

Acylation and Allied Reactions catalysed by Strong Acids. Part XII.
The Allyl and Some Related Cations.*

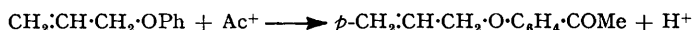
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Allyl phenyl ether is not cleaved by acetylium perchlorate but undergoes *C*-acetylation to *p*-allyloxyacetophenone. Reactions with allyl, but-2-enyl (crotyl), and cinnamyl perchlorates generally lead to the formation of complex products: the cations themselves also give "polymeric products." Cinnamoyl perchlorate reacts with anisole under a variety of conditions giving high yields of *p*-methoxyphenyl styryl ketone.

It has been postulated by Alexander ("Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, 1950, p. 42) that the benzyl and allyl cations are formed with particular ease and that the ions are stabilised by resonance. Burton and Prail (*J.*, 1951, 522) showed that the benzyl cation can be formed very easily by the action of acetylium perchlorate on an aryl benzyl ether, but found later (*J.*, 1953, 827) that when the cation was derived from benzyl perchlorate in an inert solvent (nitromethane) of relatively high dielectric constant it was markedly unstable and underwent "polymerisation": it was also noted that oxygen was probably incorporated into the polymer at some stage. In view of the well-known reactivity of allyl halides under all conditions of nucleophilic substitution and their similarity to benzyl halides, we have investigated the behaviour of allyl phenyl ether and some related ethers towards the acetylium ion and also the properties of the allyl and some substituted allyl cations, using the silver perchlorate technique.

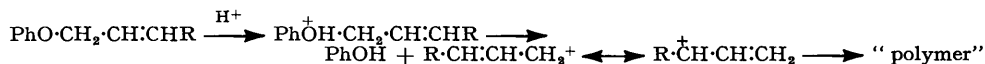
Allyl phenyl ether was converted smoothly and in high yield into *p*-allyloxyacetophenone under all the conditions previously used: the reaction occurred to some extent even in benzene as the solvent:



In one or two experiments we did observe the formation of very small amounts of phenyl acetate which must have arisen as follows:



It was apparent that under comparable conditions the allyl cation was not formed so readily as the benzyl cation. But-2-enyl (crotyl) and cinnamyl phenyl ethers behaved entirely differently giving, under all the conditions used, viscous and resinous products, respectively. The resinous materials from the cinnamyl ether were of variable composition but all appeared to contain a higher proportion of oxygen than the original ether, and the molecular weight (Rast) varied from 320 to 512. We have also found that these ethers usually produce similar polymeric products when treated with a little 70% perchloric acid in nitromethane although that from the cinnamyl ether had a higher carbon content but also a higher molecular weight (794). We were able to identify small amounts of phenol in some cases but the major portion of the products was non-phenolic. 1-Phenylallyl *p*-nitrobenzoate showed a similar behaviour towards 70% perchloric acid in nitromethane or acetic anhydride: fission was rapid and *p*-nitrobenzoic acid and polymeric material were produced. It would appear from the above results that fission of the ester, and also of the ethers, did occur but that the substituted allyl cation was unstable and "polymerised" in a manner analogous to that of the benzyl cation.



In view of the remarkable difference shown by allyl phenyl ether we decided to investigate the formation of the various allyl cations from silver perchlorate and the appropriate

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allyl halide. We again find that there is a marked difference between the unsubstituted allyl and the two γ -substituted allyl cations, although even with the allyl cation the formation of complex products often occurs especially when reactions are carried out in a medium of relatively high dielectric constant. Allyl perchlorate is hydrolysed by water to allyl alcohol and reacts with acetic anhydride forming allyl acetate; the yields of products were however not good. Resinous products were obtained from the perchlorate and *m*-xylene or mesitylene in nitromethane whilst benzene and anisole gave intractable black tars. But-2-enyl perchlorate was unstable and gave a black resin. Cinnamyl perchlorate in nitromethane in the absence of any other reactant gave resinous materials of variable composition and high molecular weight; the oxygen content of the unpurified resins was variable but persisted even when the cinnamyl perchlorate was prepared in an atmosphere of nitrogen, although the molecular weight of the product was reduced from about 860 to 430.

The products formed from anisole and phenol were approximately dimeric but the former contained methoxyl groups and the latter was phenolic, indicating that reaction had occurred. They showed only slight unsaturation towards potassium permanganate in aqueous acetone. The formation of the dimeric products may involve a cyclisation process of the type discussed by Baker, Haksar, McOmie, and Ulbricht (*J.*, 1952, 4310) but we find that allylmesitylene, in which there is no free *ortho*-position, is also converted by perchloric acid in nitromethane into a "polymeric" substance. It is also possible that addition of an allyl cation to the double linking of the allylic compound may occur.

The mode of "polymerisation" of the substituted allyl cations themselves may involve the loss of a proton to give a substituted allene which, under the influence of hydrogen ion, then polymerises. It is also possible that the incorporation of oxygen may result by simultaneous oxidation either by molecular oxygen or, more probably, by perchloric acid. The polymeric materials did not contain halogen.

In marked contrast to the results with the cinnamyl cation we find that the cinnamoyl cation closely resembles the more reactive aroyl cations previously investigated by Burton and Praill (*J.*, 1951, 529). Thus with anisole alone or in nitromethane or even benzene as a solvent we found that 91, 94, and 94% yields, respectively, of *p*-methoxyphenyl styryl ketone could be isolated when the reactions were carried out at 18–28°, 3°, and 18°, respectively, for similar times.

EXPERIMENTAL

Materials.—Silver perchlorate was dried as previously described (*J.*, 1950, 2036). Nitromethane, anisole, *m*-xylene, mesitylene, benzene, allyl bromide (b. p. 70–71°), and cinnamyl chloride (b. p. 115°/15 mm.) were all dried and redistilled. Acetic anhydride, acetyl chloride, and perchloric acid were "AnalaR" reagents. Cinnamyl bromide was prepared from the alcohol and hydrogen bromide in acetic acid and had m. p. 35°. But-2-enyl chloride, b. p. 81–83°, was fractionated from the mixture of chlorides obtained from crotyl alcohol and thionyl chloride.

p-Allyloxyacetophenone.—Allyl bromide (7.6 g.) was added to the spongy mass of yellow solid which was precipitated when potassium hydroxide (2.3 g.) in water (2.3 c.c.) was mixed with a solution of *p*-hydroxyacetophenone (4.8 g.) in dioxan (50 c.c.). After refluxing gently for 17 hr. the mixture was added to water and extracted twice with ether. The combined ethereal extracts were washed thrice with 2*N*-sodium hydroxide and then with water. The dried (Na₂SO₄) ethereal extract was evaporated, excess of dioxan being removed in a vacuum. The ketone (4.5 g.) distilled at 110–112°/0.5 mm. (Found: C, 75.3; H, 7.1. C₁₁H₁₂O₂ requires C, 75.0; H, 6.9%).

The 2 : 4-dinitrophenylhydrazones separated as red needles, m. p. 189°, from ethyl alcohol (Found: C, 57.2; H, 4.4; N, 15.6. C₁₇H₁₆O₅N₄ requires C, 57.3; H, 4.5; N, 15.7%).

Reaction of Allyl Phenyl Ether with Acetylum Perchlorate.—(a) In nitromethane Acetyl chloride (0.05 mole) in nitromethane (20 c.c.) was added during 15 min. to a cold (0–5°) solution of allyl phenyl ether (0.05 mole) and silver perchlorate (0.05 mole) in nitromethane (70 c.c.). After a further 45 min. at 0–5° the silver chloride was filtered off from the orange solution, the filtrate being allowed to fall on to crushed ice. Ethereal washings of the silver chloride were added to the filtrate and the combined extracts were washed with sodium hydrogen carbonate

solution and then with water until neutral. The residue obtained from the dried (Na_2SO_4) solution was distilled yielding fractions: (i) 0.3 g., b. p. 40—90°/0.5 mm., (ii) 8.0 g., b. p. 103—109°/0.5 mm. Fraction (i) was a mixture of unchanged allyl phenyl ether and phenyl acetate. The latter was identified by hydrolysis with boiling 2*N*-sodium hydroxide to phenol which was liberated by carbon dioxide (general procedure) and identified (standard procedure) as 2 : 4 : 6-tribromophenol, m. p. and mixed m. p. 90°. Fraction (ii) was *p*-allyloxyacetophenone, identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 188—189°.

(b) *In presence of acetic anhydride.* The experiment described under (a) was repeated but with acetic anhydride (0.05 mole) in the allyl phenyl ether-silver perchlorate-nitromethane solution. The red mixture was filtered after 30 min.; the ethereal extract showed a green fluorescence. Fractionation of the residue yielded: (i) 1.8 g., b. p. 120—122°/ca. 1 mm., (ii) 6.4 g., b. p. 116—118°/0.5 mm. Both fractions were *p*-allyloxyacetophenone; m. p.s and mixed m. p.s of the 2 : 4-dinitrophenylhydrazones, 188—189°.

(c) *In benzene.* The experiment described under (a) was repeated but with benzene (230 c.c.) instead of nitromethane as solvent. The acetyl chloride was also mixed with benzene (20 c.c.). The reaction was carried out at 8°. The orange solution was filtered after a further 30 min. The following fractions were obtained: (i) 0.8 g., b. p. 40—90°/0.5 mm., (ii) 1.0 g., b. p. 90—120° (mainly 116°)/0.5 mm., (iii) 0.7 g., b. p. 130—160°/0.5 mm., and a viscous residue (7 g.). Fraction (i) was a mixture of allyl phenyl ether and phenyl acetate. Fraction (ii) was *p*-allyloxyacetophenone, identified as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 188°.

Reaction of Allyl Phenyl Ether with a Small Amount of 70% Perchloric Acid in Acetic Anhydride.—Allyl phenyl ether (0.05 mole) in acetic anhydride (0.15 mole) was treated with two drops of 70% perchloric acid. The solution became red and the temperature rose from 15° to 40°. After 50 min. the solution was poured on to crushed ice and extracted twice with ether. The combined ethereal extracts were washed with sodium carbonate solution; a brown solid (0.3 g.), which gave an intensely fluorescent solution in ethyl alcohol, was then filtered off. The filtrate was then washed with water until neutral. The residue from the dried (Na_2SO_4) ethereal extract on fractionation yielded: (i) 2.2 g., b. p. 40—42°/0.5 mm., (ii) 0.5 g., b. p. 40—110°/0.5 mm., (iii) 2.8 g., b. p. 110—118°/0.5 mm. Fraction (i) redistilled at 178°/760 mm. and was allyl phenyl ether containing a very small amount of phenyl acetate. Fraction (iii) was *p*-allyloxyacetophenone, identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 187°.

Fission of Cinnamyl Phenyl Ether with Acetylium Perchlorate.—(a) *In nitromethane.* The ether (0.05 mole) was treated with silver perchlorate-acetyl chloride in nitromethane as described for allyl phenyl ether (above). After a further 40 min. the mixture was worked up in the usual way. A resin (9.2 g.) (Found: C, 73.1; H, 6.2%; *M*, 512) was obtained.

(b) *In presence of acetic anhydride.* The experiment was repeated but with acetic anhydride (0.05 mole) in the silver perchlorate-cinnamyl phenyl ether-nitromethane solution. The mixture was worked up after a further 30 min. The product was a brown resin (11 g.) (Found: C, 75.4; H, 6.2%; *M*, 349).

A similar resin (Found: C, 77.4; H, 8.9%; *M*, 320) was also obtained when the ether (0.025 mole) in acetic anhydride (0.2 mole) was treated with 2 drops of 70% perchloric acid. The mixture was kept for 50 min. before being worked up.

When but-2-enyl phenyl ether (0.05 mole) was treated as in (b) the product (9 g.) was a dark viscous oil from which phenyl acetate (2.7 g.), b. p. 80—84°/11 mm., was separated by fractional distillation.

Action of 70% Perchloric Acid on the Ethers in Nitromethane.—(a) *Allyl phenyl ether.* The ether (0.05 mole) in nitromethane (50 c.c.) was treated with 2 drops of 70% perchloric acid and the mixture heated on a steam-bath for 3 hr. The red solution was then cooled, poured into water, and extracted with ether. The ethereal extract was washed with sodium hydrogen carbonate solution and then with water until neutral. The residue after removal of solvent was separated into phenolic (3.1 g.) and non-phenolic (3.9 g.) portions by extracting its ethereal solution with 2*N*-sodium hydroxide. The phenolic portion was fractionated yielding: (i) 0.3 g., b. p. 90—110° (mainly 92°)/40 mm., and (ii) a viscous residue. Fraction (i) crystallised and was identified as phenol; the non-phenolic portion remained as a viscous gum.

(b) *Cinnamyl phenyl ether.* The addition of 2 drops of 70% perchloric acid to the ether (0.025 mole) in nitromethane (50 c.c.) produced an immediate deep red colour, and the temperature of the solution rose from 18° to 31°. The solution was left overnight and then heated on a steam-bath for 3 hr. On cooling the solution deposited a non-phenolic brownish red gum which dried to a "resin" (1.8 g.) in a vacuum-desiccator (Found: C, 82.6; H, 6.5%; *M*, 794). The mother-liquor was washed with sodium hydrogen carbonate solution, etc., and separated

into a phenolic portion (2.4 g.) (Found : C, 81.9; H, 7.3%; *M*, 324), and a non-phenolic portion (1.3 g.) (Found : C, 85.7; H, 8.0%; *M*, 467).

(c) *But-2-enyl phenyl ether*. The ether (0.05 mole) in nitromethane (50 c.c.) with 2 drops of 70% perchloric acid gave a golden yellow solution which darkened rapidly. After 4 hr. on a steam-bath the solution was poured into water, etc., and separated into phenolic (1.6 g.) and non-phenolic (3.7 g.) portions as described above. The latter remained as a viscous gum, whilst the phenolic portion gave on distillation phenol (0.5 g.), b. p. 80—82°/14 mm.

Fission of 1-Phenylallyl p-Nitrobenzoate.—(a) *In nitromethane*. The addition of 1 drop of 70% perchloric acid to a solution of 1-phenylallyl *p*-nitrobenzoate (1 g.) in nitromethane (10 c.c.) produced an immediate precipitate. This was filtered off and when recrystallised yielded *p*-nitrobenzoic acid, m. p. and mixed m. p. 234°, together with a little resinous material. The filtrate was diluted with ether, washed with aqueous sodium hydrogen carbonate, and water, and dried (Na₂SO₄). After removal of the solvents it yielded a "resin" (Found : C, 84.1; H, 6.8%; *M*, 840).

(b) *In acetic anhydride*. 1-Phenylallyl *p*-nitrobenzoate (1 g.) in acetic anhydride (10 c.c.) was treated with 1 drop of 70% perchloric acid. After 1 hr. the brown solution was added to cold water, extracted with ether, and separated into acidic and neutral portions with 2*N*-sodium hydroxide. The neutral portion (0.4 g.) was resinous (Found : C, 75.1; H, 6.8%; *M*, 383). The acidic portion was *p*-nitrobenzoic acid, m. p. and mixed m. p. 234°.

Reactions of Allyl Perchlorate.—(a) *In absence of other reactant*. Allyl bromide (0.05 mole) in nitromethane (20 c.c.) was added during 1 hr. to a cold (0—5°) solution of silver perchlorate (0.05 mole) in nitromethane; no gaseous product was evolved (manometer connected to apparatus) during this time or the next 90 min., after which the silver bromide was filtered off and the filtrate allowed to drop on to crushed ice. The filtrate was extracted with ether, and washed with sodium hydrogen carbonate solution, and then with water. The washings were combined with the aqueous layer, and the fraction that distilled below 98° was collected and added to the residue from the evaporated ethereal extract. The mixture with bromine yielded 2 : 3-dibromopropyl alcohol (4.2 g.), b. p. 212°, which was separated by distillation and identified by the m. p. (80°) of its phenylurethane.

(b) *With acetic anhydride*. Allyl bromide (0.05 mole) in acetic anhydride (20 c.c.) was added to a cold (0—5°) solution of silver perchlorate (0.05 mole) in acetic anhydride (20 c.c.) during 1 hr. After a further 70 min., the silver bromide was filtered off and the reaction product treated as above, except that sodium carbonate solution was used as the neutralising agent. On fractionation the residue (4.6 g.) gave : (i) 0.4 g., b. p. 94—102°, (ii) 2.3 g., b. p. 102—107° (mainly 104°), (iii) 0.7 g., b. p. 108—110°, and a black viscous residue (1 g.). Fraction (ii) was allyl acetate.

(c) *With m-xylene*. Silver perchlorate (0.05 mole) in *m*-xylene (0.05 mole) and nitromethane (70 c.c.) was treated during 1 hr. with allyl bromide (0.05 mole) in nitromethane (20 c.c.). After 2 hr. at 0—5° the silver halide was filtered off and the reaction product worked up in the usual way. A resinous product (Found : C, 87.4; H, 9.4%; *M*, 399) was obtained.

(d) *With mesitylene*. The experiment described under (c) was repeated with mesitylene (0.05 mole) in place of *m*-xylene. A "resin" (4 g.), insoluble in nitromethane, was obtained (Found : C, 86.8; H, 9.9%; *M*, 392). Viscous black tars were similarly obtained from benzene (0.75 mole) and anisole (0.05 mole).

"But-2-enyl Perchlorate".—But-2-enyl chloride (0.05 mole) in nitromethane (25 c.c.) was added to a cooled (0—5°) solution of silver perchlorate (0.05 mole) in nitromethane (70 c.c.). After 45 min. the silver chloride was filtered off and the filtrate worked up in the usual way. A black resin insoluble in nitromethane (Found : C, 80.0; H, 10.4%; *M*, 433) was isolated.

"Cinnamyl Perchlorate".—(a) Cinnamyl chloride (0.05 mole) in nitromethane (20 c.c.) was added during 30 min. to a cooled (0—5°) solution of silver perchlorate (0.05 mole) in nitromethane (75 c.c.). After a further hour the silver chloride was filtered off, the brown solution falling on to crushed ice; the silver halide was washed with ether. A yellow solid (2.4 g.), insoluble in both the ethereal and the aqueous layer separated; this was collected, washed with water and then with ether, and then dried (Found : C, 70.0; H, 5.6%; *M*, 865).

Repetition of the experiment in an atmosphere of dry nitrogen gave a buff resin (Found : C, 82.9; H, 6.7%; *M*, 428). The use of cinnamyl bromide as in (a) gave a yellow resin (Found : C, 84.9; H, 7.3%; *M*, 837).

(b) Repetition of experiment (a) but with cinnamyl bromide in presence of anisole (0.05 mole) and phenol (0.05 mole) gave an orange resin (Found : C, 82.4; H, 7.1; OMe, 11.2%; *M*, 438) and a sodium hydroxide-soluble orange resin (Found : C, 84.2; H, 6.7%; *M*, 330), respectively.

Allylmesitylene.—The Grignard reagent, from magnesium (4.9 g.) and bromomesitylene (40 g.) in ether (200 c.c.), and allyl bromide (24.2 g.) were refluxed for 6 hr. and then set aside overnight. Decomposition with ice and ammonium chloride gave a product which was repeatedly fractionated and finally distilled over sodium giving *allylmesitylene* (6.1 g.), b. p. 97—98°/10 mm. (Found : C, 89.8; H, 9.9. $C_{12}H_{16}$ requires C, 90.0; H, 10.0%).

When the hydrocarbon (1.5 g.) in nitromethane (10 c.c.) was treated with 1 drop of 70% perchloric acid the mixture darkened slowly and after a few hours tarry material separated.

Reaction of Cinnamoyl Perchlorate with Anisole.—The experiments, with silver perchlorate and anisole, were carried out as described in Part IV (*J.*, 1951, 529). The *p*-methoxyphenyl styryl ketone was identified by m. p. and mixed m. p. (107°).

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