New Addition Reactions of Acrylic Compounds with Fumaric Acid Esters Catalyzed by Tervalent Phosphorus Compounds

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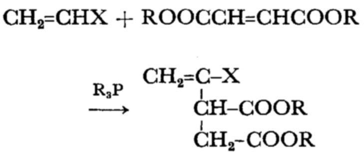
(Received April 11, 1969)

Dimerization of acrylonitrile or acrylic acid esters catalyzed by tervalent phosphorus compounds has been studied in great detail,[1,2] since the reaction furnishes industrially important products.[3] However, the study of the catalyzed reaction has been restricted only to dimerization.[4] In a previous paper,[5] we reported the reaction of acrylonitrile or acrylates with aldehydes to produce 2-(1-hydroxyalkyl)acrylonitriles or - acrylates in the presence of tertiary phosphines. This paper deals with the synthesis of 3-butene-1,2,3-tricarboxylic acid, a new tricarboxylic acid, and related compounds by the reaction of acrylic compounds with fumaric, or maleic acid esters.[6]



$$CH_2{=}CHX + ROOCCH{=}CHCOOR \xrightarrow{R_3P} \begin{array}{l} CH_2{=}C{-}X \\ \quad | \\ \quad CH{-}COOR \\ \quad | \\ \quad CH_2{-}COOR \end{array}$$

1 $X{=}CO_2CH_3$, $R{=}C_2H_5$
2 $X{=}COOH$, $R{=}H$
4 $X{=}CN$, $R{=}C_4H_9$

The reaction of 34.3 g (0.40 mol) of methyl acrylate, 67.0 g (0.39 mol) of diethyl fumarate and 1.5 g (5.4 mmol) of tricyclohexylphosphine in 100 m*l* of dioxane in an atmosphere of nitrogen at 70°C for 16 hr gave 95.7 g (95.5%, yield)[7] of 3-butene-1,2,3-tricarboxylic acid 1,2-diethyl-3-methyl ester (**1**) as a colorless liquid,[8] bp 101—102°C (3×10^{-3} mmHg); n_D^{20} 14502, $\lambda_{max}^{n\text{-hexane}}$ 213 mμ (ε, 5790); ν_{max}^{film} 1737 cm^{-1} (shoulder at 1721 cm^{-1}) (esters).

An acid hydrolysis of **1** gave 3-butene-1,2,3-tricarboxylic acid (**2**), mp 184—185°C: ν_{max}^{KBr} 1697, 1721 cm^{-1} (C=O); pK_1, 3.18, pK_2, 4.52, pK_3, 5.99. Catalytic hydrogenation of **1** over palladium charcoal followed by an acid hydrolysis furnished a mixture of diastereoisomers of 1,2,3-butanetricarboxylic acid (**3**), *i. e.*, a major component mp 181—182°C (lit., mp 182°C[9]; 184—185°C[10]) and a minor one, mp 147—148°C (lit.,[11] mp 146—147°C). Thermal decomposition of **2** at its melting point gave dimethylmaleic anhydride mp 94°C (lit.,[12] mp 95—96°C).

An analogous reaction of acrylonitrile with dibutyl fumarate in the presence of tricyclohexylphosphine at 100°C for 16 hr gave a mixture of dibutyl (1-cyanovinyl)succinate (**4**) and dibutyl (1-cyanoethylidene)succinate bp 128—129°C (0.1 mmHg); ν_{max}^{film} 1743 cm^{-1} (shoulder at 1723 cm^{-1}) (C=O), 2211 cm^{-1} (C$\equiv$N).

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1) N. Takashima and C. C. Price [*J. Am. Chem. Soc.*, **84**, 489 (1962)] found that acrylonitrile is converted into 1,1,4,4-tetracyanoethyl-1,4-dicyano-*trans*-2-butene, in the presence of triphenylphosphine, and suggested a dimer of acrylonitrile to be probably a precursor of the hexamer.

2) Dimerization of acrylontirle to 2-methyleneglutaronitrile: a) P. Carardes, C. Grard, P. Lafont and M. Thiers (to Rhone-Poulenc), French Pat. 1336081 (1964); b) J. D. McClure (to Shell Oil Co.), U. S. Pat. 3277745 (1966); c) M. M. Baizer and H. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965); d) W. H. Dietsche, *Tetrahedron Letters*, **1966**, 6347; e) D. Wittenberg and H. Mueller (to Badische Anilin & Soda-Fabrik A. G.), French Pat. 1385883 (1963); f) J. Feldman (to National Distillers & Chem. Co.), Belg. Pat. 677175 (1966); g) J. W. Nemec and R. B. Wuchter (to Rohm & Haas Co.), Belg. Pat. 689598 (1967). The dimerization to 1,4-dicyanobutene: h) J. S. McClure (to Shell Oil Co.) U. S. Pat. 3225083 (1965); i) Badische Anilin & Soda-Fabrik A. G., Belg. Pat. 698441 (1967); j) E. I. Du Pont de Nemours Co., Belg. Pat. 697162 (1967). Dimerization of acrylates to 2-methyleneglutarates; k) M. Rauhut and H. Currier (to American Cyanamid), U. S. Pat. 3047999 (1963); l) J. D. McClure (to Shell Oil Co.), U. S. Pat. 3277745 (1966); m) J. W. Nemec and R. B. Wuchter (to Rohm & Haas Co.), French Pat. 1460427 (1966), 1438745 (1966); n) Imp. Chem. Ind., Brit. Pat. 1100350 (1968).

3) L. F. Moormeier and J. Feldman, *Hydrocarbon Process Petrol. Refiner*, **44**, 151 (1965).

4) *Cf.* a) J. D. McClure (to Shell Oil Co.), U. S. Pat. 3225082 (1965); b) A. Lantz and F. Weiss (Soc. d'Electro-Chimie, d'Electron-Metallurgie, et des Acieries Electriques D'Ugine), French Pat. 1463853 (1966).

5) K. Morita, Z. Suzuki nd H. Hirose, This Bulletin, **41**, 2815 (1968).

6) The new reaction can be called Succination.

7) A trace of dimethyl methyleneglutarate was found in the product.

8) All new compounds described here gave satisfactory elemental analyses.

9) K. Alder and H. Söll, *Ann.*, **565**, 57 (1949).

10) S. Beckmann, H. Geiger and M. Schaber-Kiechle, *Chem. Ber.*, **92**, 2419 (1959).

11) K. Alder, Herbert Söll and Hanna Söll, *Ann.*, **565**, 77 (1949).

12) W. J. Bailey, R. L. Hudson and E. T. Yates, *J. Org. Chem.*, **28**, 828 (1963).