl group, *i.e.* the arrangement is as expected, with minimum interaction between phenyl group A and the 3-methyl substituent. A Dreiding molecular model of this diene shows that phenyl groups B and C overlap and lie in planes almost parallel to that of the indane nucleus, and that in the preferred conformation phenyl groups A and D are at about 45° to the plane of the indane nucleus, if steric interactions between (i) phenyl group A and the 3-hydrogen and an *ortho*-hydrogen of phenyl group B and (ii) phenyl group D and the 7-hydrogen and an *ortho*-hydrogen of phenyl group C, are to be at a minimum. The proposed conformation of phenyl group D is supported by the n.m.r. spectrum of the diene, which shows a one-proton doublet centred at τ 3·6, attributed to the 7-hydrogen. This high-field absorption is characteristic of other 1,2-bisdiphenylmethyleneindanes,[2,3] and similar shielding of the 1- and 8-hydrogens of 9-diphenylmethylenefluorenes has been reported.[4]



Ring closure of 1,2-bisdiphenylmethylene-3-methylindane (I; R = H), followed by a [1,5] hydrogen shift, could give rise to two 4b,5-dihydro-11-methyl-5,5,10-triphenyl-11*H*-benzo[*b*]fluorenes, one having the methyl group *anti* to the 4b-hydrogen (IIa; R = H), and

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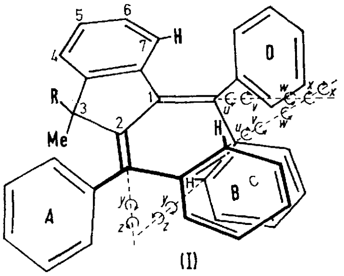
[1] Part IV, H. G. Heller and K. Salisbury, *J. Chem. Soc.* (*C*), 1970, 399.

[2] H. G. Heller, D. Auld, and K. Salisbury, *J. Chem. Soc.* (*C*), 1967, 1084.

[3] H. G. Heller, D. Auld, and K. Salisbury, *J. Chem. Soc.* (*C*), 1967, 2457.

[4] E. D. Bergmann, M. R. Rabinowitz, and I. Agranat, *J. Chem. Soc.* (*B*), 1967, 1281.

the other having a *syn* arrangement (IIb; R = H). A Dreiding model shows that the methyl group is shielded by one of the 5-phenyl groups only when it is *anti* to the 4b-hydrogen. The *anti*-isomer (IIa; R = H), m.p. 209—210°, is the sole product from the photochemical rearrangement of the diene (I; R = H). Its structure follows from the close similarity of its characteristic u.v. spectrum to that of the dimethyl derivative (II; R = Me), and its n.m.r. spectrum, which shows the strongly shielded methyl group as a doublet centred at τ 9·85. The n.m.r. spectrum of the dimethyl derivative (II; R = Me) shows signals for the shielded methyl group *anti* to the 4b-hydrogen (τ 9·6), and the *syn*-methyl group (τ 8·8).[2]



(I)

A Dreiding molecular model of diene (I; R = H) indicates that several modes of ring closure are not feasible because of the severe steric interactions between phenyl groups B and C which would be involved (*e.g.* disrotatory mode *v*, and conrotatory modes *x* and *y*). Other modes of ring closure (*e.g.* disrotatory mode *u* and conrotatory modes *w* and *z*) are comparatively free from steric interactions. Cyclisation by mode *w*, followed by a [1,5] hydrogen shift, gives the *anti*-isomer (IIa; R = H), the sole product of the reaction. This photochemical conrotatory ring closure is in accord with the Woodward–Hoffmann rules for electrocyclic reactions.[5] As the *syn*-isomer (IIb; R = H) could not be detected in the reaction, it is assumed that ring closure by disrotatory mode *u* does not occur.

The photochemical reaction of diene (I; R = Me) yields the dimethyltriphenylbenzofluorenes (II; R = Me) and (III; R = Me) in 70 and 20% yields respectively, after chromatographic separation.[2] The reason why ring closure by conrotatory mode *z* is less easy for diene (I; R = H) than for diene (I; R = Me) is of interest. We tentatively suggest that the energy barrier to rotation of phenyl group A past a 3-methyl substituent should be approximately the same for both dienes, but because of the greater steric interaction between phenyl group A and a 3-methyl substituent in diene (I; R = Me), the ground state energy of this compound is higher, and hence its activation energy for ring closure by mode *z* is lower than that for diene (I; R = H). As dienes (I; R = H) and (I; R = Me) are stable up to 300°, their thermal rearrangement reactions were not investigated.

EXPERIMENTAL

U.v. spectra were measured for solutions in n-hexane with a Unicam SP 500 spectrometer and n.m.r. spectra for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) spectrometer.

1,2-*Bisdiphenylmethylene*-3-*methylindane* (I; R = H).—Diphenylketen (1·6 g.) and 2-diphenylmethylene-3-methylindan-1-one (1·2 g.) were heated under nitrogen at 140° for 14 hr. The resulting yellow glass, in benzene, was chromatographed on alumina (Camag 507-C-1) and developed with light petroleum in the dark to give a yellow band which yielded 1,2-*bisdiphenylmethylene*-3-*methylindane* (1·5 g.), yellow crystals, m.p. 199—201° (from ethanol) (Found: C, 93·4; H, 6·3. $C_{36}H_{28}$ requires C, 93·9; H, 6·1%). Its u.v. spectrum [$\lambda_{max.}$ 278, 335, and 342 nm. (log ε 4·41, 4·00, and 4·00)] resembled that of 1,2-bisdiphenylmethylene-3,3-dimethylindane.[2] The n.m.r. spectrum showed τ 2·5—3·3 (23H, complex m, aromatic), 3·55 (1H, d, *J* 8 Hz, shielded 7-proton), 6·5 (1H, q, *J* 7 Hz, 3-proton), and 8·4 (3H, d, *J* 7 Hz, Me).

The diene (I; R = H) (0·5 g.) in light petroleum (600 ml.) was exposed (20 hr.) to 366 nm. radiation from a 125 w mercury vapour discharge lamp, until the yellow colour of the solution disappeared. The product, after removal of solvent, showed only one spot on t.l.c. and had a u.v. spectrum almost identical with that of the pure *anti*-isomer of 4b,5-dihydro-11-methyl-5,5,10-triphenyl-11*H*-benzo[*b*]fluorene (IIa; R = H) m.p. 209—210°, which was obtained by recrystallisation of the product from benzene and light petroleum (Found: C, 93·75; H, 6·3. $C_{36}H_{28}$ requires C, 93·9; H, 6·1%). Its u.v. spectrum [$\lambda_{max.}$ 272, 290, and 294 nm. (log ε 4·09, 3·79, and 3·81)] closely resembled those of 4b,5-dihydro-5,5,10-triphenyl-11*H*-benzo[*b*]fluorene and its 11,11-dimethyl derivative (IIa; R = Me).[2] The n.m.r. spectrum showed τ 2·4—3·5 (23H, complex m, aromatic), 4·55 (1H, s, 4b-proton), 5·9 (1H, q, *J* 7 Hz, 11-proton), and 9·85 (3H, d, *J* 7 Hz, Me).

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[5] R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, 1968, **1**, 17.