587. *Interaction of Acrylonitrile and Benzaldehyde.*

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The interaction of acrylonitrile and benzaldehyde in the presence of methanol, piperidine, and 2-nitropropane has been studied and the nature of the products elucidated.

Bruson and Riener [1] showed that reaction of acrylonitrile with benzaldehyde in the presence of aqueous Triton B gave two products. Wasserman, Suryanarayana, and Grassetti [2] showed that these had the structures (I) and (II). Before the paper of Wasserman *et al.* appeared we had independently elucidated these structures by a similar method. We found that both compounds (I) and (II) gave benzaldehyde when boiled with alkali and were converted into a chloro- (IV) and a bromo-nitrile (V) by the appropriate hydrogen halide. The bromo-nitrile was hydrolysed to the alcohol (VI) which on oxidation gave benzylidenecyanoacetic acid (X).

The mechanism proposed [2] to account for the formation of the nitriles (I) and (II) may be regarded as an interference by benzaldehyde at the second step in the cyanoethylation of water; that is, benzaldehyde and protons compete for addition to the intermediate anion $^{-}CH(CN){\cdot}CH_2{\cdot}OH$. Since similar intermediate species have been postulated as existing in the cyanoethylation of methanol,[3] nitroalkanes,[4] and amines [3,5] it was of interest to carry out the cyanoethylation of methanol, 2-nitropropane, and piperidine in the presence of benzaldehyde to seek evidence for a similar interference.

$CHPh{:}C(CN){\cdot}CH_2{\cdot}O{\cdot}[CH_2]_2{\cdot}CN$ (I)

$CHPh{:}C(CN){\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C(CN){:}CHPh$ (II)

$CHPh{:}C(CO_2H){\cdot}CH_2Cl$ (III)

$CHPh{:}C(CN){\cdot}CH_2R$
(IV) $R = Cl$
(V) $R = Br$
(VI) $R = OH$
(VII) $R = OMe$
(VIII) $R =$ piperidino
(IX) $R = CMe_2{\cdot}NO_2$

$CHPh{:}C(CN){\cdot}CO_2H$ (X)

$HO{\cdot}CHPh{\cdot}CH(CN){\cdot}CH_2R$
(XI) $R = OMe$
(XII) $R =$ piperidino
(XIII) $R = CMe_2{\cdot}NO_2$

When a mixture of benzaldehyde, methanol, and Triton B or sodium methoxide had been treated with acrylonitrile, a large amount of benzaldehyde was recovered, and some methoxyproponitrile was obtained, together with small amounts of α-methoxymethylcinnamonitrile (VII) and β-hydroxy-α-methoxymethyl-β-phenylpropionitrile (XI). Analyses, Zeisel determinations, and infrared spectra were consistent with these formulations. Only the nitrile (VII) gave benzaldehyde when boiled with aqueous sodium hydroxide, and only it (VII) gave the bromo-nitrile (V) on treatment with hydrobromic acid.

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[1] Bruson and Riener, U.S.P. 2,353,687/1944.
[2] Wasserman, Suryanarayana, and Grassetti, *J. Amer. Chem. Soc.*, 1956, **78**, 2808.
[3] Ogata, Okano, Furuya, and Tabushi, *J. Amer. Chem. Soc.*, 1956, **78**, 5426.
[4] Bergmann, Ginsberg, and Pappo, *Org. Reactions*, 1959, **10**, 179.
[5] Taylor, Selcer, Montgomery, and Hughes, *J. Amer. Chem. Soc.*, 1959, **81**, 5333.

The nitrile (XI) was characterised as an alcohol by the formation of a 3,5-dinitrobenzoate and was readily dehydrated to give compound (VII).

Piperidine and benzaldehyde, in presence of Triton B, reacted exothermally with acrylonitrile. Benzaldehyde was recovered from the mixture together with 1-(cyanoethyl)piperidine and a small amount of a mixture of two bases that could not be separated by distillation. The mixture was converted into the oxalates, and analysis indicated that the two compounds (VIII) and (XII) were present in the proportion 1 : 2. Dehydration of the mixture gave a single substance (VIII) identical with an authentic specimen prepared from the bromo-nitrile (V) and piperidine.

A mixture of benzaldehyde, 2-nitropropane, and Triton B in dioxan was then treated with acrylonitrile. Benzaldehyde and 2,2′-cyanoethyl-2-nitropropane were isolated, together with a high-boiling alcohol $C_{13}H_{16}N_2O_3$. The alcohol was readily dehydrated to an olefin which gave benzaldehyde when boiled with aqueous sodium hydroxide. By analogy with the previous reactions these two compounds were assigned the structures (XIII) and (IX), respectively.

Thus, the cyanoethylation of methanol, piperidine, and 2-nitropropane in the presence of benzaldehyde proceeds normally, but a small amount of the aldehyde enters into reaction with a cyanoethylation intermediate to produce two compounds, an alcohol, and the corresponding cinnamonitrile. According to Ogata *et al.*[3] the rate-determining step in the cyanoethylation of methanol is the attack of the methoxide ion on acrylonitrile, and this is followed by rapid protonation of the intermediate carbanion. Similarly, in the case of amines, the slow step is the attack of the amine on the nitrile, being followed by a rapid proton-transfer process.[3,5] Thus in both these cases, and probably also for a nitroalkane,[4] the benzaldehyde is in competition with a rapid protonation. Reaction of acrylonitrile with water is slow and, since cyanoethylation of primary alcohols is generally fast,[6] the rate-determining step in the formation of di-(2-cyanoethyl) ether is probably the formation of ethylene cyanohydrin. Reaction of acrylonitrile with water and benzaldehyde is very fast and gives a high yield of products containing benzaldehyde. This suggests that the rate-controlling step is the protonation of the intermediate $^{-}CH(CN){\cdot}CH_2{\cdot}OH$, because the relatively long life of this carbanion permits considerable reaction with benzaldehyde. The extent to which benzaldehyde " interferes " in a cyanoethylation may thus give some measure of the rate of protonation of the intermediate carbanion.

In the new reactions just described, the alcohols corresponding to the substituted cinnamonitriles have always been isolated, and their ease of dehydration suggests that they are the true products of these reactions, and that the unsaturated compounds arise during the isolation involving high-vacuum distillation (water is formed during these distillations). It is thus probable that these reactions proceed without an intermediate dehydration step.

EXPERIMENTAL

Reaction between Benzaldehyde and Acrylonitrile.—Bruson and Riener's method [1] gave the ethers (I), b. p. 158—163°/0·3 mm., and (II), needles (from methanol), m. p. 73—74°.

Alkaline Hydrolysis of Compound (I).—This nitrile (1·3 g.) and 2N-aqueous sodium hydroxide (13 ml.) were boiled and the volatile product was distilled in steam. Ammonia was detected in the distillate and the oil therein was converted into a 2,4-dinitrophenylhydrazone (0·7 g.), m. p. 242—244°, undepressed on admixture with the authentic derivative from benzaldehyde. The compound (II) similarly gave benzaldehyde 2,4-dinitrophenylhydrazone.

Treatment of Compound (I) *with Hydrochloric Acid.*—The nitrile (7·0 g.) was heated for 3 days at 100° in a sealed tube with acetic acid (15 ml.) and concentrated hydrochloric acid (15 ml.). The mixture was cooled and filtered, to give *α-chloromethylcinnamic acid* (III) (1·3 g.), plates, m. p. 158—159° (from aqueous methanol) (Found: C, 61·4; H, 4·9; Cl, 18·0. $C_{10}H_9ClO_2$ requires C, 61·1; H, 4·6; Cl, 18·1%). The filtrate was evaporated, and the residue separated into the same acid (0·7 g.), m. p. 140—150°, and neutral *α-chloromethylcinnamonitrile* (IV) (3·3 g.), prisms, m. p. 44—45·5° [from light petroleum (b. p. 60—80°)] (Found: C, 67·7; H, 4·7; Cl,

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[6] Bruson and Riener, *J. Amer. Chem. Soc.*, 1943, **65**, 23.

19·6; N, 7·85. $C_{10}H_8ClN$ requires C, 67·6; H, 4·6; Cl, 20·0; N, 7·9%). Compound (IV) gave a *thiouronium derivative*, plates (from ethanol–ether), m. p. 194—195° (Found: C, 52·0; H, 4·8; Cl, 14·1; N, 16·4; S, 12·7. $C_{11}H_{12}ClN_3S$ requires C, 52·1; H, 4·7; Cl, 14·0; N, 16·6; S, 12·6%).

In another experiment a small amount of an acid, $C_{13}H_{13}NO_3$, was isolated as the S-*benzylthiouronium salt*, m. p. 142—143° (Found: C, 63·3; H, 5·86; N, 9·9; S, 8·6. $C_{13}H_{13}NO_3,C_8H_{10}N_2S$ requires C, 63·5; H, 5·79; N, 10·6; S, 8·1%).

Compound (II) similarly yielded the acid (III) and the nitrile (IV).

Hydrolysis of the Bromo-compound (V).—The solid [2] (5·0 g.) was heated with sodium carbonate (3·75 g.) in ethanol (40 ml.) and in water (20 ml.) for 4 hr., then evaporated to a low bulk. The salts were dissolved in water and the oil was isolated by extraction with ether and distillation, to give α-hydroxymethylcinnamonitrile (VI) (2·25 g.), b. p. 136—139°/0·1 mm. (lit.,[2] b. p. 135—140°/0·2 mm.) (Found: C, 75·9; H, 6·45; N, 8·1. Calc. for $C_{10}H_9NO$: C, 75·5; H, 6·45; N, 8·8%). The 3,5-*dinitrobenzoate* formed needles, m. p. 151—152°, from aqueous acetone (Found: C, 57·7; H, 3·2; N, 11·9. $C_{17}H_{11}N_3O_6$ requires C, 57·8; H, 3·1; N, 11·9%).

Oxidation of the Alcohol (VI).—The alcohol (14·4 g.) in acetone (432 ml.) was treated with chromium trioxide (11·7 g.) and sulphuric acid (10·2 ml.) in water (48 ml.) during 1 hr. at 20°. After a further 1 hr. the mixture was poured into water (864 ml.), and the acetone evaporated under reduced pressure at 20°. The solution was kept at 0° overnight and the crystalline precipitate (11·5 g.) filtered off and triturated with benzene, to yield benzylidenecyanoacetic acid (10·0 g.), m. p. 182—184°; this and its methyl ester, m. p. 89—90°, were identical with authentic specimens. The benzene extract yielded an aldehyde (1·1 g.), prisms, m. p. 99—100° (from aqueous methanol) (Found: C, 76·8; H, 4·6; N, 8·9. Calc. for $C_{10}H_7NO$: C, 76·5; H, 4·5; N, 8·9%) [2,4-dinitrophenylhydrazone, scarlet needles, m. p. 283—284° (decomp.), from 2-ethoxyethanol (Found: C, 57·5; H, 3·95; N, 19·5. Calc. for $C_{16}H_{11}N_5O_4$: C, 57·0; H, 3·27; N, 20·1%)] (lit.,[2] m. p. 99—100° and 274—275°).

Reaction of Benzaldehyde, Methanol, and Acrylonitrile.—Acrylonitrile (53 g.) was added dropwise to benzaldehyde (53 g.) in methanol (50 ml.) containing Triton B (40% w/v aqueous solution; 5 ml.) during 25 min. at 35—40°. The mixture was left at room temperature for 16 hr., and then poured into dilute hydrochloric acid. The products were extracted with ether and distilled, to give fractions, (i) b. p. <165°/15 mm., (ii) b. p. 165—190°/16 mm., and (iii) (7·5 g.) b. p. 190—210°/15 mm. Redistillation of (i) gave a fraction (51 g.), b. p. 168—176°/760 mm., consisting of methoxypropionitrile (40%) (lit.,[7] b. p. 164°) and benzaldehyde (60%). Redistillation of fraction (ii) gave *α-methoxymethylcinnamonitrile* (5·0 g.), b. p. 164—166°/15 mm., n_D^{21} 1·5430 (Found: C, 75·6; H, 6·9; N, 8·4; OMe, 17·4. $C_{11}H_{11}NO$ requires C, 76·3; H, 6·4; N, 8·1; OMe, 17·9%). Redistillation of fraction (iii) gave *β-hydroxy-α-methoxymethyl-β-phenylpropionitrile* (6·0 g.), b. p. 200—202°/13 mm., n_D^{22} 1·5272 (Found: C, 69·6; H, 6·3; N, 7·7; OMe, 14·9. $C_{11}H_{13}NO_2$ requires C, 69·4; H, 6·3; N, 7·4; OMe, 16·5%) [3,5-*dinitrobenzoate* needles, m. p. 139·5—141°, from aqueous acetone (Found: C, 56·6; H, 4·2; N, 10·85; OMe, 8·2. $C_{18}H_{15}N_3O_7$ requires C, 56·1; H, 3·9; N, 10·9; OMe, 8·05%)].

A similar result was obtained when the reaction was carried out with sodium methoxide in place of Triton B.

Hydrolysis of α-Methoxymethylcinnamonitrile.—The nitrile (2·7 g.), 48% w/v hydrobromic acid (10·8 ml.), and acetic acid (10·8 ml.) were heated at 100° for 10 hr., then poured into water (200 ml.). The oil solidified, to give α-bromomethylcinnamonitrile, m. p. 52—54°, identical with the specimen previously prepared.

Dehydration of β-Hydroxy-α-methoxymethyl-β-phenylpropionitrile.—The nitrile (1·8 g.) in dry pyridine (3·0 ml.) was heated with toluene-*p*-sulphonyl chloride (2·0 g.) at 100° for 30 min. The product was isolated and distilled, to give α-methoxymethylcinnamonitrile, b. p. 158—162°/12 mm., identical with the sample previously prepared.

α-Piperidinomethylcinnamonitrile Oxalate.—α-Bromomethylcinnamonitrile (1·0 g.) and piperidine (1·0 ml.) were heated at 100° for 30 min. Dilute hydrochloric acid was added and the mixture cooled in ice. The salt was filtered off and converted into the *hydrogen oxalate* (0·5 g.), m. p. 225—226° (decomp.) (from water) (Found: C, 65·2; H, 6·5; N, 8·6%; equiv., 158 and 326. $C_{15}H_{18}N_2,C_2H_2O_4$ requires C, 64·9; H, 6·3; N, 8·8%; equiv., 158 and 316).

Reaction of Benzaldehyde, Piperidine, and Acrylonitrile.—Acrylonitrile (26·5 g.) was added

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[7] MacGregor and Pugh, *J.*, 1945, 536.

dropwise at 30—35° during 30 min. to benzaldehyde (53 g.) and piperidine (42·5 g.) in dioxan (100 ml.) containing Triton B (40% w/v aqueous solution; 2·5 ml.). After 1 hr. the solution was poured into water and the products were isolated by extraction with ether and distillation, to give (i) benzaldehyde, (ii) 1-2′-cyanoethylpiperidine (20·24 g.), b. p. 109—114°/13 mm. (lit.,[8] b. p. 116°/18 mm.), (iii) an intermediate fraction, b. p. 114—140°/13 mm., and (iv) a fraction (4·1 g.), b. p. 140°/15 mm. to 200°/0·2 mm. Fraction (iv), a mixture, lost water on attempted refractionation and was therefore converted into the oxalate (3·2 g.), m. p. 174—177° (decomp.). Analysis showed this to be a 1 : 2 mixture of the oxalates of α-piperidinomethylcinnamonitrile and β-hydroxy-β-phenyl-α-piperidinomethylpropionitrile [Found: C, 62·1; H, 6·8; N, 8·5%; H_2O, 0; equiv., 166. Calc. for $1(C_{15}H_{18}N_2,C_2H_2O_4) + 2(C_{16}H_{20}N_2O,C_2H_2O_4)$: C, 62·2; H, 6·5; N, 8·5%; equiv., 164].

The mixed oxalates (0·5 g.) in dry pyridine (10 ml.) were heated with toluene-*p*-sulphonyl chloride (0·9 g.) at 100° for 30 min. Water (10 ml.) was added and the solution evaporated under reduced pressure. The residue was treated in water (3 ml.) with an excess of oxalic acid, and the precipitated salt (0·35 g.) was recrystallised, giving an oxalate, m. p. 225—226° (decomp.), undepressed by the oxalate of 1-piperidinomethylcinnamonitrile described above.

Reaction of Benzaldehyde, 2-Nitropropane, and Acrylonitrile.—Acrylonitrile (53 g.) was added dropwise with stirring during 50 min. at 30—35° to benzaldehyde (106 g.), 2-nitropropane (89 g.), dioxan (150 ml.), and Triton B (40% w/v aqueous solution; 5·0 ml.). The mixture was left at room temperature overnight, then poured into water, and the resultant oil extracted with ether. The combined extracts were dried and distilled, to give fractions, (i) (24·4 g.) chiefly 2-nitropropane, b. p. <70°/20 mm., (i) benzaldehyde (67·6 g.), b. p. 70—80°/20 mm., (iii) (10·8 g.) b. p. 80—151°/20 mm., (iv) 2-2′-cyanoethyl-2-nitropropane (71·5 g.), b. p. 151—153°/17 mm., n_D^{21} 1·4509 (lit.,[9] b. p. 135—138°/6 mm.), (v) (12·9 g.), b. p. 60—195°/0·2 mm., n_D^{21} 1·4790, and (vi) (23·6 g.), b. p. 195—202°/0·2—0·25 mm., n_D^{21} 1·5308 (water was formed during the distillation of this fraction).

Fraction (vi) solidified and was crystallised successively from ether and light petroleum (b. p. 100—120°), to give *α-hydroxybenzyl-γ-methyl-γ-nitrovaleronitrile* as needles, m. p. 118·5—120° (Found: C, 62·8; H, 6·7; N, 11·3. $C_{13}H_{16}N_2O_3$ requires C, 62·9; H, 6·4; N, 11·3%). The 3,5-*dinitrobenzoate* formed needles, m. p. 184—185°, from 2-ethoxyethanol (Found: C, 54·3; H, 4·4; N, 12·7. $C_{20}H_{18}N_4O_8$ requires C, 54·3; H, 4·1; N, 12·7%).

This alcohol (16 g.) was heated with toluene-*p*-sulphonyl chloride (9·0 g.) in pyridine (48 ml.) at 100° for 1 hr., then poured into dilute hydrochloric acid. The product was isolated by extraction with ether and distilled. The fraction (3·4 g.), b. p. 160—165°/0·25 mm., crystallised from light petroleum (b. p. 60—80°), giving α-(*2-methyl-2-nitropropyl*)*cinnamonitrile* as needles, m. p. 70—71·5° (Found: C, 67·7; H, 6·25; N, 12·4. $C_{13}H_{14}N_2O_2$ requires C, 67·8; H, 6·1; N, 12·2%), which gave benzaldehyde when boiled with aqueous sodium hydroxide.

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[8] Clemo, Ormston, and Ramage, *J.*, 1931, 3185.

[9] Hopff, von Schickh, and Wiest, G.P. 851,342/1952.