

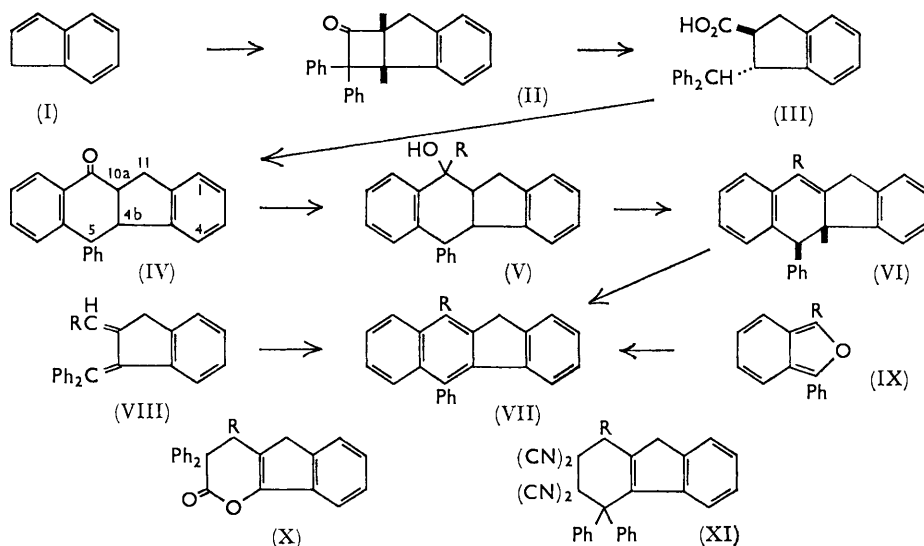
1017. *The Interaction of Indene and Diphenylketen*

By NEIL CAMPBELL and HARRY G. HELLER

Indene and diphenylketen react to form 2,2a,7,7a-tetrahydro-2,2-diphenylcyclobut[*a*]inden-1-one (II), whose structure was established by ring-closure to the stereoisomeric 4b,5,10a,11-tetrahydro-5-phenylbenzo[*b*]fluorene-10-ones (IV). The stereoisomerism of these ketones is discussed.

THEORETICALLY diphenylketen can add to the double bond of indene (I) in two ways, but in our hands only one product was isolated. The structure of this product (II) was rigidly established by converting it into a derivative (IV) of 5-phenyl-10*H*-benzo[*b*]fluorene. The alternative structure would have yielded a 10-phenyl derivative.

Alkaline ring-fission of the cyclobutane product (II) gave 1-benzhydrylindane-2-carboxylic acid (III), which underwent ring-closure with hydrogen fluoride or *via* the acid chloride with aluminium chloride to give two ketones (IV), whose isomerism is discussed



below. Each ketone reacted with *p*-methoxyphenylmagnesium bromide to give a carbinol (V; R = C₆H₄·OMe in this and subsequent formulæ), each of which yielded by dehydration the same dihydrobenzofluorene derivative (VI). Dehydrogenation of this yielded 10-*p*-methoxyphenyl-5-phenylbenzo[*b*]fluorene (VII), identical with a sample prepared

by either of the following methods. 2-*p*-Methoxybenzylideneindan-1-one with diphenylketen yielded the δ -lactone (X) and benzhydrylidene compound (VIII), which when kept in daylight for 6 months underwent cyclic dehydrogenation to give the hydrocarbon (VII), whose structure is thus unequivocally established.¹ In the second method 2-*p*-methoxyphenyl-5-phenyl-3,4-benzofuran (IX) with indene also gave this hydrocarbon (VII) although two products are possible.

Some of the above reactions have stereochemical implications and it is tempting to regard both ketones (IV) as containing *cis*-hydrogen atoms at 4b and 10a, thus making the configuration of the C-5 atom responsible for the isomerism. This explanation must, however, be abandoned since the same hydrocarbon (VI) is obtained by the dehydration of the two carbinols (V). The isomerism of the ketones (and consequently of the carbinols) is therefore due to the relative configuration of the carbon atoms 4b and 10a. Since in many pentane-hexane annellations the *cis*-configuration is more stable and since the ketone A, m. p. 196–198° is epimerised by boiling methanolic potassium hydroxide solution or methanolic hydrochloric acid to the lower melting ketone B it is plausible to assume that the ketone A and B possess the *trans*- (IVa) and the *cis*-configurations (IVb), respectively. This is in harmony with the findings of House and his co-workers² on the isomeric 1,1a,2,3,4,4a-hexahydrofluorenes and with the n.m.r. spectra of the ketones. If the ketone A has the rigid strained structure (IVa) in which the 4b-hydrogen atom is *trans* to those



at positions 5 and 10a, Dreiding models show that the 5-phenyl group will be quasi-equatorial and will shield the 4 proton, thus accounting for the high-field aromatic doublet in the n.m.r. spectrum at τ 3.7. The hydrocarbon (VI) also exhibits this doublet and consequently possesses a similar configuration at 4b and 5. The models also show that the isomeric ketone B with a *cis*-configuration at 4b and 10a has a flexible structure and can be "flipped" into a conformation in which the 5-phenyl group is axial. The phenyl group is thus removed too far from the other benzene nuclei to influence them and this ketone in consequence lacks the doublet at τ 3.7. The acid-catalysed epimerisation of the C-10a atom with its neighbouring group has many analogies, particularly that encountered in 1,1a,2,3,4,4a-hexahydrofluorenone.²

It seems probable that the acid (III) is the *trans*-compound both because this is the configuration adopted by the more stable isomeric acids of this type³ and because on cyclisation it yields mainly the *trans*-ketone A. Since the adduct (II) from its mode of formation must be *cis* it follows that epimerisation must have occurred during ring-fission of the ketone.

EXPERIMENTAL

Ultraviolet spectra were measured in ethanol and n.m.r. spectra in deuteriochloroform.

2,2a,7,7a-Tetrahydro-2,2-diphenylcyclobut[a]inden-1-one.—Diphenylketen (69.5 g.) and freshly distilled indene (45.4 g.) were heated at 120° for 4 hr. The ketone solidified on cooling, and was washed with light petroleum and crystallised from ethanol; it had m. p. 123° (68 g.) (Found: C, 88.5; H, 5.6. C₂₃H₁₆O requires C, 89.0; H, 5.9%); ν_{\max} , 1780s ("4"-ring ketone), 1600m, and 1580m cm.⁻¹ (C:C). The adduct (62 g.) was boiled with 10% methanolic potassium hydroxide (250 ml.) for 3 hr. and poured into water. Acidification with hydrochloric acid yielded 1-benzhydrylindane-2-carboxylic acid (59 g.), m. p. 201–202° after crystallisation from ethanol (Found: C, 83.8; H, 6.0. C₂₃H₂₀O₂ requires C, 84.2; H, 6.0%), *p*-nitrobenzyl ester, m. p. 149–150°

¹ Cf. N. Campbell, P. Davidson, and H. G. Heller, *J.*, 1963, 993.

² H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Amer. Chem. Soc.*, 1960, **82**, 1457.

³ R. N. McDonald and A. C. Kovelesky, *J. Org. Chem.*, 1963, **28**, 1433.

(Found: N, 3.9. $C_{30}H_{25}N$ requires N, 3.9%); *methyl ester*, prisms (from methanol), m. p. 117—118° (Found: C, 84.0; H, 6.6. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.5%).

4b,5,10a,11-Tetrahydro-5-phenylbenzo[b]fluoren-10-ones.—The above acid (17.5 g.) was left in hydrogen fluoride (600 ml.) for 2 days. Evaporation of the hydrogen fluoride gave a residue which was dissolved in benzene and shaken with sodium carbonate solution. The dried (Na_2SO_4) benzene solution on evaporation yielded the *ketone A* (11.4 g.), m. p. 196—198° after several crystallisations first from ethanol or light petroleum and later from benzene (Found: C, 88.7; H, 5.5. $C_{23}H_{18}O$ requires C, 88.9; H, 5.8%); ν_{max} . 1700s ("6"-ring CO) and 1600m cm^{-1} (C:C). From the filtrates a second *ketone B* was obtained, m. p. 118° after crystallisation from light petroleum (Found: C, 88.7; H, 5.8%); ν_{max} . 1675s and 1595 cm^{-1} . The ketone can be obtained as a dimorph, m. p. 128°, both forms having identical infrared spectra in carbon disulphide. Ketone A with lithium aluminium hydride in ether gave 4b,5,10a,11-tetrahydro-5-phenyl[b]benzofluoren-10-ol, as needles (from aqueous ethanol), m. p. 237—238° (Found: C, 88.2; H, 6.5. $C_{23}H_{20}O$ requires C, 88.4; H, 6.5%). Ketone B similarly yielded an isomeric alcohol, m. p. 190°.

1-Benzylhydriindane-1-carboxylic acid (1 g.) was converted by thionyl chloride into the acid chloride which was heated (2 hr.) with aluminium chloride (1 g.) and benzene, trichloroethylene, or methylene chloride (20 ml.). Working up the mixture gave ketone A (50 mg.), m. p. 196—198°, after crystallisation from ethanol.

The acid chloride from 8 g. of acid was heated with aluminium chloride (2 g.) in nitrobenzene (20 ml.) at 100° and poured into water. Steam-distillation left a brown gum which was chromatographed in benzene on alumina. Elution of a pale yellow fraction gave ketone B (0.5 g.), m. p. 118°, after crystallisation from benzene.

4b,5,10a,11-Tetrahydro-10-p-methoxyphenyl-5-phenyl[b]benzofluoren-10-ols.—The ketone A (3.1 g.) in benzene (10 ml.) was added to *p*-methoxyphenylmagnesium bromide, prepared from *p*-bromoanisole (5.6 g.) and magnesium (0.72 g.) in ether (100 ml.) and the mixture boiled for 15 min. The *alcohol*, isolated in the usual way, crystallised from ethanol in prisms, m. p. 214° (Found: C, 85.9; H, 6.3. $C_{30}H_{26}O_2$ requires C, 86.1; H, 6.3%); ν_{max} . 3550m (OH), 1610m (C:C), and 1240s cm^{-1} (OMe). The ketone B similarly gave an isomeric *alcohol*, m. p. 210°, depressed to 190° when admixed with the above alcohol (Found: C, 86.9; H, 6.6%); ν_{max} . 3600m, 1605m, and 1250s cm^{-1} .

The alcohols were dehydrated by boiling formic acid or ethanol containing a few drops of hydrochloric acid and yielded in each instance 4b,5-dihydro-10-p-methoxyphenyl-5-phenyl[b]benzofluorene, crystals (from ethanol), m. p. 167—168° (Found: C, 89.3; H, 6.1. $C_{30}H_{24}O$ requires C, 89.0; H, 6.0%). The dihydro-compound (0.4 g.) was boiled with chloranil (0.25 g.) in xylene (3 ml.) for 5 hr. and chromatographed on alumina. Development with benzene gave a blue fluorescent fraction containing 10-p-methoxyphenyl-5-phenylbenzo[b]fluorene, needles (from light petroleum and then ethanol), m. p. 199°, not depressed when admixed with the substance prepared below (Found: C, 90.1; H, 5.7. $C_{30}H_{22}O$ requires C, 90.3; H, 5.5%); λ_{max} . 270 μ ($\log \epsilon$ 4.84), 314 μ ($\log \epsilon$ 4.29), and 323 μ ($\log \epsilon$ 4.33), similar to that of 5,10-diphenylbenzo[b]fluorene.¹

1-Benzhydrylidene-2-p-methoxybenzylideneindane.—2-*p*-Methoxybenzylideneindan-1-one⁴ (7 g.) and diphenylketen (5.4 g.) were heated together under nitrogen for 3½ hr. at 140—150° and the product boiled with light petroleum (200 ml.) and filtered. The residue gave 1-benzhydrylidene-2-p-methoxybenzylideneindane, pale yellow crystals (from benzene and light petroleum), m. p. 186° (Found: C, 89.0; H, 6.3. $C_{30}H_{24}O$ requires C, 89.0; H, 6.0%). The filtrate deposited the δ -lactone (X), m. p. 219°, after crystallisation from benzene and light petroleum (Found: C, 83.6; H, 5.8. $C_{31}H_{24}O_3$ requires C, 83.6; H, 5.5%); ν_{max} . 1750s (δ -lactone CO), 1600m (C:C), 1260s cm^{-1} (OMe). The hydrocarbon in benzene and light petroleum was kept in daylight for 6 months. The solution was evaporated and the residual gum in a small volume of benzene was chromatographed on alumina. Development with light petroleum gave a blue fluorescent fraction, yielding 10-*p*-methoxyphenyl-5-phenylbenzo[b]fluorene, m. p. 199°. A bright yellow fraction gave a gum which yielded bright yellow needles, m. p. 206°, after crystallisation from ethanol, probably of 10-*p*-methoxyphenyl-5-phenylbenzo[b]fluoren-11-one (Found: C, 86.4; H, 4.3. $C_{30}H_{20}O_2$ requires C, 87.4; H, 4.9%); ν_{max} . 1710s (CO), 1610m (C:C), and 1230s cm^{-1} (OMe); λ_{max} . 288 μ ($\log \epsilon$ 4.83).

Benzhydrylidene-2-*p*-methoxybenzylideneindane (0.2 g.) and tetracyanoethylene (0.07 g.)

⁴ P. Pfeiffer and E. Milz, *Ber.*, 1938, **71**, 272.

in benzene (10 ml.) were boiled (1 hr.), half the solvent was evaporated, and light petroleum (5 ml.) was added. *2,2,3,3-Tetracyano-1,2,3,4-tetrahydro-1-p-methoxyphenylfluorene* (XI) separated and crystallised from benzene and light petroleum in needles of no definite m. p. (Found: C, 81.3; H, 4.6; N, 11.6. $C_{36}H_{24}N_4O$ requires C, 81.8; H, 4.6; N, 11.6%). Reduction of compound (VIII) by aluminium amalgam in moist ether⁵ for 2 days yielded *3-benzhydryl-2-p-methoxybenzylindene* as needles (from ethanol), m. p. 82° (Found: C, 89.0; H, 6.5. $C_{30}H_{26}O$ requires C, 89.5; H, 6.5%).

2-p-Methoxyphenyl-3-phenyl-3,4-benzofuran.—*p*-Methoxyphenylmagnesium bromide, prepared from *p*-bromoanisole (10.3 g.) and magnesium (12 g.) in ether (200 ml.) was added dropwise with stirring to phenylphthalide (9.75 g.) in benzene (150 ml.). The mixture was boiled (10 min.) and poured on to ice and hydrochloric acid. Evaporation of the organic layer gave an oil which was boiled in ethanol (100 ml.) and hydrochloric acid (1 ml.) for 5 min. The cooled solution deposited the bright yellow *2-p-methoxyphenyl-5-phenyl-3,4-benzofuran*, m. p. 95° (Found: C, 84.2; H, 5.6. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.4%). Hydrogen chloride was passed through a suspension of the benzofuran (3 g.) and indene (1.25 g.) in ethanol for 1 hr. A solid (2.2 g.) separated and was chromatographed in benzene on alumina. Development with light petroleum gave a blue fluorescent fraction which on evaporation yielded *10-p-methoxyphenyl-5-phenylbenzo[*b*]fluorene* as needles (from light petroleum and then from ethanol), m. p. and mixed m. p. 199°.

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THE UNIVERSITY, EDINBURGH.

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⁵ J. Thiele and K. Merck, *Annalen*, 1918, **415**, 266.