J. Chem. Soc. (C), 1967

Overcrowded Molecules. Part II.¹ The Interaction of Diphenylketen with 2-Benzylidene-1,3-indanedione

By H. G. Heller, D. Auld, and K. Salisbury, Edward Davies Chemical Laboratory, University College of Wales, Aberystwyth

Diphenylketen and 2-benzylidene-1,3-indanedione react at 160° to yield 5,10-diphenylbenzo[b]fluoren-11-one, 5,10-diphylco-5,10-diphenyl-11-diphenylmethylene-11H-benzo[b]fluorene, and 3,4-dihydro-3,3,4-triphenyl-5-diphenylmethyleneindeno[1,2-b]pyran-2-one. The first two products are believed to be formed by the dehydro-cyclisation and cyclisation of 2-benzylidene-3-diphenylmethylene-1-indanone and 1,3-bisdiphenylmethylene-2-benzylideneindane, respectively.

PREVIOUS work has shown that 2-benzylidene-1-diphenylmethyleneindane undergoes dehydrocyclisation to yield 5,10-diphenyl-11*H*-benzo[*b*]fluorene,² while 1,2bisdiphenylmethyleneindane rearranges to dihydrotriphenyl-11*H*-benzo[*b*]fluorenes.¹ The reaction of 2-benzylidene-1,3-indanedione (I) with diphenylketen was carried out in an attempt to synthesise 1,3-bisdiphenylmethylene-2-benzylideneindane (IV), so that its rearrangement reactions could be compared to those described above.

We find that on heating the keten with the dione (I) at 160° , 5,10-diphenylbenzo[b]fluoren-11-one (V), 5,10-dihydro-5,10-diphenyl-11-diphenylmethylene-11H-

benzo[b]fluorene (VII), and the δ -lactone, 3,4-dihydro-3,3,4-triphenyl-5-diphenylmethyleneindeno[1,2-b]pyran-2-one (VI), are produced. The ketone (V) was identical with a sample prepared by another method.³ The structure of the hydrocarbon (VII), which has a characteristic diphenylbenzofulvene spectrum,² follows from its dehydrogenation by N-bromosuccinimide to 5,10-diphenyl-11-diphenylmethylene-11H-benzo[b]-

fluorene (IX), which was identical to a sample prepared by dehydrating the alcohol (VIII), prepared by the reaction of diphenylbenzofluorenone (V) with diphenylmethyl-lithium. Dreiding models show that hydrocarbon (VII) will have the 10 proton shielded by a phenyl of the diphenylmethylene group, thus accounting for the high-field doublet at τ 6.22, J = 7 c./sec. in its n.m.r. spectrum The 5 proton exhibits a doublet at 5.13, J =7 c./sec. Large homo-allylic coupling has been observed in 1-phenyl-1,4-dihydrobenzene $(J_{1-4} = 9 \text{ c./sec.}),4$ and in 1-phenyl-1,4-dihydronaphthalene $(J_{1-4} = 6 \text{ c./sec.}).^5$ Confirmation of the structure of the δ -lactone (VI) was supplied by ozonolysis to give benzophenone, and by hydrogenation to give the dihydro-derivative (X), and by the characteristic u.v. and i.r. spectra of the δ -lactones (VI) and (X).

It is suggested that these products are formed as follows. Diphenylketen reacts with the dione (I) to give 2-benzylidene-3-diphenylmethylene-1-indanone (III) through the β -lactone intermediate (II). The ketone (III) then undergoes dehydrocyclisation to give the

¹ Part I, H. G. Heller, D. Auld, and K. Salisbury, J. Chem. Soc. (C), 1967, 682.

² N. Campbell, P. S. Davison, and H. G. Heller, J. Chem. Soc., 1963, 993.

³ R. Weiss and A. Beller, Monatsh., 1932, 61, 143.

⁴ L. J. Durham, J. Studebaker, and M. J. Perkins, Chem. Comm., 1965, 456.

⁵ W. Carruthers and G. E. Hall, J. Chem. Soc. (B), 1966, 863.



The rearrangement of the triene (IV) is pictured as occurring through the diradical intermediate [(XIIa) and (XIIb)] to give a dihydro-intermediate (XIII) which undergoes a 1,3-hydrogen shift to yield the fulvene (VII).⁶



A possible reason why the intermediate (XIII) undergoes rearrangement instead of dehydrocyclisation may

⁶ P. G. Jones, Chem. Comm., 1966, 894.

⁷ L. Geita and G. Vanags, *Zhur. obshchei Khim.*, 1957, **27**, 3109. 5 K be the high energy state of hydrocarbon (IX) caused by the steric interactions of the 10 phenyl substituent with a phenyl of the diphenylmethylene group.

EXPERIMENTAL

Ultraviolet spectra were measured for n-hexane solutions on a Unicam SP 500 spectrometer and the n.m.r. spectra on a Varian HA 100 spectrometer.

Interaction of Diphenylketen and 2-Benzylidene-1,3-indandione (I).—Diphenylketen ($6\cdot0$ g., $0\cdot031$ mol) and 2-benzylidene-1,3-indanedione ⁷ ($3\cdot5$ g., $0\cdot015$ mol.) were heated (10 hr.) under nitrogen at 160°. The product in benzene was chromatographed on neutral alumina (Camag 507-C-1) and developed with light petroleum. The yellow first fraction, having a bright green fluorescence, yielded 5,10-dihydro-5,10-diphenyl-11-diphenylmethylene-11H-benzo[b]-

fluorene (VII) (1.4 g.), m. p. 271-272° (from benzenelight petroleum) (Found: C, 94.1; H, 5.8. C42H30 requires C, 94·3; H, 5·7%), λ_{max} 260, 302, and 364 mµ (log ε 4·50, 4·54, and 4·51), λ_{min} 276 and 327 mµ (log ε 4·35 and 4·29); n.m.r. (CDCl₃) τ (28) 2·4—3·7, multiplet, aromatic protons; τ (1) 5.12 doublet, J = 7 c./sec., 5 proton; τ (1) 6.22 doublet, J = 7 c./sec., 10 proton. Evaporation of the yellow second fraction gave the δ-lactone, 3,4-dihydro-3,3,4triphenyl-5-diphenylmethyleneindeno[1,2-b]pyran-2-one (VI) (2 g.), m. p. 245-246° (from benzene-light petroleum) (Found: C, 89.0; H, 5.4. C42H30O2 requires C, 89.0; H, 5.3%); ν_{max} 1780s (C:O) and 1630w cm.⁻¹ (C:C); λ_{max} 347 mm (log ϵ 4·18), $\lambda_{\rm min.}$ 318 mm (log ϵ 4·03) $\lambda_{\rm infl.}$ 288 mm (log ε 4.24). Ozone was passed into the δ -lactone (0.6 g.) in carbon tetrachloride (70 ml.) until the ozonide separated. Steam distillation gave first solvent and then benzophenone, identified by m. p., mixed m. p., and dinitrophenylhydrazone. Hydrogenation at 1 atmos. of the δ-lactone in ethanol with a palladium on charcoal catalyst gave 3, 4-dihydro-3, 3, 4-triphenyl-5-diphenylmethylindeno-[1,2-b]pyran-2-one (X), m. p. 262-264° (from benzene-light petroleum) (Found: C, 88·1; H, 5·6. C42H32O2 requires C, 88.7; H, 5.7%), ν_{max} 1786s cm.⁻¹ (C.O). The third yellow fraction yielded 5,10-diphenylbenzo[b]fluoren-11-one (V) (0.5 g.), m. p. 206-207° (from ethanol) (lit.,³ m. p. 208°), undepressed when admixed with an authentic sample (Found: C, 90.9; H, 4.6. Calc. for C₂₉H₁₈O: C, 91.1; H, 4.7%), v_{max} 1715s cm.⁻¹ (C:O); λ_{max} 290 mµ (log ε 4.78). Unlike fluorenone,⁸ diphenylbenzofluorenone (V) does not react with diphenylketen at 160°.

5,10-Diphenyl-11-diphenylmethylene-11H-benzo[b]fluorene (IX).—The dihydro-compound (VII) (0·2 g.) reacted with N-bromosuccinimide (0·1 g.) in carbon tetrachloride (10 ml.) with evolution of hydrogen bromide. Succinimide was filtered off, the filtrate evaporated, and the residual oil chromatographed on alumina. Development with light petroleum gave an orange band, which on evaporation gave the fluorene (IX) (0·1 g.), yellow needles, m. p. 296—297° (from benzene-light petroleum) undepressed with a sample prepared as follows. 5,10-Diphenylbenzo[b]fluoren-11-one (V) (0·4 g.), prepared by chromic acid oxidation of diphenylbenzofluorene,³ was dissolved in tetrahydrofuran and treated with a solution of diphenylmethyl-lithium ⁹ in tetrahydrofuran until the red colour of the reagent persisted. The reaction mixture was stirred for 10 min.,

⁸ N. Kon and H. Staudinger, Annalen, 1911, 384, 133.

⁹ C. Tamorski, G. J. Moore, and E. J. Soloski, *Chem. and Ind.*, 1962, 696.

1554

J. Chem. Soc. (C), 1967

poured on ice and ammonium chloride, and worked up. Trituration with ether gave tetraphenylethane (0.3 g.), m. p. 211°, identified by mixed m. p. with an authentic sample. Evaporation of the ether solution left 5,10-diphenyl-11-diphenylmethyl-11H-benzo[b]fluoren-11-ol (VIII), pale yellow cubes, m. p. 207—208°, after crystallisation from petroleum b. p. 100—120° (Found: C, 91·5; H, 5·7. C₄₂H₃₀O requires C, 91·6; H, 5·5%), v_{max} 3530s cm.⁻¹, sharp, (OH). The fluorenol (VIII) (0·03 g.) in ethanol (25 ml.) was saturated with hydrogen chloride and boiled (3 hr.). The fluorene (IX) separated on cooling and was recrystallised as before (Found: C, 94.25; H, 5.6. $C_{42}H_{28}$ requires C, 94.7; H, 5.3%); λ_{max} 270 mµ (log ϵ 4.6); λ_{min} 239 mµ (log ϵ 4.35). The n.m.r. (CCl₄) spectrum showed τ 2.3—3.6, multiplet, aromatic protons only. The *fluorene* (IX) in ethanol could not be hydrogenated at 1 atmos. with platinum, or a palladium on charcoal catalyst.

We thank Miss A. Heinrich, Varian Associates Ltd., for measuring the n.m.r. spectra.

[7/227 Received, February 24th, 1967]