

170. *Acylation and Allied Reactions catalysed by Strong Acids. Part VIII.* A Comparison of the Action of Acetyl and Benzyl Perchlorates on Benzene and Related Compounds.*

By H. BURTON and P. F. G. PRAILL.

The yield of aryl methyl ketone from acylium perchlorate and aromatic hydrocarbons is: benzene \ll toluene \ll *m*-xylene. Addition of acetic anhydride diminishes the yield of ketone in the first two cases but increases that from *m*-xylene. Benzyl perchlorate with benzene at room temperature rapidly gives high yields of diphenylmethane and, under suitable conditions, higher substitution products. The benzyl cation is shown to be unstable.

IN Part III (*J.*, 1951, 522) we showed that acetyl cations derived from acylium perchlorate were capable of displacing benzyl cations from suitably constituted benzyl ethers and that if the reaction was carried out in benzene a considerable amount of diphenylmethane was formed. We had also shown in Parts I and II (*J.*, 1950, 1203, 2034) that acylium perchlorate was a very efficient *C*-acetylating agent for anisole. It therefore appeared of interest to compare the reactivity of acylium perchlorate with that of benzyl perchlorate towards benzene. It must be pointed out that in our work on the benzyl ethers we found no indication of the formation of acetophenone. Further, Diels and Alder (*Ber.*, 1927, **60**, 716) have shown that, whilst acylium perchlorate reacts readily with acetophenone, toluene, or *o*-xylene in hot acetic anhydride to give substituted pyrylium salts, benzene fails to react under similar conditions.

We now show, as briefly reported earlier (*Chem. and Ind.*, 1951, 939), that only traces of ketone are produced from benzene solutions of acylium perchlorate after 24 hours at room temperature. The yield of acetophenone was \sim 5% when the reaction was carried out in nitromethane: some intractable material was also produced. The yield was not markedly affected by the addition of small amounts of acetic acid but was reduced to less than 1% by addition of acetic anhydride. It appeared from the results in nitromethane that some of the ketone might be attacked further to produce the intractable material and this assumption was tested by treating acetophenone with acylium perchlorate: after 4 hours, 0.2 mole of benzoylacetone per mole of acylium perchlorate could be isolated, together with much intractable material. Some highly insoluble orange solid was also formed which was undoubtedly a pyrylium salt of the type described by Dilthey (*J. pr. Chem.*, 1916, **94**, 75).

In view of the similarity of the acylium and benzoylium ions (*J.*, 1951, 529) and because benzophenone is unlikely to undergo further condensation under the conditions employed, we also carried out similar reactions with benzoylium perchlorate. In benzene alone less than 0.02 mole of ketone per mole of the perchlorate was produced after 24 hours at room temperature, but in nitromethane the yield was increased to 0.24 mole.

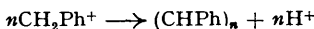
In marked contrast to these results benzyl perchlorate reacted rapidly with benzene alone to give 0.7 mole of diphenylmethane and small amounts of more highly substituted products: the yield of the latter was much increased in nitromethane solution. The formation of the more highly substituted products should be favoured in nitromethane because, in the absence of the "dilution effect" due to a large amount of benzene, diphenylmethane would be more susceptible to attack than benzene. Similar results were obtained with toluene.

Acylium perchlorate reacts with toluene to give *p*-methylacetophenone (0.44 mole); the yield was markedly increased (to 0.57 mole) in nitromethane. These yields were decreased by the addition of acetic acid or acetic anhydride and in the latter case an oil was produced which had the properties of a β -diketone. When the more reactive *m*-xylene was used the amount of ketone formed was increased by the addition of acetic anhydride as was found for anisole (*loc. cit.*).

The effect of adding anhydride to the benzene and toluene experiments is readily

* Part VII, *J.*, 1952, 4457.

halide" a resinous product was obtained which corresponded in amount to that to be expected from the reaction :



This type of "polymerisation" of the benzyl cation was postulated by Monicelli and Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 1722) and was remarked upon in a previous communication (Part III).

It is clear from these experimental facts that, whilst in the process of acylation the hydrocarbon-silver perchlorate system is not necessary for the reaction to occur, in alkylation it may be. In the case of benzyl perchlorate it is not easy to devise experiments which will give an unequivocal answer to this point. If the production of diphenylmethane depends upon an attack on the benzene-silver perchlorate complex by benzyl perchlorate (or the benzyl cation) it is not apparent how this process occurs, for the aromatic nucleus in such a complex might be expected to have at least a partial positive charge. A similar difficulty obtains in some of the reaction mechanisms postulated for the normal Friedel-Crafts reaction on benzene. It is possible that the reaction between the benzyl cation and the aromatic compound takes place on the surface of the silver halide. The concentration of ionic species in hydrocarbon solutions would not be expected to be appreciable at any time but it must be apparent that if organic ions are present then these can react with the hydrocarbon and allow more of the perchlorate to dissociate. It is not unlikely that the dissociation is aided to some extent by the polar properties of the hydrocarbon under investigation, this would account for the particularly sluggish activity of benzene. The present work shows that if organic cations are formed in the presence of hydrocarbons they are extremely active entities. It also shows that the benzyl cation is much more reactive, and hence less stable, than the acetyl or the benzoyl cations. This may be attributed to the presence of the oxygen atom in the latter which enables the positive charge to be more evenly distributed than is possible in the case of the benzyl ion.

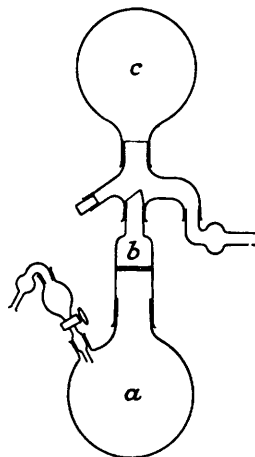
The work now described was undertaken to examine the overall effects of organic perchlorates on hydrocarbons and is of a semi-quantitative nature. Although all reasonable precautions were taken to exclude moisture, we do not claim to have used completely anhydrous conditions as would be required for kinetic measurements. We do not think that this invalidates any of our general arguments but we draw attention to it here because we hope subsequently to investigate the kinetics of some of the reactions.

EXPERIMENTAL

Materials.—Acetyl chloride, acetic acid, and acetic anhydride were "AnalaR" reagents. Traces of sulphur compounds in "AnalaR" benzene were removed by several hours' refluxing with Raney nickel before drying over sodium wire and redistilling. This procedure was found advisable in order to prevent the formation of small amounts of solid perchlorates in the reaction product. Toluene was sulphur-free. Silver perchlorate was treated as described in Part II (*J.*, 1950, 2034). Benzyl bromide was of laboratory-reagent quality, and benzoyl chloride was freshly treated with thionyl chloride and redistilled. All other reagents were dried and re-distilled.

General Procedure A.—The acid chloride or benzyl bromide (0.05 mole) was added during 10–15 minutes to a solution of silver perchlorate (0.05 mole) in a suitable quantity of hydrocarbon (depending on the solubility of the silver salt), with or without nitromethane. After an appropriate time the mixture was filtered rapidly through a sintered plate on to crushed ice, and the filter was washed with ether and then with water. The filtrate was extracted thrice with ether and the combined ethereal solutions were washed with water until the washings no longer gave an acid reaction (Congo). The dried (Na_2SO_4) extract was then evaporated and the residue was fractionated in a vacuum.

General Procedure B.—The apparatus used was of the type illustrated in the Figure. Silver perchlorate was weighed in stoppered flask *a* and this was kept for at least 24 hours in a vacuum-desiccator (P_2O_5) and reweighed before use. The silver salt was dissolved in nitromethane



(125 g.) and the flask was then fitted with a dropping funnel, and a sintered filter *b* with a three way adapter; the latter was fitted with a calcium chloride tube and a second flask *c*. The solution was cooled in ice-salt for 30—60 minutes and the organic halide, in an equal weight of nitromethane, was then added with shaking, during the next 10—15 minutes. After 15—30 minutes the apparatus was inverted and the solution was sucked into *c*. The silver halide was then washed rapidly with nitromethane (21 g.) and sucked as dry as possible. Flask *a* and the filter were then replaced by a thermometer. The hydrocarbon (0.2 mole) was added and the mixture was left for an appropriate period before working up as in procedure A.

Acylation experiments.

Reactions with Benzene.—When benzene was used as solvent it was necessary to use a relatively large amount (230 g.) owing to the low solubility of the silver salt. Procedure A was employed and acetyl chloride was added at 10—15°; the mixture was then left at room temperature for 24 hours. The small amount of acetophenone was isolated as the 2 : 4-dinitrophenylhydrazone (0.0003 mole), m. p. and mixed m. p. 230°. When benzoyl chloride was substituted for acetyl chloride the yield of ketone (as 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p.) did not exceed 0.001 mole. No ketone could be detected when benzoic acid (0.05 mole) was added to the mixture.

Experiments in nitromethane (thrice the combined weight of benzene and acid chloride) were carried out with benzene (0.2 mole) for 24 hours at room temperature. Under these conditions approx. 0.002 mole of acetophenone was obtained together with 0.9—1.1 g. of intractable material. By reducing the reaction period to 2 hours the total weight of product was less but the amount of ketone isolated was 0.003 mole.

When a mixture containing an excess of silver perchlorate (0.05 mole) in benzene (0.4 mole) and nitromethane (104 g.) was kept for 2 hours at room temperature the amount of ketone isolated was 0.0015 mole.

Similar results were obtained in the presence of acetic acid (0.05—0.1 mole), but when acetic anhydride (0.2 mole) was added to the mixture only traces of ketone were produced.

In nitromethane benzoyl chloride gave rise to benzophenone (0.012 mole) and some non-distillable residue (1.5 g.). When procedure B was employed the yields were benzophenone 0.009 mole, and residue 1.0 g.

Reactions with Toluene.—In procedure A the silver perchlorate was dissolved in toluene (0.2 mole) and the mixture was left for 24 hours at room temperature. The fraction, b. p. 100—110° (mainly 105—106°)/15 mm. (0.022 mole), was redistilled at atmospheric pressure (b. p. 215—220°), and characterised as the 2 : 4-dinitrophenylhydrazone, bright red needles [from ethyl acetate-chloroform (1 : 1)], m. p. 256° (decomp.), which did not depress the m. p. of *p*-methylacetophenone 2 : 4-dinitrophenylhydrazone. There was also a small fraction (0.6 g.) of higher-boiling material (140—165°/15 mm.) and a viscous residue (0.8 g.).

When the reaction was carried out in nitromethane (36.8 g.) for 2 hours the yield of ketone increased to 0.028 mole.

Similar experiments in which acetic anhydride (0.15 mole) was added before the acetyl chloride gave only traces of *p*-methylacetophenone. The main product (1.3 g.) boiled in the region of 150° at 20 mm.; it was a pale yellow, sweet-smelling oil, failed to give a 2 : 4-dinitrophenylhydrazone, but gave a crystalline sodium salt with 2*N*-sodium hydroxide and an intense reddish-violet colour with alcoholic ferric chloride.

Reactions with m-Xylene.—Silver perchlorate was dissolved in *m*-xylene (0.2 mole) and nitromethane (37 g.); the mixture was left for 2 hours at room temperature. The ketonic fraction (0.043 mole) distilled at 82°/5—6 mm., and at 225°/1 atm. Only a small residue (0.3 g.) remained. 2 : 4-Dimethylacetophenone was characterised as the 2 : 4-dinitrophenylhydrazone, bright orange-red needles (from ethyl acetate), m. p. 169—170° (Found : C, 58.1; H, 4.9; N, 17.2. C₁₆H₁₆O₄N₄ requires C, 58.5; H, 4.9; N, 18.0%), and as the semicarbazone, m. p. 191° (Heilbron's "Dictionary of Organic Compounds" gives m. p. 185—187°).

When the experiment was repeated with the addition of acetic anhydride (0.15 mole) and more nitromethane (15 g.), the yield of ketone was increased to 0.053 mole. The intractable residue (2.3 g.) from the distillation contained traces of nitrogen (Lassaigne's test).

The initial experiment was repeated with the addition of acetic acid (0.37 mole); the yield of ketone was then only 0.009 mole.

When procedure B was used and the reaction mixture kept at 10—15° for 45 minutes the yield of 2 : 4-dimethylacetophenone was 0.032 mole. In a second experiment under identical

conditions but in the presence of excess of silver perchlorate (0.05 mole) the yield of ketone was 0.029 mole.

Reactions with Acetophenone and p-Methylacetophenone.—Acetyl chloride (0.26 mole) was added during 25 minutes to a precooled solution of silver perchlorate (0.26 mole) in nitromethane (270 g.) and acetophenone (0.26 mole). The mixture was kept for 4 hours during which the temperature was allowed to rise slowly from 5° to 14°. The dark mixture was then worked up in the usual way.

Acetophenone (0.16 mole) was recovered. Benzoylacetone (0.054 mole) distilled at 118—120°/9 mm. as a pale yellow oil which rapidly solidified on cooling; recrystallisation from methanol gave long colourless needles, m. p. 56°. (Beyer and Claisen, *Ber.*, 1887, 20, 2180, give m. p. 60—61°.) The structure was confirmed by alkaline fission to acetophenone and a little benzoic acid.

When the reaction was carried out with *p*-methylacetophenone and the mixture kept for 2 hours, about half of the ketone was recovered. The *p*-methylbenzoylacetone (0.053 mole), b. p. 126—132°/5—6 mm., distilled as a sweet-smelling pale yellow oil (Found: C, 74.8; H, 7.1. C₁₁H₁₂O₂ requires C, 75.0; H, 6.8%). Alkaline fission of the oil (2.0 g.) gave *p*-methylacetophenone (1.2 g.) and *p*-toluic acid (0.3 g.) (m. p. and mixed m. p.).

S-Benzylthiuronium *p*-toluate recrystallised from ethanol as colourless needles, m. p. 188—189° (Vogel, "Practical Organic Chemistry," Longmans, Green & Co., London, 1948, p. 737, gives m. p. 164°).

Reactions using 72% Perchloric Acid.—Series A. 72% Perchloric acid (0.05 mole) was added during 5—10 minutes to acetic acid (0.18 mole) and acetic anhydride (0.31 mole) cooled in ice water. The hydrocarbon (0.1 mole) was added during 5 minutes at 6—8° and the mixture was then left at 10—15° for 4 hours (48 hours in the case of benzene and 2 hours in the case of anisole). The mixture was poured on crushed ice and then extracted thrice with ether. The combined ethereal extracts were washed successively with aqueous sodium carbonate, 2*N*-sodium hydroxide, and water. The dried (Na₂SO₄) solution was evaporated and the residue was fractionated.

Series B. A mixture of the hydrocarbon (0.2 mole) with acetic anhydride (0.16 mole) and nitromethane (36.8 g.) was cooled to below 5° and 72% perchloric acid (0.05 mole) was added during 15 minutes, so that the temperature did not rise above 15°. The mixture was left at room temperature for 18 hours before being worked up as in series A.

The amounts of ketone formed (in moles) were:

	C ₆ H ₆	PhMe	<i>m</i> -C ₆ H ₄ Me ₂	PhOMe
Series A	Trace	Trace	0.004	0.033
Series B	Trace	0.0044	0.026	0.040

Alkylation experiments.

Reactions with Benzene.—Silver perchlorate in benzene (230 g.) was allowed to react with benzyl bromide at 5—6° for 45 minutes, procedure A being used. As a slight variation of technique the whole reaction mixture was poured on crushed ice and left for several hours before filtration; this prevented separation of solid benzene on the sintered plate. Distillation of the residue gave a little (0.7 g.) unchanged benzyl bromide—possibly owing to the inhomogeneity of the reaction mixture. The main fraction consisted of diphenylmethane (0.036 mole), b. p. 130—140° (mainly 134—135°)/16 mm., m. p. and mixed m. p. 25—26°. There was a viscous high-boiling residue (1.0 g.).

When the reaction was carried out with benzene (0.2 mole) and nitromethane (72.8 g.), the diphenylmethane (0.021 mole) was accompanied by a fraction (1.4 g.), b. p. 165—200° (mostly 185—190°)/4—5 mm., which partly solidified on cooling. The solid crystallised from alcohol and from methanol as colourless needles which had almost completely melted at 65° but did not become clear until 74° (Found: C, 93.1; H, 7.1. Calc. for C₂₀H₁₈: C, 93.0; H, 7.0%). There was a non-distillable residue (1.8 g.).

When procedure B was used all but a trace of the material derived from the benzyl perchlorate was retained by the silver bromide which was rather greasy in appearance; it was washed with water and dried. The powdered material (13.9 g.) was extracted (Soxhlet) with chloroform; the adsorbed substance was not completely extractable with ether in which it was sparingly soluble. Evaporation of the extract left a resin (4.2 g.) (Found: C, 87.6; H, 6.8. Calc. for C₇H₆: C, 93.3; H, 6.7%), which was obviously impure. It appears probable that oxygen was incorporated in the product at some stage.

Reactions with Toluene.—The above experiments were repeated with toluene (0.2 mole). *p*-Methyldiphenylmethane (0.032 mole), b. p. 120—130° (mainly 128—130°)/7 mm., was charac-

terised by oxidation with chromic acid to *p*-methylbenzophenone, identified as the 2 : 4-dinitrophenylhydrazone, orange-red needles (from ethyl acetate), m. p. 198—201° (Found : C, 63·7; H, 4·1; N, 14·7. Calc. for C₂₀H₁₆O₄N₄ : C, 63·8; H, 4·3; N, 14·9%). There was a high-boiling residue (1·9 g.).

In nitromethane (72·8 g.) the same amount of *p*-methyldiphenylmethane (0·032 mole) was obtained but there was more residue (2·4 g.).

We thank the Chemical Society and Imperial Chemical Industries Limited for grants.

KING'S COLLEGE OF HOUSEHOLD & SOCIAL SCIENCE,
(UNIVERSITY OF LONDON), W.8.

[Received, November 18th, 1952.]
