426. *The Preparation of Some Substituted Butadienes.*

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1-Cyanobuta-1 : 3-diene is prepared by pyrolysis of esters of 1-cyanobut-3-en-2-ol, acetaldol cyanohydrin, and crotonaldehyde cyanohydrin. 2-Chloro-1-cyanobuta-1 : 3-diene is similarly obtained by pyrolysis of 1-acetoxy-2-chloro-1-cyanobut-2-ene, and the alkyl buta-1 : 3-diene-1-carboxylates from alkyl 1-acetoxybut-2-ene-1-carboxylates.

Burns, Jones, and Ritchie (*J.*, 1935, 400, 714) showed that α-hydroxy-esters and -nitriles could conveniently be converted into the corresponding αβ-unsaturated compounds by pyrolysis of their acyl derivatives. We have applied this procedure to the preparation of a number of conjugated dienes, *viz.*, buta-1 : 3-diene and its 1-cyano-, 2-chloro-1-cyano-, and 1-carbalkoxy-derivatives. The preparation of buta-1 : 3-diene by pyrolysis of 2 : 3-diacetoxybutane was subsequently developed in America on a semi-commercial scale and an excellent account of the development work is already available (Morell, Geller, and Lathrop, *Ind. Eng. Chem.*, 1945, **37**, 877). Others of our results have already been very briefly described elsewhere (B.P. 483,989, 515,737, 520,272, 523,080) but they are now being presented in greater detail, together with some related work.

1-Cyanobuta-1 : 3-diene was first obtained by Coffmann (*J. Amer. Chem. Soc.*, 1935, **57**, 1981) in poor yield by reaction of 1-chlorobuta-2 : 3-diene with sodium cyanide. We obtained the diene in good yields by the following three routes :

(i) $CH_2Cl{\cdot}CH(OH){\cdot}CH{:}CH_2 \longrightarrow CN{\cdot}CH_2{\cdot}CH(OAc){\cdot}CH{:}CH_2$

(ii) $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO \longrightarrow CH_3{\cdot}CH(OAc){\cdot}CH_2{\cdot}CH(OAc){\cdot}CN \longrightarrow CH_2{:}CH{\cdot}CH{:}CH{\cdot}CN$

(iii) $CH_3{\cdot}CH{:}CH{\cdot}CHO \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CH(OAc){\cdot}CN$

Since this work was completed, two variants of route (i) have been published (Wingfoot, U.S.P. 2,473,486; Bissinger *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 2955). On using route (ii), two isomeric by-products were obtained with the composition ($C_7H_9O_2N$) of a compound formed by the fission of one molecule of acetic acid, but these products were not characterised. The third route, in which the elimination of acetic acid from the acetate of crotonaldehyde cyanohydrin was accompanied by migration of the double bond, was the most convenient. This method has since been used by Snyder, Stewart, and Myers (*J. Amer. Chem. Soc.*, 1949, **71**, 1055) who preferred to use the benzoate rather than the acetate; they showed that in either case the cyanobutadiene formed is a mixture of the *cis*- and the *trans*-isomer, which can be separated by distillation. The third type of route was also found convenient for the preparation of 2-chloro-1-cyanobuta-1 : 3-diene from 1-acetoxy-2-chloro-1-cyanobut-2-ene. In this instance the fission was very sensitive to temperature; at temperatures very slightly higher than that required for efficient splitting, a side reaction set in with elimination of hydrogen chloride. From the high-boiling by-products of the reaction a crystalline dimeride of 2-chloro-1-cyanobuta-1 : 3-diene was deposited in a state of high purity.

Crotonaldehyde was also the starting point for the preparation of alkyl buta-1 : 3-diene-1-carboxylates, crotonaldehyde cyanohydrin being converted into the alkyl 1-hydroxybut-2-ene-1-carboxylates, which were acetylated and pyrolysed :

$$CH_3{\cdot}CH{:}CH(OH){\cdot}CN \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CH(OAc){\cdot}CO_2R \longrightarrow CH_2{:}CH{\cdot}CH{:}CH{\cdot}CO_2R$$

When R is ethyl or a higher alkyl group, pyrolysis can take an alternative course, with the fission of butadiene-1-carboxylic acid from the ester to form the olefin derived from R (cf. Burns, Jones, and Ritchie, *loc. cit.*); *e.g.*, the methyl, ethyl, and *n*-butyl esters on pyrolysis at 480—500° gave 73, 40, and 35% yields respectively of the corresponding alkyl buta-1 : 3-diene-1-carboxylates; the ethyl ester yielded much ethylene, and from the butyl ester but-1-ene was isolated equivalent to 34% of the ester pyrolysed.

EXPERIMENTAL.

(Analyses are by Mr. E. S. Morton. M. p.s are uncorrected.)

Apparatus.—The pyrolysis equipment consisted essentially of a Pyrex-glass tube 1 m. long and of 5 cm. internal diameter packed with ½-in. Raschig rings of unglazed porcelain or stainless steel. The tube was mounted in a vertical, electrically heated furnace, and the operating temperature was determined by means of an iron–constantan thermocouple sliding in a glass tube of 1 cm. diameter lying along the axis of the pyrolysis tube. The ester was fed at room temperature into the tube, the upper section (30 cm.) of which acted as a preheater and vapouriser, and the pyrolysate was collected in a water-cooled flask.

A. 1-*Cyanobuta*-1 : 3-*diene*.—(a) *From* 2-*acetoxy*-1-*chlorobut*-3-*ene*. 1-Cyanobut-3-en-2-ol (cf. Bissinger *et al.*, *loc. cit.*) was acetylated with acetic anhydride in pyridine to give 2-*acetoxy*-1-*cyanobut*-3-*ene*, b. p. 118°/20 mm. (Found : N, 9·8. $C_7H_9O_2N$ requires N, 10·1%). The ester (14 g.) was fed at 3 g. per minute to the pyrolysis tube kept at 500—510°. The condensate was washed free from acid with aqueous sodium carbonate, dried ($MgSO_4$), and distilled to give 1-cyanobuta-1 : 3-diene (4·5 g.; 57%), b. p. 48—50°/24 mm. (Found : C, 75·4; H, 6·3; N, 17·2. Calc. for C_5H_5N : C, 76·0; H, 6·3; N, 17·7%).

(b) *From acetaldol.* Acetaldol (88 g.; b. p. 57—60°/3 mm.), prepared by twice fractionating technical acetaldol through a short column, was converted into its cyanohydrin and acetylated under the conditions described for crotonaldehyde [see (c), below]. Fractionation of the crude acetylation product gave 1 : 3-*diacetoxy*-1-*cyanobutane* (155 g., 78%), b. p. 150°/22 mm.; n_D^{20} 1·4304 (Found : C, 54·6; H, 6·6; N, 7·1. $C_9H_{13}O_4N$ requires C, 54·2; H, 6·5; N, 7·0%). The di-ester (199 g.) was fed at 5 g. per minute into the pyrolysis tube kept at 480—500°, and from the condensed pyrolysate 1-cyanobuta-1 : 3-diene (47·5 g., 60%) was isolated as described under (c), below. Two higher-boiling isomeric fractions were also obtained : (i) b. p. 95—97°/13 mm., n_D^{20} 1·4368 (Found : C, 60·8; H, 6·8; N, 10·0%), and (ii) b. p. 104—107°/12 mm., n_D^{20} 1·4460 (Found : C, 61·0; H, 6·7; N, 9·9. $C_7H_9O_2N$ requires C, 60·5; H, 6·5; N, 10·1%). On pyrolysis these *compounds* gave high yields of 1-cyanobuta-1 : 3-diene.

(c) *From crotonaldehyde.* Acid-free crotonaldehyde (70 g.) was added with stirring, during ½ hour, to 98% technical hydrogen cyanide (28 g.) containing triethylamine (1 g.) at 20—30°. The mixture was cooled to −20° and then acidified with acetic acid (5 g.), and the crude cyanohydrin was run into refluxing acetic anhydride (102 g.) containing sulphuric acid (0·2 g.) at such a rate as to keep the mixture gently boiling, and then refluxed for ½ hour. The cooled reaction mixture was washed free from acid with aqueous sodium carbonate, and the separated oil was dried ($MgSO_4$) and distilled to give 1-acetoxy-1-cyanobut-2-ene (114 g., 82%), b. p. 97—100°/20 mm. The ester (139 g.) was fed at 5 g. per minute into the pyrolysis tube kept at 490—510°. The condensed pyrolysate was washed free from acid with aqueous sodium carbonate, and the separated oil dried ($MgSO_4$), treated with quinol (0·1 g.), and fractionated to give 1-cyanobuta-1 : 3-diene (63·5 g., 80%), b. p. 48—50°/24 mm., n_D^{20} 1·4878. Snyder *et al.* (*loc. cit.*) give *cis*-, b. p. 49·5°/31·5 mm., n_D^{20} 1·4852, and *trans*-, b. p. 57·3°/31·5 mm., n_D^{20} 1·4960.

Other esters of crotonaldehyde cyanohydrin were prepared by the action of the appropriate acid chloride : *propionate*, b. p. 95—96°/12 mm., n_D^{20} 1·4383 (Found : C, 62·8; H, 7·1; N, 9·0. $C_8H_{11}O_2N$ requires C, 62·7; H, 7·2; N, 9·1%); benzoate, b. p. 159—160°/12 mm.; *methyl carbonate*, b. p. 108°/20 mm., n_D^{20} 1·4383 (Found : C, 54·0; H, 6·0; N, 9·0. $C_7H_9O_3N$ requires 3, 54·2; H, 5·8; N, 9·0%). Pyrolysis of these esters at 500° also gave 1-cyanobuta-1 : 3-diene.

B. 2-*Chloro*-1-*cyanobuta*-1 : 3-*diene*.—By using the conditions described above for crotonaldehyde cyanohydrin, α-chlorocrotonaldehyde cyanohydrin was prepared and acetylated to give 1-*acetoxy*-2-*chloro*-1-*cyanobut*-2-*ene* (yield 85%), b. p. 104°/17 mm., n_D^{20} 1·4582 (Found : N, 8·0; Cl, 20·9. $C_7H_8O_2NCl$ requires N, 8·1; Cl, 20·4%). The ester (347 g.) was fed at 8 g. per minute to the pyrolysis tube kept at 490—500°, and when the condensate was worked up as described under 1-cyanobuta-1 : 3-diene three fractions were obtained : (i) b. p. 54—58°/25 mm. (59 g.); (ii) b. p. 58—100°/25 mm. (59 g.); (iii) b. p 100—120°/25 mm. (35 g.); residue 15 g. Fraction (i) on redistillation gave 2-*chloro*-1-*cyanobuta*-1 : 3-*diene*, b. p. 51—52°/20 mm., n_D^{20} 1·5150 (Found : C, 53·1; H, 3·8; N, 12·5; Cl, 30·9. C_5H_4NCl requires C, 52·9; H, 3·6; N, 12·3; Cl, 31·2%). When heated at 100°, the diene became viscous and set to a rubbery gel after a few hours. Fraction (iii) was mainly unchanged ester. Fraction (ii) on being kept deposited about half its weight of a crystalline *dimeride*, m. p. 120° (from benzene), of 2-chloro-1-cyanobuta-1 : 3-diene [Found : C, 52·8; H, 3·7; N, 12·6; Cl, 30·4%; *M* (cryoscopic in benzene), 230. $(C_5H_4NCl)_2$ requires C, 52·9; H, 3·6; N, 12·3; Cl, 31·2%; *M*, 227]. The pyrolysis temperature was unusually critical; below 480° splitting was inefficient, and above 500° much tar was formed together with gaseous by-products including hydrogen chloride.

C. *Alkyl Buta*-1 : 3-*diene*-1-*carboxylates*.—(a) *Alkyl* 1-*hydroxybut*-2-*ene*-1-*carboxylates*.—A solution of 35% hydrochloric acid (125 c.c.) and hydrogen chloride (160 g.) in methyl alcohol (480 g.) was added with stirring to crude crotonaldehyde cyanohydrin (527 g.) in methyl alcohol (480 g.) at 70°. After 3 hours the deposited ammonium chloride was collected and the filtrate distilled to give *methyl* 1-*hydroxybut*-2-*ene*-1-*carboxylate* (440 g., 71%), b. p. 80—84°/15 mm. (Found : sap. equiv., 130·8. $C_6H_{10}O_3$ requires sap. equiv., 130). The ethyl ester (b. p. 90°/20 mm.) and the *n*-butyl ester (b. p. 110°/15 mm.) were prepared similarly.

(b) *Esters of* 1-*acetoxybut*-2-*ene*-1-*carboxylic acid.* Methyl 1-hydroxybut-2-ene-1-carboxylate was acetylated by the method used for crotonaldehyde cyanohydrin to give *methyl* 1-*acetoxybut*-2-*ene*-1-*carboxylate* (yield 92%), b. p. 100°/10 mm., n_D^{18} 1·4396 (Found : sap. equiv., 85·2. $C_8H_{12}O_4$ requires sap. equiv., 86). The acetyl derivatives of the ethyl ester (b. p. 110—115°/15 mm.) and the *n*-butyl ester (b. p. 130°/15 mm.) were also prepared.

(c) *Esters of buta*-1 : 3-*diene*-1-*carboxylic acid.* (i) Methyl buta-1 : 3-diene-1-carboxylate. Methyl 1-acetoxybut-2-ene-1-carboxylate (172 g.) in benzene (344 g.) was fed at 6 g. of solution per minute to the pyrolysis tube maintained at 480—500°. The condensate was worked up as before and twice distilled to give methyl buta-1 : 3-diene-1-carboxylate (82 g., 73%), b. p. 50—52°/20 mm. (Kohler and Butler, *J. Amer. Chem. Soc.*, 1926, **48**, 1041, give b. p. 77—80°/25 mm.); n_D^{20} 1·4765, d_4^{20} 0·9618 (Found : C, 63·6; H, 7·4%; sap. equiv., 112; $[R]_D$, 32·87. Calc. for $C_6H_8O_2$: C, 64·1; H, 7·2%; sap. equiv., 112;

[*R*]$_D$, 30·58). Hydrolysis with aqueous potassium hydroxide gave buta-1 : 3-diene-1-carboxylic acid, m. p. 70—73° (Nottbohm, *Annalen*, 1917, **412**, 73, gives m. p. 70—72°). The ester (5 g.) reacted vigorously with maleic anhydride (2·5 g.) on being warmed to give an adduct, m. p. 109—110° (from benzene).

(ii) Ethyl buta-1 : 3-diene-1-carboxylate. Pyrolysis of ethyl 1-acetoxybut-2-ene-1-carboxylate under the above conditions gave ethyl buta-1 : 3-diene-1-carboxylate (40% yield), b. p. 63—65°/18 mm., d_4^{20} 0·946, n_D^{20} 1·4785 (Found : C, 66·5; H, 8·5. Calc. for $C_7H_{10}O_2$: C, 66·6; H, 8·6%). Von Auwers (*Annalen*, 1923, **432**, 68) gives b. p. 59·9°/18 mm., $d_4^{17.5}$ 0·9382, $n_{He}^{17.5}$ q·4780). Ethylene was evolved during the pyrolysis.

(iii) *n*-Butyl buta-1 : 3-diene-1-carboxylate. Pyrolysis of *n*-butyl 1-acetoxybut-2-ene-1-carboxylate at 6 g. per minute and 480—500° gave n-*butyl buta*-1 : 3-*diene*-1-*carboxylate* (35% yield), b. p. 91—93°/20 mm., n_D^{17} 1·4745 (Found : C, 70·2; H, 9·1%; sap. equiv., 155·5. $C_8H_{14}O_2$ requires C, 70·1; H, 9·1%; sap. equiv., 154). But-1-ene equivalent to 34% of the ester pyrolysed was also isolated.

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