794. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part VII.* The Production of* p-tert.*-Butylphenyl and* iso*But-1-enyl* tert.*-Butyl Ketones from Pivaloyl Chloride.*

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The formation of *tert.*-butyl *p-tert.*-butylphenyl ketone when pivaloyl chloride is slowly added to a mixture of benzene and aluminium chloride (Pearson, *J. Amer. Chem. Soc.*, 1950, **72**, 4169) results from the reaction between *p-tert.*-butylbenzene, which is the first product, and the acid chloride (compare Rothstein and Saville, Part II, *J.*, 1949, 1950). The diminution of the first-order velocity constant in the course of the reaction (*idem*, Part III, *ibid.*, p. 1954) which occurs even in the absence of benzene is now shown to be due to *iso*but-1-enyl *tert.*-butyl ketone. This ketone is formed by condensation of *iso*butylene (arising from the decomposition of pivaloyl chloride) with unchanged pivaloyl chloride; when it is added to a Friedel–Crafts reaction mixture it completely deactivates the catalyst and thus prevents all further reaction.

It was noted in Part III (*J.*, 1949, 1954) that the rate of disappearance of pivaloyl chloride when mixed with aluminium chloride diminished appreciably towards the end of the reaction, *i.e.*, the curve formed by a plot of the logarithm of the concentration against time tended to flatten out towards the time axis. Since then, even more marked examples of the phenomenon have been encountered, notably when solutions of the acid halide in pure nitrobenzene were used. In such cases the reaction, which initially is very rapid, soon ceases and proceeds to a limited extent only if a further quantity of catalyst is added. Neither addition of more acid chloride nor dilution of the solvent with benzene will restart the reaction (details will be given in a later communication). It proceeds normally if it is catalysed by the pre-formed complex of aluminium chloride and nitrobenzene provided that the latter is only a small proportion of the total solvent. The reason therefore for the deactivation of the aluminium chloride is evidently the rapid formation of a by-product with which it forms a stable compound.

The foregoing largely invalidates the explanation offered by Wertyporoch and Adamus (*Z. physikal. Chem.*, 1934, **168**, 38) for the inactivity of nitrobenzene solutions of aluminium halides towards alkyl and acyl halides. They considered that the very stable complex formed by the solvent with the catalyst was responsible for the ineffectiveness of the latter. This, however, is inconsistent with the normal catalytic activity shown when a solution of the complex is added to a mixture of an acyl halide and benzene. The non-reactivity of nitrobenzene evidently should be ascribed to the deactivation of the benzene nucleus, and this is doubtless true for the results Wertyporoch *et al.* obtained for halogen-substituted benzene as well.

The necessity for using more than one molecule of aluminium chloride in Friedel–Crafts acylation reactions is of course due to progressive loss of catalytic efficiency as a result of compound formation with the product (see also Part IV, *J.*, 1949, 1959). Recently, Pearson (*J. Amer. Chem. Soc.*, 1950, **72**, 4169) reported a yield of over 46% of *tert.*-butylpivalophenone † (*tert.*-butyl *tert.*-butylphenyl ketone, $CMe_3{\cdot}C_6H_4{\cdot}CO{\cdot}CMe_3$) when pivaloyl chloride was *slowly* added during 20—60 minutes to a stirred mixture of aluminium chloride and benzene. In this case it is quite clear that primarily *tert.*-butylbenzene is formed and that further reaction furnishes the ketone, provided that the acid chloride is added slowly enough. If the addition is in one portion the 87% yield of carbon monoxide (Part II, *loc. cit.*) shows that hydrocarbon must be the main product. The substitution of *tert.*-butylbenzene for benzene as the solvent reduced the yield of carbon monoxide to 65% and correspondingly the ketone was isolated in 26·3% yield. Acylation is thus particularly sensitive to changes both in solvent (none occurred when a carbon disulphide solution of *tert.*-butylbenzene was used) and in concentration (unpublished work). It

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* Part VI, *J.*, 1951, 1459.

† Recalculated on the basis of acid chloride employed. For reasons given in Part II we do not consider that yields calculated on the final products isolated are reliable.

would be perhaps over-simplification to assume that the sole factor is the slow addition of pivaloyl chloride which then allows the *tert.*-butylbenzene to be further acylated, but, on using the condition described by Pearson and varying the time of addition, there is a variation in the yield of ketone (as shown below) though in no case was it quite as high as that obtained by him.

Time of addition, min.	20	45	50
Yield of ketone, %	16*	32·5	36·9

* Yield of CO, approx. 84%.

The gradual accumulation of this ketone would undoubtedly slow down the main reaction, especially in cases where the molecular concentration of aluminium chloride was low compared to the concentration of the acid chloride. A ratio of 1 : 10 was used in the kinetic experiments described in Part III. However, no *tert.*-butylpivalophenone was ever detected in these dilute solutions and, further, neither in carbon disulphide nor in nitrobenzene solution is its formation possible.

Although Pearson reported that there was no product when he repeated his reaction in nitrobenzene, it appeared to us that his experiments were inadequate. It was found, for example, that, when the reactants were mixed, a proportion of the acid chloride rapidly disappeared, and in these particular experiments there was an accompanying evolution of carbon monoxide amounting to about 10% of that theoretically possible. Now the first product in the decomposition of pivaloyl chloride is *iso*butylene (Boëseken, *Rec. Trav. chim.*, 1910, **24**, 85), which usually polymerises, but neither *iso*butylene nor its polymer hinders the subsequent reaction, and consequently it was desirable to search for some other substance, probably of a ketonic nature. Fractionation afforded an unsaturated ketone, $C_9H_{16}O$, b. p. 58°/15 mm. (semicarbazone, m. p. 119—120°), possessing the expected inhibitory action when added to aluminium chloride. The most likely structures suggesting themselves were *iso*but-1-enyl *tert.*-butyl ketone (I) and *tert.*-butyl 2-methylallyl ketone (II) both of which can result from reaction between *iso*butylene and pivaloyl chloride :

$$\mathrm{CMe_2{:}CH_2 + Cl{\cdot}CO{\cdot}CMe_3 \longrightarrow \underset{(I)}{CMe_2{:}CH{\cdot}CO{\cdot}CMe_3}}\ \textit{or}\ \mathrm{\underset{(II)}{CH_2{:}CMe{\cdot}CH_2{\cdot}CO{\cdot}CMe_3}}$$

Less likely possibilities were hexamethyldiacetyl and hexamethylacetone, both of which were synthesised in order to make a direct comparison. Neither of these yielded semicarbazones, and the boiling points of both were substantially different from that of the above ketone.

The reaction leading to (I) and (II) is very similar to the production of mesityl oxide from *iso*butylene and acetyl chloride with zinc chloride as catalyst (Kondakov, *J. Russ. Phys. Chem. Soc.*, 1894, **26**, 5), or to the formation of a β-chloro-ketone by addition of acetyl chloride to trimethylethylene, which is then followed by elimination of hydrogen chloride (Wieland and Bettag, *Ber.*, 1922, **55**, 2246). Some confirmation was obtained in that when *iso*butylene was mixed with pivaloyl chloride and aluminium chloride in carbon disulphide solution the unsaturated ketone was isolated in 20% yield. Its independent synthesis from 2-methylbut-2-enoyl chloride, as below, confirmed it to be the *iso*butenyl ketone.

$$\mathrm{CMe_2{:}CH{\cdot}COCl + Cl{\cdot}Mg{\cdot}CMe_3 \longrightarrow CHMe_2{:}CH{\cdot}CO{\cdot}CMe_3}$$

EXPERIMENTAL

The reaction between pivaloyl chloride and benzene was carried out as nearly as possible as described by Pearson (*loc. cit.*), except that the times of addition were measured more exactly. These times were (i) 20, (ii) 45, and (iii) 50 minutes. The products were : (i) Approx. vol. of carbon monoxide 1488 c.c.; *tert.*-butylbenzene, b. p. 58°/15 mm., 3·36 g. (33·6%); *tert.*-butyl *tert.*-butylphenyl ketone, b. p. 147°/12 mm., 2·79 g. (17%) (Found : C, 82·7; H, 10·1. Calc. for $C_{15}H_{22}O$: C, 82·6; H, 10·1%) [oxime, m. p. 205° (Found : C, 77·1; H, 9·6; N, 6·3. Calc. for $C_{15}H_{23}ON$: C, 77·2; H, 9·9; N, 6·0%)]. (ii) *tert.*-Butylbenzene, 1·7 g. (17%); ketone, 5·3 g. (32·5%). (iii) *tert.*-Butylbenzene, 0·85 g. (8·5%); ketone, 6·02 g. (37%).

Preparation of But-1-enyl tert.*-Butyl Ketone.*—(a) *From pivaloyl chloride.* A solution of pivaloyl chloride (24·2 g., 0·2 mol.) in nitrobenzene (50 c.c.) was slowly added to freshly distilled aluminium chloride (14 g., 0·105 mol.) dissolved in the same solvent (100 c.c.) and cooled to 0°. After 1 hour's stirring, more aluminium chloride (7 g., 0·055 mol.) in nitrobenzene (30 c.c). was added, and after another hour the liquid was warmed to 40—50° for 0·5 hour. The product was decomposed with ice and 10% hydrochloric acid, the organic layer separated, and an ethereal extract of the aqueous layer added to it. The combined layers were dried (Na_2SO_4). Fractionation afforded iso*but*-1-*enyl* tert.-*butyl ketone* (4·5 g., 20%), b. p. 58°/15 mm. (Found : C, 77·1; H, 11·9%; *M*, 142. $C_9H_{16}O$ requires C, 77·1; H, 11·4%; *M*, 140). The *semicarbazone*, prepared in pyridine, separated from water in needles, m. p. 119—120° (Found : C, 61·2; H, 9·6; N, 21·3. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·6; N, 21·3%).

(b) *From* iso*butylene*. The gas generated from *tert.*-butyl alcohol by the action of 30% sulphuric acid (Barkenbus and Kelly, *J. Chem. Educ.*, 1945, **22**, 356) was passed for 1 hour into a carbon disulphide (100 c.c.) solution of pivaloyl chloride (12 g., 0·1 mol.) at −12°. Whilst the passage of the *iso*butylene was continued, aluminium chloride (26 g., 0·2 mol.) was added from a dropping tube, the temperature being kept between −12° and −20°. More acid chloride (3 g.) was added, and the temperature then allowed to rise gradually to that of the room. Initially there was a vigorous reaction, and towards the end oily drops of polymerised *iso*butylene separated. After decomposition with ice and subsequent extraction, the product was fractionated, yielding, together with other material including unchanged pivalic acid, polymerised product, etc., the above ketone (2·2 g.) (Found : C, 77·0; H, 12·2%). The semicarbazone, which appeared to be identical (m. p. and mixed m. p.) with that noted above, also gave rather poor analytical figures (Found : C, 60·4; H, 8·7; N, 20·6%).

(c) *From 2-methylbut-2-enoyl chloride*. The acid (*Org. Synth.*, 1943, **23**, 27) was converted into the acid chloride with thionyl chloride (Schindler and Reichstein, *Helv. Chim. Acta*, 1942, **25**, 551), the yield of product, b. p. 145—150°, being 90%. An ethereal (50 c.c.) solution of the acid chloride (12 g., 0·1 mol.), containing quinol (0·1 g.), was slowly added to a stirred solution in ether of *tert.*-butylmagnesium chloride prepared from *tert.*-butyl chloride (12 g.) and magnesium (2·5 g.). The liquid was warmed for 30 minutes on the steam-bath and then decomposed with ice. The ketone, b. p. 58°/15 mm., was obtained in 14% yield (2 g.), together with unchanged acid and some undistillable tar. The semicarbazone was identical (m. p. and mixed m. p.) with that obtained from the product of the Friedel–Crafts reactions (*a*) and (*b*) (Found : C, 60·8; H, 9·6; N, 21·2%).

Preparation of Hexamethyldiacetyl.—This was prepared by a method similar to that used by Mushenko (*Chem. Abs.*, 1943, **37**, 5697), pivaloyl chloride being substituted for the bromide. A mixture of pivaloyl chloride (12 g.), " molecular " sodium (3 g.), and ether (100 c.c.) furnished approximately 4 g. of the pure ketone, b. p. 168°. It did not afford a semicarbazone.

Preparation of Hexamethylacetone.—Only a poor yield of the ketone (b. p. 153°) was obtained by reaction of pivaloyl chloride with acetone (Whitmore, *Rec. Trav. chim.*, 1938, **57**, 566). Better yields resulted from the condensation of methyl pivalate (Richard, *Ann. Chim.*, 1910, **21**, 335) with *tert.*-butyl chloride in the presence of sodium, and oxidation of the mixture of di-*tert.*-butylcarbinol and hexamethylacetone with concentrated nitric acid (Bartlett and Schneider, *J. Amer. Chem. Soc.*, 1945, **67**, 141). A semicarbazone could not be obtained.

Friedel–Crafts Reaction with iso*But*-1-*enyl* tert.-*Butyl Ketone.*—The ketone (0·7767 g.) was mixed with nitrobenzene (140 c.c.) and to this were added first a solution of freshly prepared aluminium chloride (0·6320 g.) in nitrobenzene (20 c.c.) and then pivaloyl chloride (5·6664 g.) in the same solvent (20 c.c.). There was no reaction and no carbon monoxide was evolved.

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