476. *The Uncatalyzed Reaction of Olefins with Acyl Chlorides. Part I. Reaction of* 1 : 1-*Diphenylethylene.**

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Since 1 : 1-diarylethylenes undergo substitution at the β-carbon atom by strongly polar reagents such as phosphorus pentachloride, oxalyl chloride, and thionyl chloride, we examined the condensation of 1 : 1-diphenylethylenes with acyl chlorides. This reaction can be carried out only in the absence of a Friedel–Crafts catalyst. Condensation took place with the chlorides of benzoic, cinnamic, fumaric, and phenylacetic acid, but not with saturated aliphatic acyl chlorides, because the latter are not thermally stable. The structures of the various reaction products are discussed.

Certain strongly polar reagents cause substitution at the β-carbon atom of 1 : 1-diarylethylenes; *e.g.*, phosphorus pentachloride (E. Bergmann and Bondi, *Ber.*, 1930, **63**, 1158; 1931, **64**, 1455), oxalyl chloride (Kharasch, Kane, and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 333; F. Bergmann *et al.*, *ibid.*, 1948, **70**, 1612), and thionyl chloride (Patai and F. Bergmann, *ibid.*, 1950, **72**, 1034) eliminate hydrogen chloride, giving $CR_2{:}CH{\cdot}PCl_4$, $CR_2{:}CH{\cdot}COCl$, and $CR_2{:}CH{\cdot}SOCl$, respectively. It has now been found that certain acyl chlorides react similarly at high temperatures in the absence of a catalyst.† Aluminium chloride could not be used because it attacks the double bond, producing dimerization and subsequent cyclization (E. Bergmann and Weiss, *Annalen*, 1930, **480**, 49; Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021), and it also promotes nuclear acylation (cf. the analogous reaction with styrene; Ralston and van der Wal, U.S.P., 2,197,709/1940). It is however, known that the acylation of aromatic hydrocarbons can be carried out at high temperatures in the absence of a catalyst (*e.g.*, benzoylation of naphthalene and anthracene; Nenitzescu, Isacescu, and Ionescu, *Annalen*, 1931, **491**, 210).

(1) When 1 : 1-diphenylethylene and benzoyl chloride in a molar ratio of 1 : 1·1 are heated to 190—200°, a slow reaction takes place, which can be followed semiquantitatively by titration of the hydrogen chloride removed in a current of nitrogen. After 30 hours, 65% of the theoretical amount of hydrogen chloride was obtained, and the expected

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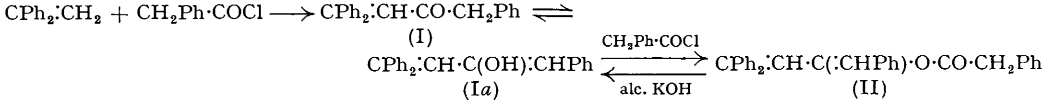
† Patent pending.

product, 1-benzoyl-2 : 2-diphenylethylene, was isolated in about 50% yield (cf. Vorländer, Osterberg, and Meyer, *Ber.*, 1923, **56**, 1139). Analogous reactions were observed with cinnamoyl chloride and fumaroyl chloride, the latter reacting only with one mol. of diphenylethylene.

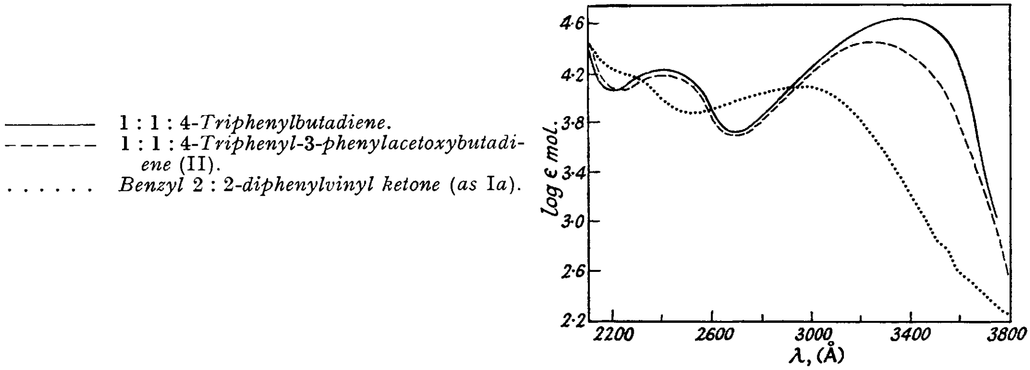
(2) Similarly 1 : 1-diphenylethylene and phenylacetyl chloride afforded two products: (*a*) white prisms, m. p. 141—142°, and (*b*) white rods, m. p. 136°. The first, resulting from condensation of the hydrocarbon with 2 moles of the acyl chloride, was converted by alcoholic potash into a ketone (I), and, as its absorption spectrum closely resembled that of 1 : 1 : 4-triphenylbutadiene (see Fig.), we regard it as the ester (II) of the enolic form (I*a*) of the ketone (I), formed as follows:



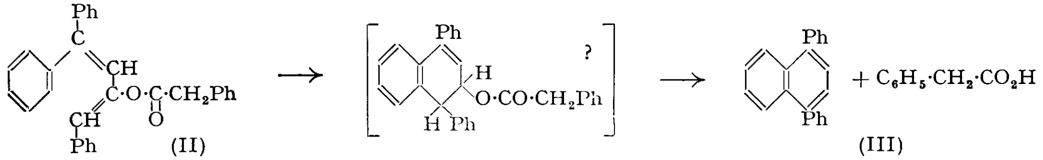
$$\mathrm{CPh_2{:}CH_2 + CH_2Ph{\cdot}COCl \longrightarrow \underset{(I)}{CPh_2{:}CH{\cdot}CO{\cdot}CH_2Ph} \rightleftharpoons}$$

$$\underset{(Ia)}{\mathrm{CPh_2{:}CH{\cdot}C(OH){:}CHPh}} \underset{\text{alc. KOH}}{\overset{\mathrm{CH_2Ph{\cdot}COCl}}{\rightleftarrows}} \underset{(II)}{\mathrm{CPh_2{:}CH{\cdot}C({:}CHPh){\cdot}O{\cdot}CO{\cdot}CH_2Ph}}$$

The absorption spectrum of the ketone (I) is different from that of (II), but the shoulder at 2230 Å occurs at the same place as the first minimum in the spectrum of the enol ester (see Fig.), so the ketone is assumed to be in equilibrium with its enolic form in solution. This assumption was confirmed by measurement of the infra-red absorption spectrum of (I) in carbon tetrachloride: besides the band at 1694 cm.$^{-1}$, due to the αβ-unsaturated keto-group, a weak band occurs at 3390 cm.$^{-1}$, indicating the presence of a free hydroxyl group. From the relative intensities of the two bands it was estimated that about 10% of the enol form is present in the equilibrium mixture at room temperature. The enol ester (II) showed absorption at 1764 cm.$^{-1}$, indicating the presence of an αβ-vinyl ester (cf. Grove and Willis, *J.*, 1951, 877, who give the frequency for such vinyl esters as 1770 cm.$^{-1}$).



The product (*b*) was 1 : 4-diphenylnaphthalene (III), presumably formed from (II) as follows:



(II) (III)

Alternatively, the enol (I*a*) could undergo cyclization directly under the conditions of the experiment, but this cyclization did not occur when (I) or (II) was heated either alone or in a stream of hydrogen chloride to 200°.

If the hydrogen chloride is removed in a rapid current of inert gas, formation of (II) in preference to (III) is favoured, and increase of the proportion of phenylacetyl chloride has the same effect. On the other hand, (III) is favoured by accumulation of hydrogen chloride or by increase of temperature.

On hydrogenation of (II), 3 mols. of hydrogen were absorbed and one mol. of phenylacetic acid was set free. The product was identified as 1 : 1 : 4-triphenylbutane by a method to be described later.

Experiments with the next higher homologue of phenylacetic acid, *viz.*, β-phenylpropionic acid, at 185° gave as the only product indan-1-one in small yield. Saturated aliphatic acyl chlorides (acetyl chloride or acetic anhydride; lauroyl and stearoyl chloride) did not react with 1 : 1-diphenylethylene at temperatures below their thermal decomposition points. This work is being continued.

EXPERIMENTAL

M. p.s are uncorrected.

Reaction of 1 : 1-*Diphenylethylene.*—(1) *With benzoyl chloride.* A three-necked flask was equipped with gas inlet and outlet tubes, thermometer, and reflux condenser, the latter protected by a calcium chloride tube.

A mixture of 1 : 1-diphenylethylene (18 g.; 0·1 mole) and benzoyl chloride (16 g.; 0·11 mole) was heated to 190—200°, while dry nitrogen was bubbled through. The gas was passed through a solution of 0·1N-sodium hydroxide, which was changed every hour for titration. During 30 hours a total of 2·4 g. of hydrogen chloride was absorbed (65% of the theoretical amount). The mixture was now dissolved in ether and washed with 3% potassium hydroxide solution (2 × 50 ml.). The organic layer was dried, and the solvent distilled off. The residue from the ether crystallized on trituration with ethanol. From *n*-propanol the 1-benzoyl-2 : 2-diphenylethylene was obtained in lemon-yellow crystals (13 g., 46%), m. p. 88—89° (cf. Vorländer, Osterberg, and Meyer, *loc. cit.*) (Found: C, 88·6; H, 5·4. Calc. for $C_{21}H_{16}O$: C, 88·7; H, 5·6%). Its oxime crystallized from ethanol in yellow prisms, m. p. 142° (Dilthey and Last, *J. pr. Chem.*, 1916, **94**, 50). From the mother-liquor of the ketone a small amount of the open-chain dimer of 1 : 1-diphenylethylene (Bergmann and Weiss, *loc. cit.*) was isolated (m. p. 118°).

(2) *With cinnamoyl chloride.* The ethylene (6 g., 1/30 mole) and cinnamoyl chloride (b. p. 146—148°/21 mm.; m. p. 35—36°; 10 g., 1/15 mole) in dry xylene (10 ml.) were heated at 165—170° during 16 hours in a continuous stream of nitrogen. 1·2 g. of hydrogen chloride (100% of theoretical) were collected. The mixture was cooled, and dry ethanol (5 ml.) added to destroy the excess of cinnamoyl chloride. Solvents and starting materials were removed by vacuum-distillation, and the solid residue was recrystallized twice from ethanol. Yellow-brown prisms, m. p. 88°, were obtained (2 g., 20%). Analysis corresponds to 1 : 1 : 5-*triphenylpentadien*-3-*one* (Found: C, 88·7; H, 5·4. $C_{23}H_{18}O$ requires C, 89·0; H, 5·8%). With 2 : 4-dinitrophenylhydrazine this afforded a deep red colour but no crystals.

(3) *With fumaroyl chloride.* 1 : 1-Diphenylethylene (6 g., 1/30 mole) and fumaroyl chloride (5 g., 1/30 mole) in dry xylene (10 ml.) were refluxed at 147—149°. During 22 hours 1·2 g. of hydrogen chloride (100% of theoretical) were absorbed in the sodium hydroxide solution, and the colour of the mixture changed from orange to deep red. The starting materials were removed *in vacuo*, and the residue was dissolved in ether and extracted with dilute sodium carbonate solution. From the aqueous layer 4-*keto*-6 : 6-*diphenylhexa*-2 : 5-*dienoic acid* was precipitated by acidification with cold dilute sulphuric acid; it crystallized from dilute acetic acid in yellow needles (2 g., 22%), m. p. 128° (Found: C, 77·3; H, 5·3. $C_{18}H_{14}O_3$ requires C, 77·6; H, 5·0%). No crystalline neutral product could be isolated from the ethereal layer. The same acid was the only product when the mixture contained the ethylene and the acyl chloride in a molar ratio of 2·2 : 1, no diketone being obtained. The acid did not respond to carbonyl reagents.

(4) *With phenylacetyl chloride.* (*a*) Under the same conditions as above a mixture of the ethylene (27 g., 0·15 mole) and phenylacetyl chloride (30 g., 0·2 mole) was heated at 195—200°. During 4 hours 5·4 g. of hydrogen chloride (100% of theoretical) were collected. The excess of starting materials was removed *in vacuo*, and the residue extracted with ice-cold ether.

(i) The ether-insoluble residue crystallized from ethanol in colourless prisms, m. p. 141—142°. 1 : 4 : 4-*Triphenylbutadien*-2-*yl phenylacetate* (II) (Found: C, 86·3; H, 5·8%; sap. equiv., 410. $C_{30}H_{24}O_2$ requires C, 86·5; H, 5·8%; sap. equiv., 416) was thus obtained in a yield of 11 g. (18% on diphenylethylene, 27% on phenacetyl chloride). In contact with concentrated sulphuric acid the crystals become green-yellow and dissolve slowly with a green-blue colour.

(ii) The ethereal solution was washed with alkali, the solvent evaporated, and the residue fractionated. The fraction of b. p. 275°/3 mm. crystallized promptly on trituration with ethanol and acetone. 1 : 4-Diphenylnaphthalene, recrystallized from ethanol, forms long colourless needles (1·5 g.), m. p. 136—137° (Found : C, 94·2; H, 5·9. Calc. for $C_{22}H_{16}$: C, 94·3; H, 5·7%), unchanged in admixture with authentic hydrocarbon (cf. Weiss *et al.*, *Monatsh.*, 1932, **61**, 162; Allen and Gilman, *J. Amer. Chem. Soc.*, 1936, **58**, 939).

(*b*) When the ethylene (8·5 g.) and phenylacetyl chloride (8 g.) were heated as before for 8 hours, but without use of inert gas, 8 g. (60%) of 1 : 4-diphenylnaphthalene and only 0·3 g. (1·1%) of the enol ester (III) were isolated.

(*c*) When 9 g. (0·05 mole) of 1 : 1-diphenylethylene and 17 g. (0·11 mole) of the acyl chloride were heated in a stream of nitrogen for 4 hours, the enol ester (III) was isolated in 48% yield (10 g.), and the naphthalene derivative in 3·5% yield (0·5 g.).

Saponification of the enol ester (II). The ester (2·5 g.) was refluxed with N-ethanolic potassium hydroxide (10 ml.) for 2 hours. The solvent was evaporated, and the residue extracted with ether and purified by distillation. A yellow oil (1·7 g.), b. p. 183—185°/1 mm., was obtained, which crystallized as needles, m. p. 44° (Found : C, 88·3; H, 5·9. $C_{22}H_{18}O$ requires C, 88·6; H, 6·0%). *Benzyl* 2 : 2-*diphenylvinyl ketone* (I) dissolves in concentrated sulphuric acid with a green-blue colour. Its *semicarbazone* crystallized from dilute ethanol in colourless prismatic needles, m. p. 166° (Found : N, 12·0. $C_{23}H_{21}ON_3$ requires N, 11·8%). Its 2 : 4-*dinitrophenylhydrazone* was obtained in two modifications, from dilute acetic acid as orange-red needles, m. p. 74° (Found : N, 11·7. $C_{28}H_{22}O_4N_4$ requires N, 11·7%), and from glacial acetic acid as red needles, m. p. 156° (Found : N, 11·5%).

Catalytic Hydrogenation and Hydrogenolysis of the Enol Ester (II).—The ester (2 g.) in ethanol (80 ml.) was reduced over Raney nickel at 19°/694 mm. During 90 minutes 350 ml. of hydrogen were absorbed (Calc. for 2 double bonds : 252 ml.). The solvent was evaporated, and the oily residue dissolved in ether. The ether was extracted with a measured amount of 0·2N-sodium hydroxide, and the excess of base determined by back-titration (NaOH consumed : 23·2 ml. Calc. : 24 ml.). The ethereal layer left an oily residue, which crystallized very slowly. 1 : 1 : 4-*Triphenylbutane* crystallized from ethanol in glistening scales, m. p. 78—79° (Found : C, 92·4; H, 7·5. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%).

Preparation of 1 : 1 : 4-*Triphenylbutadiene*.—This compound, which had been prepared by Staudinger (*Ber.*, 1909, **42**, 4258) from diphenylketen and cinnamaldehyde, was synthetised by us as follows : A mixture of diphenylacraldehyde (8·5 g.), phenylacetic acid (5·5 g.), lead monoxide (4·9 g.), and acetic anhydride (6 ml.) was heated at 180° during 5 hours, then poured into boiling dilute acetic acid (10%), and the precipitate recrystallized twice from ethanol. 1 : 1 : 4-Triphenylbutadiene was obtained in long colourless needles (55%), m. p. 101—102° (Found : C, 93·7; H, 6·3. Calc. for $C_{22}H_{18}$: C, 93·6; H, 6·4%). It dissolves in concentrated sulphuric acid with an intense yellow colour.

Ultra-violet absorption spectra were measured in 95% ethanol with a Beckman quartz spectrophotometer. We thank Dr. S. Pinchas, of the Weizmann Institute of Science, for the infra-red absorption measurements.

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