

618. Polymerisation of Benzyl and Some Substituted Benzyl Perchlorates.

By P. F. G. PRAILL.

Solutions of benzyl perchlorate in nitromethane deposit polymer of relatively low molecular weight. If an aromatic hydrocarbon is present in the mixture, the diarylmethane is formed. The polymer contains benzyl groups since with aluminium chloride in benzene it gives diphenylmethane. Substituted benzyl perchlorates behave similarly.

RECENT work on the polymerisation of benzyl derivatives^{1,2} prompts us to record some observations with benzyl perchlorates.³ The formation of a resinous polymer by a solution of benzyl perchlorate in nitromethane is doubtless an example of the well-known polymerisation of benzyl derivatives by strong acids. Indeed, it has been shown⁴ that perchloric acid polymerises benzyl alcohol in a similar way to sulphuric acid. Among the more recent examples of polymerisations of this type are the decomposition of benzyl toluene-*p*-sulphonates⁵ and the polymerisation of benzyl halides by various Lewis acids.^{1,2,6}

We found that when benzyl bromide was added to a solution of silver perchlorate in nitromethane in the presence of an aromatic component such as benzene or toluene, nuclear substitution occurred to give diphenylmethane or phenyltolylmethane, respectively. In the absence of the hydrocarbons, a polymeric substance was adsorbed on the silver bromide. The polymer had properties similar to those mentioned in the works quoted above, but its molecular weight (cryoscopic, 700—800) was somewhat lower.

The material was depolymerised when a dilute solution in benzene was refluxed with aluminium chloride;⁷ a considerable amount of the original material was accounted for by the diphenylmethane produced. This indicates that, in the polymer, the benzyl group remains essentially unmodified, in agreement with the structure proposed by Haas *et al.*²

We have found that the necessity for free *ortho*- or *para*-positions for polymerisation is excluded by the ready polymerisation of 2 : 4 : 6-trimethylbenzyl perchlorate. As in the work of Haas and others, we have found that electron-releasing substituents such as *p*-methoxy increase the ease of polymerisation, and that polymerisation of the 4-chloro-derivative still occurs. In general, the polymers from these compounds resemble that from benzyl perchlorate, the molecular weights indicating 4—7 monomer units.

p-Nitrobenzyl perchlorate in nitromethane does not polymerise, but instead is largely converted into *p*-nitrobenzaldehyde. Ingold and Ingold⁸ obtained this aldehyde instead of the expected 4-nitrobenzyl fluoride on distilling *p*-nitrobenzyltrimethylammonium fluoride. In our case, it seems that the aldehyde results from oxidation by perchloric acid since it is also formed in absence of oxygen. Further, the aldehyde is not produced in systems that contain magnesium oxide, which would neutralise any perchloric acid, the water formed being removed by the resulting magnesium perchlorate. From some of the experiments a small amount of di-4-nitrobenzyl ether was obtained. These observations form an interesting contrast to those in which metal halides and 4-nitrobenzyl halides are allowed to react under similar conditions. It has been shown⁹ that the nitrobenzyl

¹ Valentine and Winter, *J.*, 1956, 4768.

² Haas, Livingston, and Saunders, *J. Polymer Sci.*, 1955, **15**, 503.

³ Burton and Prail, *J.*, 1953, 827; Prail, Ph.D. Thesis, London, 1954.

⁴ Shriner and Berger, *J. Org. Chem.*, 1941, **6**, 305.

⁵ Kochi and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3443.

⁶ Korshak, Lebedev, and Tsipershtein, *J. Gen. Chem. (U.S.S.R.)*, (U.S. transl.), 1949, **19**, 647; Illari, *Ann. Chim. (Italy)*, 1950, **40**, 483.

⁷ Wertyporoch and Farnik, *Annalen*, 1931, **491**, 265.

⁸ Ingold and Ingold, *J.*, 1928, 2249.

⁹ Boeseken, *Rec. Trav. chim.*, 1904, **23**, 98.

halide can be recovered unchanged and this may be partly attributed to a preferential interaction of the metal halide with the nitro-group rather than with the halogen atom.¹⁰

During our experiments with 4-nitrobenzyl perchlorate we observed formation of variable amounts of *p*-nitrobenzaldehyde di-4-nitrobenzyl acetal, almost certainly formed as a by-product during the working-up.

The formation of polymers under acid conditions and the influence of various substituents on the ease of polymerisation indicate that carbonium ions may be involved. However, as Valentine and Winter¹ observed, the exact nature of the reaction has not yet been elucidated.

EXPERIMENTAL

Materials.—Silver perchlorate was treated as described previously.¹¹ Nitromethane was dried (CaCl₂) and redistilled. 4-Methoxybenzyl chloride was prepared by the method of Livshits *et al.*¹² and 2 : 4 : 6-trimethylbenzyl chloride was by the method of Varon and Bolle.¹³

General Procedure.—The benzyl chloride or bromide (0.05 mole), or a solution of the halide in nitromethane, was added during 10–20 min. to a chilled (5–15°) solution of silver perchlorate (0.05 mole) in nitromethane (94 g.). Immediate precipitation of silver halide occurred. The mixture was left at room temperature for 18–24 hr. and then filtered through a sintered filter into ice-water. After being washed with chloroform and water the solid material was dried. The filtrate was extracted thrice with chloroform, and the combined extracts were washed with water until free from acid, dried (Na₂SO₄), and evaporated. Any nitromethane was removed at the water-pump and the gummy, or resinous, residue was mixed with any polymer extracted from the silver halide. The latter was extracted (Soxhlet) with chloroform and any adsorbed material was isolated in the normal way. Recovery of silver halide was 98–100%.

Benzyl Perchlorate.—About 80% of the total polymeric material was extracted from the silver halide. The polymer was a light brown, brittle resin (4.0–4.2 g.) (Found: C, 89.2; H, 6.4; Cl, 1.9%; *M*, 710. Calc. for C₇H₆: C, 93.3; H, 6.7%). Its ultraviolet spectrum (in CHCl₃) had a broad absorption band at 250–290 mμ, with small peaks at 264 and 270 mμ, the latter being the main peak. The specific extinction coefficient, *E* [(optical density)/(path length in cm.) (concn. in g. per l.)] was 5.0. Apart from the absence of a peak at 266 mμ this is in close agreement with the observations by Valentine and Winter.¹

As other workers have found, attempts to obtain useful information about structure by oxidative degradation were not successful. Pyrolysis of the polymer gave a colourless liquid which was predominantly toluene, b. p. 110°, *n*_D²⁰ 1.5063, and some intractable higher-boiling, viscous, brown material.

Some of the polymer (5.0 g.) was dissolved in benzene (200 c.c.) and heated under reflux for 2 hr. with aluminium chloride (10 g.). The mixture was worked up in the usual way. Distillation of the product gave a pale yellow oil (6.2 g.), b. p. 138–144° (mainly 138–140°)/18 mm., which was mainly diphenylmethane (m. p. and mixed m. p. 23°). It also gave some pale yellow, rectangular plates, m. p. 205°, that did not depress the m. p. of anthracene.

Steam-distillation of the main gummy residue gave some yellow oil (0.5 g.) which also yielded a small quantity of impure anthracene (m. p. and mixed m. p.).

4-Methoxybenzyl Perchlorate.—This preparation was carried out in the presence of magnesium oxide (2.0 g.) in an attempt to avoid catalytic polymerisation of the halide by liberated perchloric acid. The mixture was left for 40 min. at –5° to 2°. Hardly any of the light orange polymer (5.2 g.) was adsorbed on the silver halide. The resin (Found: C, 78.5; H, 6.6; OMe, 21.2%; *M*, 790. Calc. for C₈H₈O: C, 80.0; H, 6.7; OMe, 25.8%) gave a broad absorption band in chloroform at 258–298 mμ with a single peak at 280 mμ. The specific extinction coefficient was high, as expected, *E* = 22.6.

¹⁰ Olivier and Berger, *Rec. Trav. chim.*, 1926, **45**, 710.

¹¹ Burton and Prail, *J.*, 1950, 2034.

¹² Livshits, Bazilevskaya, Bainova, Dobrovinskaya, and Preobrazhenskii, *J. Gen. Chem. (U.S.S.R.)*, 1947, **17**, 1671.

¹³ Varon and Bolle, *Compt. rend.*, 1937, **204**, 1826.

2 : 4 : 6-*Trimethylbenzyl Perchlorate*.—Left at 0—5° for 1 hr. this gave a pale orange gum (5.0 g.) (Found : C, 87.3; H, 8.9%; *M*, 555. Calc. for $C_{10}H_{12}$: C, 90.9; H, 9.1%), about 8% of which was adsorbed on the silver chloride; it had ultraviolet adsorption at 255—300 $m\mu$ with a single peak at 273 $m\mu$ (*E* 10.3).

4-*Chlorobenzyl Perchlorate*.—60—70% of the polymer was adsorbed on the silver halide. The gummy polymer (6.4 g.) contained a small amount of aldehyde. The latter was removed by repeated extraction of the polymer with hot ethanol; it gave a semicarbazone, m. p. 230° (*p*-chlorobenzaldehyde semicarbazone, m. p. 232°). The extracted polymer was a dark brown resin (Found : C, 63.5; H, 3.9; Cl, 28.8%; *M*, 665. Calc. for $(C_7H_6Cl)_n$: C, 66.9; H, 4.8; Cl, 28.3%). In chloroform the material had a broad absorption band at 250—295 $m\mu$ with a maximum at 271 $m\mu$ (*E* 8.3).

The above results indicate that the polymers probably contain oxygen. However, no attempt was made to purify the resins.

4-*Nitrobenzyl Perchlorate*.—Here the reaction product (7.5 g.) was a waxy solid, almost completely soluble in hot ethanol though a small amount was insoluble (m. p. 206°). The solution gave a 2 : 4-dinitrophenylhydrazone equivalent to 4.2 g. of *p*-nitrobenzaldehyde. The 2 : 4-dinitrophenylhydrazone crystallised from xylene as orange-yellow needles, m. p. 305° (decomp.) (Vogel¹⁴ gives m. p. 320°).

The alcoholic solution also deposited some 4-nitrobenzyl alcohol (m. p. and mixed m. p.) on storage.

Experiments carried out in a nitrogen atmosphere gave similar results.

The material, m. p. 206°, proved to be *p*-nitrobenzaldehyde di-4-nitrobenzyl acetal.

When the reaction was carried out in the presence of an excess of magnesium oxide (0.1 mole), and the suspension was shaken mechanically for 24 hr., only a trace of aldehyde was detected. The product was a sticky solid (7.7 g.); crystallised from benzene and from water it gave colourless needles, m. p. and mixed m. p. with 4-nitrobenzyl alcohol, 92—93°.

From a similar experiment with magnesium oxide the product was allowed to crystallise slowly from ethanol; almost colourless prisms (0.9 g.) of di-4-nitrobenzyl ether were obtained. Recrystallisation from benzene and then from ethanol gave prisms, m. p. 97—98° (Found : C, 58.4; H, 4.0; N, 10.3. Calc. for $C_{14}H_{12}O_5N_2$: C, 58.3; H, 4.2; N, 9.8%).

p-*Nitrobenzaldehyde Di-4-nitrobenzyl Acetal*.—*p*-Nitrobenzaldehyde (0.75 g.) and 4-nitrobenzyl alcohol (1.5 g.) were heated together at 95—100° for 3 hr. The hard yellow *acetal* was boiled with 96% ethanol (20 c.c.), filtered, and washed with hot ethanol. It melted at 209—210° (yield 2.0 g.); crystallisation from acetone gave colourless needles, m. p. 213° (Found : C, 57.1; H, 3.8; N, 9.7%; *M*, 410. $C_{21}H_{17}O_8N_3$ requires C, 57.4; H, 3.9; N, 9.6%; *M*, 439).

Dissolving this material in hot 60—70% acetic acid reconverted it into the aldehyde and alcohol.

The author is indebted to the University of London for a grant from the Central Research Fund. He also thanks Professor H. Burton for his encouragement and Miss M. Seidenberg for technical assistance.

QUEEN ELIZABETH COLLEGE,
CAMPDEN HILL ROAD, LONDON, W.8.

[Received, March 20th, 1957.]

¹⁴ Vogel, "Practical Organic Chemistry," Longmans, London, 1948.