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J. Chem. Soc. (C), 1967

Some Reactions of Biphenyl-2,2'-dialdehyde

CH2 · CH · CO2R

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The reactions of biphenyl-2,2'-dialdehyde with zinc and ethyl bromoacetate, with malonic acid and with the phosphorane derived from 2-bromomethylnaphthalene, are described.

THE Paper by Hall and Prakobsantisukh,¹ who reported recently on reactions in the biphenyl-2,2'-dialdehyde (I) series, prompts us to describe briefly some analogous experiments.

The reaction product of (I) and ethyl bromoacetate and zinc did not give the expected doubly unsaturated diethyl ester (II; $R = C_2 H_5$) upon acid decomposition, but a compound which contained one molecule of water more, was saturated towards hydrogen, and showed only the absorption of biphenyl (251 m μ); it was very probably the 6,8-diethoxycarbonyl-5,6,8,9-tetrahydrodibenz[d, f]oxonin (III). The acid (II; R = H) can be obtained from (I) by the Knoevenagel reaction, and has been prepared previously by Mayer ² by way of the Perkin synthesis; it has also been reported by Hall.¹ Compound (II; R = Me) absorbed, as expected, at 278 mµ.

Hall¹ has described the reaction of the diphosphorane (IV) with benzaldehyde which gave 2,2'-distyrylbiphenyl. Analogously, β -naphthaldehyde gave 2,2'-bis- $[2-(\beta-naphthyl)vinyl]$ biphenyl (V). The same compound was obtained, although in lower yield, from (I) and 2 mole of the phosphorane (VI), derived from 2-bromomethylnaphthalene.

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EXPERIMENTAL

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6, 8-Diethoxy carbonyl-5, 6, 8, 9-tetrahydrodibenz [d,f] oxonin.-A mixture of biphenyl-2,2'-dialdehyde (I) (25.0 g.),

¹ D. M. Hall and B. Prakobsantisukh, J. Chem. Soc., 1965, 6311.

² F. Mayer, Ber., 1911, 44, 2298.

ethyl bromoacetate (39.5 g.), mossy zinc (15.5 g.), and iodine in benzene (100 ml.) was heated, until an exothermic reaction set in; after this had subsided, heating was continued for a further 3 hr. after which the mixture was decomposed with cold 25% sulphuric acid. The product boiled (after initial spontaneous dehydration) at 230-235° (1 mm.) (30 g., 73%) (Found: C, 72.0; H, 6.5. $C_{22}H_{24}O_5$ requires C, 71.7; H, 6.5%), λ_{max} (EtOH) 251 mµ (4.06); ν_{max} (liq.) 1725 (ester), 1160 (C–O–C), and 1450 cm.⁻¹ (o-disubstituted benzene).

Biphenyl-2,2'-diacrylic acid (II; R = H).—A mixture of (I) (21 g.), malonic acid (20.8 g.), pyridine (250 ml.), and piperidine (2 ml.) was heated at 100° for 3 hr. and then boiled for 5 min. after which time the theoretical quantity of carbon dioxide had been liberated. The liquid was concentrated to one third of its volume and poured into an excess of 10% hydrochloric acid, and the solid material so obtained extracted with hot 10% sodium hydroxide solution (1 l.). The filtered solution was treated with charcoal, acidified, and the precipitate recrystallised from glacial acetic acid, to give the acid (23 g., 78%) as colourless crystals of m. p. 285-287° (decomp.) (lit.,^{1,2} m. p. 295° and 294-296°, respectively) (Found: C, 73.5; H, 4.5. Calc. for $C_{18}H_{14}O_4$: C, 73.4; H, 4.8%). λ_{max} (EtOH) 278 mm (4.20); v_{max} (KBr) 1690 (conjugated carboxyl) and 1634 cm.⁻¹ (C=C).

The dimethyl ester, m. p. 124-125° (MeOH) (lit.,¹ m. p. 123–124°), λ_{max} EtOH 278 mµ (4·28); ν_{max} KBr 1724 cm.-1.

2,2'-Bis(triphenylphosphoniomethyl)biphenyl Dibromide.-The title compound was best obtained not in xylene,¹ but in dimethylformamide. A mixture of 2,2'-bis-bromomethylbiphenyl³ (5.0 g.), triphenylphosphine (8.3 g.), and dimethylformamide (40 ml.) was heated under reflux for 3 hr. in a nitrogen atmosphere and the solid product (9.7 g.), after cooling, was filtered off and washed with ether. An additional crop (3.4 g.) precipitated from the motherliquor on standing, bringing the total yield to 98%. The dibromide can be recrystallised from acetonitrile; m. p. above 300° (Found: C, 69.2; H, 5.0; Br, 18.8. Calc. for $C_{50}H_{42}Br_2P_2$: C, 70.0; H, 4.9; Br, 18.5%).

2,2'-Bis $[2-(\beta-naphthyl)vinyl]$ biphenyl (V). (a) An 0.4Nsolution of lithium ethoxide in ethanol (50 ml.) was added, with stirring, to a mixture of the previously described dibromide (5.0 g.), β -naphthaldehyde (1.8 g.), and absolute ⁴ ethanol (75 ml.). After 12 hr., the product (V) (9 g., 73%) was filtered and recrystallised from cyclohexane; it melted at 144-146° (Found: C, 94.6; H, 5.8. C36H26 requires C, 94.3; H, 5.7%. λ_{max} (dioxan) 225 (4.63), 255 (4.40), 276 (4.45), and 325 m μ (4.48); ν_{max} (KBr) 1620 (C=C) and 970 cm.⁻¹ (trans-1,1-disubstituted ethylene).

<sup>L. A. Carpino, J. Amer. Chem. Soc., 1963, 85, 2144.
A. I. Vogel, "Practical Organic Chemistry," Longmans,</sup> London, 1961, p. 167.

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(b) The same product was obtained when a stirred solution of (I) (1.5 g.) and 2-naphthylmethyl triphenylphosphonium bromide ⁵ (VI) (6.8 g.) in absolute ethanol (25 ml.) and under a nitrogen atmosphere was treated, with an 0.4N-solution of lithium ethoxide in alcohol (40 ml.). The product (1.5 g., 48%) crystallised spontaneously;

it was identical (undepressed m. p.) with that obtained in the previous experiment.

[6/483 Received, April 21st, 1966]

⁵ J. D. Geerts and R. H. Martin, Bull. Soc. chim. belges, 1960, 69, 563.