22. *The Action of Phosphorus Pentachloride on Non-symmetrically Substituted Acetones.*

By Ahmad Zaki and Youssef Iskander.

The action of phosphorus pentachloride on boiling benzene solutions of the five ketones mentioned below gave equilibrium mixtures of chloro-olefins. The reactivity of the chlorine atom, as tested by sodium ethoxide, was increased by the presence of nitro-groups: the mononitro-compound gave a mixture of the corresponding ethyl ether and acetylenic compound by boiling, whereas the dinitro-compound gave only the acetylenic compound and in the cold.

Attempts to prepare a non-symmetrically substituted acetone from *ethyl α-2 : 4-dinitrophenyl-γ-phenylacetoacetate* led to the formation of substituted naphthalenes.

Ketones, $Ar{\cdot}CH_2{\cdot}CO{\cdot}CH_2R$ [Ar = Ph and R = H, Me, or Et; or R = H and Ar = p-$C_6H_4{\cdot}NO_2$ or 2 : 4-$C_6H_3(NO_2)_2$], react with phosphorus pentachloride in boiling benzene with evolution of hydrogen chloride and formation of chloro-olefins, $Ar{\cdot}CH{:}CCl{\cdot}CH_2R$ and $Ar{\cdot}CH_2{\cdot}CCl{:}CHR$. These were separated by fractional distillation or in suitable cases by crystallisation. Their structures were determined by ozonolysis in chloroform, $Ar{\cdot}CH{:}CCl{\cdot}CH_2R$ giving $Ar{\cdot}CHO$ and $R{\cdot}CH_2{\cdot}COCl$, and $Ar{\cdot}CH_2{\cdot}CCl{:}CHR$ giving $Ar{\cdot}CH_2{\cdot}COCl$ and $R{\cdot}CHO$. These products were difficult to separate, so the ozonolysis was effected in alcohol–chloroform, giving separable mixtures of esters, aldehydes, and acids, the last produced by partial oxidation of the aldehydes.

The two chloro-olefinic isomers obtained by distillation were individual substances, but changed in course of time into the same equilibrium mixture, the components of which were either separated by distillation or identified by ozonolysis.

The chlorine atom in the chloro-olefins showed fair stability towards boiling alcoholic sodium ethoxide, except in the case of the mononitro-compounds, which were readily converted into β-*ethoxy*-α-p-*nitrophenyl*-Δ^{α}-*propylene* and α-p-*nitrophenylallylene*, and in the case of β-*chloro*-α-2 : 4-*dinitrophenyl*-Δ^{α}-*propylene*, which gave only α-2 : 4-*dinitrophenylallylene* with cold sodium ethoxide solution.

Methods of Synthesis.—p-Nitrobenzyl methyl ketone, first obtained as a by-product of the action of diazomethane on p-nitrophenylacetaldehyde (*Ber.*, 1929, **62**, 51), has been prepared in 20% yield by West and Soliman of the Egyptian University (private information) by the action of *p*-nitrophenylacetyl chloride on acetoacetic ester (sodio-derivative) in dry benzene, hydrolysis of the resulting α-*p*-nitrophenylacetylacetoacetic ester with dilute aqueous ammonia at 40°, and hydrolysis of the product, γ-*p*-nitrophenylacetoacetic ester, with dilute sulphuric acid. By substituting malonic ester for acetoacetic ester, we have increased the yield to 40%.

In an attempt to prepare 2 : 4-dinitrodibenzyl ketone *ethyl* α-2 : 4-*dinitrophenyl-γ-phenylacetoacetate* was prepared by the action of ethyl γ-phenylacetoacetate (sodio-derivative) on 1-chloro-2 : 4-dinitrobenzene in absolute alcohol. The product was resinified by concentrated sulphuric acid and unchanged by dilute sulphuric or hydrochloric acid; boiling with 5% sodium hydroxide solution produced 1 : 3-*dihydroxy*-2-2′ : 4′-*dinitrophenylnaphthalene*. When the ester was boiled with the equivalent amount of alcoholic sodium ethoxide, 3-*hydroxy*-1-*ethoxy*-2-2′ : 4′-*dinitrophenylnaphthalene* was formed, hydrolysis of which by boiling dilute alkali gave the preceding 1 : 3-dihydroxy-derivative.

EXPERIMENTAL.

Ethyl p-*Nitrophenylacetylmalonate*.—Sodium (23 g.; 1 mol.) in absolute alcohol (500 c.c.) and *p*-nitrophenylacetyl chloride (99·5 g.; 0·5 mol.) in dry benzene (400 c.c.) were successively added during 4 hours to ethyl malonate (80 g.; 0·5 mol.) in absolute alcohol (375 c.c.), cooled in a freezing mixture. The mixture was then stirred for 1 hour longer and kept in the ice-chest overnight. The precipitated sodio-derivative was acidified, and the liberated oil extracted with ether and washed with sodium bicarbonate solution (yield, 65 g.). It was converted, by addition to the required amount of sodium ethoxide in absolute alcohol, into the *sodio*-derivative of ethyl *p*-nitrophenylacetylmalonate, which separated from absolute alcohol in yellowish microcrystalline cubes (Found: C, 48·9; H, 4·6; N, 4·3; Na, 6·6. $C_{15}H_{16}O_7NNa$ requires C, 48·7; H, 4·7; N, 4·1; Na, 6·7%).

p-Nitrobenzyl methyl ketone, prepared from ethyl *p*-nitrophenylacetylmalonate by means of hydrochloric acid (*d* 1·1), crystallised from light petroleum (b. p. 70—80°) in scales, m. p. 65°, not depressed by an authentic specimen. Yield, 40%.

p-*Nitrophenylacetic anhydride*, prepared from *p*-nitrophenylacetyl chloride and sodium *p*-nitrophenylacetate in boiling benzene and crystallised from acetone, had m. p. 153° (Found: C, 55·7; H, 3·6; N, 8·1. $C_{16}H_{12}O_7N_2$ requires C, 55·8; H, 3·5; N, 8·1%).

Ethyl α-2 : 4-*Dinitrophenyl-γ-phenylacetoacetate*.—Ethyl γ-phenylacetoacetate (31 g.; 2 mols.) (Sonn and Litten, *Ber.*, 1933, **66**, 1512) was treated with sodium (3·46 g.; 2 mols.) in absolute alcohol (400 c.c.), and 1-chloro-2 : 4-dinitrobenzene (15·25 g.; 1 mol.) in ether (100 c.c.) then added. The mixture was left in the cold for 24 hours and acidified. The precipitated *ethyl* α-2 : 4-*dinitrophenyl-γ-phenylacetoacetate* (19 g.) crystallised from alcohol in thick yellow needles, m. p. 127° (Found: C, 58·2; H, 4·5; N, 7·5. $C_{18}H_{16}O_7N_2$ requires C, 58·1; H, 4·3; N, 7·5%). In acetone it gave a red coloration with ferric chloride.

3-*Hydroxy*-1-*ethoxy*-2-2′ : 4′-*dinitrophenylnaphthalene*, prepared by boiling the preceding ester with the equivalent amount of sodium ethoxide for 4 hours, crystallised from alcohol in long, yellow, silky needles, m. p. 179° (Found: C, 61·1; H, 4·1; N, 7·9. $C_{18}H_{14}O_6N_2$ requires C, 61·0; H, 3·95; N, 7·9%). The *acetyl* derivative (acetic anhydride–sulphuric acid method) crystallised from benzene–alcohol in long, yellow, silky needles, m. p. 191—192° (Found: C, 60·1; H, 4·1; N, 7·3. $C_{20}H_{16}O_7N_2$ requires C, 60·6; H, 4·0; N, 7·1%).

1 : 3-*Dihydroxy*-2-2′ : 4′-*dinitrophenylnaphthalene*, obtained by boiling the above acetoacetate for 30 minutes, or the preceding naphthalene derivative for 5 minutes, with 5% aqueous sodium hydroxide and acidifying the solution, had m. p. 279° after crystallisation from benzene–alcohol (Found: C, 59·0; H, 3·2; N, 8·6. $C_{18}H_{10}O_6N_2$ requires C, 58·9; H, 3·1; N, 8·6%).

α-Chloro-α-benzylethylene and β-Chloro-α-phenyl-Δ^{α}-propylene.—Benzyl methyl ketone (67 g.) and phosphorus pentachloride (110 g.) in dry benzene (300 c.c.) were boiled for 4 hours, the benzene and phosphoryl chloride removed under reduced pressure, ice added, and the mixture left overnight in the ice-chest. The chloro-olefins were extracted with ether and washed successively with dilute pyridine, dilute hydrochloric acid, and sodium bicarbonate solution (yield, 80 g.). Fractional distillation gave: (1) 35 g., b. p. 105—107°/26 mm. (Found: C, 70·9; H, 6·1; Cl, 23·1. C_9H_9Cl requires C, 70·8; H, 5·9; Cl, 23·3%); (2) 20 g., b. p. 120—124°/26 mm. (Found: C, 70·9; H, 6·0; Cl, 22·8%); (3) 6 g., above 124°.

Ozonisation of fraction (1), *immediately* after distillation, in chloroform containing alcohol gave ethyl phenylacetate (detected and estimated by hydrolysis to the acid), denoting that (1) consisted entirely of *α-chloro-α-benzylethylene*. When the same fraction was ozonised a few days later, benzoic acid was detected in the products, the amount of ethyl phenylacetate being correspondingly decreased. Fraction (2) gave the same ozonisation products as those obtained in the second ozonisation of (1). When redistilled many days after their first fractionation, fractions (1) and (2) were found to have attained the same composition—that of an equilibrium mixture of the two chloro-olefins. One can safely say, therefore, that fraction (1) is α-chloro-α-benzylethylene and fraction (2) is β-chloro-α-phenyl-Δ^{α}-propylene (cf. Farmer and Hose, J., 1933, 965) and that these exist in the ratio 35 : 20 in the equilibrium mixture. Boiling the equilibrium mixture with concentrated alcoholic sodium ethoxide for 24 hours failed to eliminate all the chlorine.

α-Chloro-α-benzyl-Δ^{α}-propylene and β-Chloro-α-phenyl-Δ^{α}-butylene.—Benzyl ethyl ketone (74 g.) was treated with phosphorus pentachloride exactly as in the case of benzyl methyl ketone. After the washing, the product gave (1) 42 g., b. p. 114—116°/23 mm. (Found: Cl, 21·1%); (2) 19 g., b. p. 123—125°/23 mm. (Found: Cl, 20·9. $C_{10}H_{11}Cl$ requires Cl, 21·3%); (3) 7 g., above 130°.

In course of time fraction (1), *α-chloro-α-benzyl-Δ^{α}-propylene*, and fraction (2), *β-chloro-α-phenyl-Δ^{α}-butylene*, changed into the same equilibrium mixture, about 70% of the products of ozonisation of which consisted of ethyl phenylacetate.

α-Chloro-α-benzyl-Δ^{α}-butylene and β-Chloro-α-phenyl-Δ^{α}-amylene.—The product obtained in the same way from benzyl propyl ketone (81 g.) gave on distillation (1) *α-chloro-α-benzyl-Δ^{α}-butylene* (46 g.), b. p. 134—135°/22 mm. (Found: Cl, 19·2%); (2) *β-chloro-α-phenyl-Δ^{α}-amylene* (22 g.), b. p. 145—147°/22 mm. (Found: Cl, 19·2. $C_{11}H_{13}Cl$ requires Cl, 19·7%); (3) 7 g., above 150°.

Fractions (1) and (2) ultimately changed into the same equilibrium mixture, about 70% of the products of ozonisation of which consisted of ethyl phenylacetate.

*α-Chloro-α-*p*-nitrobenzylethylene and β-Chloro-α-*p*-nitrophenyl-Δ^{α}-propylene*.—*p*-Nitrobenzyl methyl ketone (35·8 g.) and phosphorus pentachloride (45 g.) in dry benzene (120 c.c.) were refluxed for 4 hours. After the usual treatment and washing, the chloro-olefins were obtained as a liquid containing 10% of a solid, m. p. 78° after crystallisation from light petroleum (b. p. 60—70°) (Found: C, 54·6; H, 4·0; N, 6·7; Cl, 18·1. $C_9H_8O_2NCl$ requires C, 54·7; H, 4·1; N, 7·1; Cl, 18·0%); 70% of the product was a liquid, b. p. 161—162°/11 mm. or 134—136°/3 mm. (Found: C, 54·5; H, 4·1; N, 7·0; Cl, 18·4%); the remaining 20% was a high-boiling liquid.

Ozonisation of the solid proved it to be *β-chloro-α-*p*-nitrophenyl-Δ^{α}-propylene*. Ozonisation of the liquid ***immediately*** after distillation gave mostly ethyl *p*-nitrophenylacetate, m. p. and mixed m. p. 65°, thus proving it to be *α-chloro-α-*p*-nitrobenzylethylene*. When the liquid was ozonised a few days after distillation, *p*-nitrobenzaldehyde, m. p. 106°, and *p*-nitrobenzoic acid, m. p. 238°, were obtained in amounts approximating to 23% of the products. Attempts to precipitate a solid from this liquid failed. This was taken to indicate that 23% of the equilibrium mixture is not the solid, m. p. 78°, but its liquid geometrical isomer. Crystals, m. p. 78°, were, however, formed in the liquid after about 1 year.

Action of dilute alkali solution. The solid did not give a coloration with aqueous or alcoholic alkali. The liquid equilibrium mixture gave a dark violet coloration with very dilute alkali solution. An ethereal solution of the liquid was washed with 5% sodium hydroxide solution until the washings ceased to be red. The ethereal solution, after cooling, deposited the solid, m. p. 78°.

Action of sodium ethoxide. The solid was boiled for 1 hour with alcoholic sodium ethoxide, and the mixture diluted, acidified, and shaken with ether, which extracted yellow *β-ethoxy-α-*p*-nitrophenyl-Δ^{α}-propylene*, m. p. 96° after crystallisation from light petroleum (b. p. 60—70°) (Found : C, 63·6; H, 6·3; N, 6·7. $C_{11}H_{13}O_3N$ requires C, 63·7; H, 6·3; N, 6·8%). When the boiling was prolonged to 4 hours, this substance was again produced together with *α-*p*-nitrophenylallylene*, which crystallised from light petroleum (b. p. 60—70°) in long prisms, m. p. 108° (Found : C, 67·1; H, 4·4; N, 8·6. $C_9H_7O_2N$ requires C, 67·1; H, 4·4; N, 8·7%). The liquid equilibrium mixture also was treated with alcoholic sodium ethoxide; the solution became dark violet. After 1 hour's boiling, the above ether and the acetylenic compound were isolated, but more than half of the product was an unidentified brown-red solid insoluble in ether.

α-Chloro-α-2 : 4-dinitrobenzylethylene and β-Chloro-α-2 : 4-dinitrophenyl-Δ^{α}-propylene.—2 : 4-Dinitrobenzyl methyl ketone (22·4 g.) and phosphorus pentachloride (22·5 g.) in dry benzene (60 c.c.) were refluxed for 4 hours and the chloro-olefins were isolated after the usual treatment and washing. *β-Chloro-α-2 : 4-dinitrophenyl-Δ^{α}-propylene*, which crystallised from dilute alcohol in straw-coloured needles, m. p. 91—93° (Found : C, 44·2; H, 3·0; N, 11·4; Cl, 14·7. $C_9H_7O_4N_2Cl$ requires C, 44·5; H, 2·9; N, 11·5; Cl, 14·6%), formed 10% of the product; its constitution was shown by ozonolysis. The rest was a heavy liquid, which was ozonised in chloroform containing alcohol; about one-fourth of the products of ozonisation was 2 : 4-dinitrobenzaldehyde, m. p. 71—72°, and 2 : 4-dinitrobenzoic acid, m. p. 183°. The solid product gave no colour with alcoholic sodium ethoxide, but sodium chloride was precipitated in the cold. After dilution ether extracted *α-2 : 4-dinitrophenylallylene*, which crystallised from light petroleum (b. p. 60—70°) in small yellowish lumps, m. p. 77° (Found : C, 52·0; H, 3·0; N, 13·2. $C_9H_6O_4N_2$ requires C, 52·4; H, 2·9; N, 13·6%). No ether was formed. The crude liquid chloro-olefin gave a dark violet coloration with sodium ethoxide and a dark brown-red solid insoluble in ether (not investigated) was obtained.

FOUAD I UNIVERSITY, CAIRO, EGYPT.

[*Received, October 7th*, 1942.]