BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3484—3485 (1971)

Dimerization of Malononitrile by Palladium and Platinum Complex Catalysts

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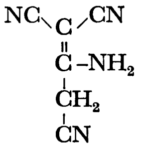
(Received July 20, 1971)

Previously we reported the palladium catalyzed reactions of 1,3-dienes with active methylene compounds.[1] In the course of the studies a novel catalytic dimerization of malononitrile has been found.

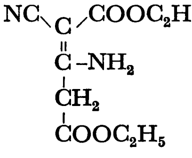
As described in the previous report,[1] malononitrile reacts with butadiene in the presence of a palladium catalyst to give 2,7-octadienyl and bis(2,7-octadienyl)-malononitrile in high yields. However, in the presence of a platinum catalyst, *e.g.*, tetrakis(triphenylphosphine)-platinum(0), the reaction gave only a small amount of the 2,7-octadienyl derivatives, with a large amount of a yellow solid product. The yellow product was insoluble in benzene. The elemental analysis and molecular weight measurement indicated that the product (mp 168—169°C) was a dimer of malononitrile. The dimer exhibited IR absorptions at 3350 and 3230 cm^{-1} (νN-H), 2180 cm^{-1}(νC≡N) and the NMR signals at τ 6.24 (s, 2H), 1.19 and 1.08 (broad, 2H). Its UV spectrum showed the maximum absorption at 274 mμ (ε 14000 in ethanol) due to conjugated double bonds. These spectral characteristics suggest the following structure (I).



(I)

Carboni[2] prepared the malononitrile dimer (I) for the first time using bases and acids. The IR and NMR spectra of the present product were identical with those of the dimer prepared by the Carboni's method.

Ethyl cyanoacetate also dimerized by the platinum catalyst to give 1-cyano-1,3-diethoxycarbonyl-2-amino-1-propene (II). Ethyl cyanoacetate was not so reactive as malononitrile. The dimer (II) showed IR absorptions at 3420, 3300, and 3230 cm^{-1}(νN-H), 2200 cm^{-1}(νC≡N), and 1740 cm^{-1}(νC=O, ester). The NMR spectrum of II in CCl_4 exhibited signals at τ 8.69 (t, 6H, J=7.0 Hz, –O–C–CH_3), 6.43 (s, 2H, =C–CH_2–CO), 5.80 and 5.77 (two quartet, J=7.0 Hz, –CO–O–CH_2–), 2.55 and 0.68 (broad, 2H, N–H, equal intensities). The maximum absorption of UV spectrum was at 277 mμ (ε 17600 in ethanol).

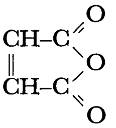


(II)

Tetrakis(triphenylphosphine)platinum is most efficient for the dimerization of malononitrile, but inefficient for the reaction of malononitrile with 1,3-butadiene.[1] A combination of dichloro bis(triphenylphosphine) platinum (II) and sodium phenoxide also showed the catalytic activity. The palladium catalysts, which are quite effective for the reaction of malononitrile with butadiene, was found to be effective for the dimerization reaction of malononitrile, as shown in Table 1, but their activities were low as compared with those of the platinum ones.

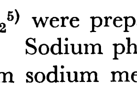
It was confirmed that triphenylphosphine or sodium phenoxide alone had no catalytic activity under the present reaction conditions. From the fact that the zerovalent platinum and palladium complexes are effective catalysts, the zerovalent metal atoms appear to play an important role in the catalytic dimerization reactions of malononitrile and ethyl cyanoacetate.

TABLE 1. DIMERIZATION OF MALONONITRILE BY PLATINUM AND PALLADIUM COMPLEXES

Catalyst mmole	Reaction time hr	Dimer yield %
$Pt(Ph_3P)_4$ 0.25	1	82.1
$PtCl_2(Ph_3P)_2$–C_6H_5ONa 0.25	20	80.3
$Pd(Ph_3P)_4$ 0.25	4	39.5
$Pd(Ph_3P)_2$  0.25	20	13.6
$PdCl_2(Ph_3P)_2$–C_6H_5ONa 0.25 2.5	20	33.4

malononitrile 0.1 mol, benzene 20 m*l*, 80°C

Experimental

Catalysts. $Pd(Ph_3P)_4$,[3] $Pd(Ph_3P)_2$  ,[4] $PdCl_2(Ph_3P)_2$,[3] $Pt(Ph_3P)_4$,[5] and $PtCl_2(Ph_3P)_2$[5] were prepared by the methods described in the literatures. Sodium phenoxide was prepared by the usual method from sodium metal and phenol.

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[1] G. Hata, K. Takahashi, and A. Miyake, *Chem. Ind.* (London), **1969**, 1836.

[2] R. A. Carboni, D. D. Coffman, and E. G. Howard, *J. Amer. Chem. Soc.*, **80**, 2838 (1958).

[3] L. Malatesta and M. Angolleta, *J. Chem. Soc.*, **1957**, 1186.

[4] S. Takahashi, K. Sonogashira, and N. Hagihara, *Nippon Kagaku Zasshi*, **87**, 610 (1966).

[5] L. Malatesta and C. Cariells, *J. Chem. Soc.*, **1958**, 2323.

Dimerization of malononitrile by Pt(Ph_3P)$_4$. In a two-necked 50 m*l* round-bottomed flask were placed 6.6 g (0.1 mol) of malononitrile, 0.31 g (0.00025 mol) of tetrakis(triphenylphosphine)platinum(0) and 20 m*l* of benzene. The mixture was stirred at 80°C for 1 hr under an argon atmosphere. The precipitated yellow solid was separated by filtration, washed several times with hot benzene and dried to give 5.4 g (82.1% yield) of 1,1,3-tricyano-2-amino-1-propene (I); mp 168—169°C (lit,[2]) mp 172—173°C); IR(KBr): 3350, 3230, 2180, 1655, 1555, 1387, 1309, and 906 cm^{-1}; NMR (in hexadeuterodimethyl sulfoxide): 6.24 (s, 2H), 1.19 (broad, 1H), and 1.08 (broad, 1H); UV (in ethanol): λ_{max} 274 mμ (ε 14000). Found: C, 54.42; H, 3.17; N, 42.44%; mol wt, 135.7. Calcd for $C_6H_4N_4$: C, 54.54; H, 3.05; N, 42.41; mol wt, 132.1.

Dimerization of Ethyl Cyanoacetate. The mixture of 11.4 g (0.1 mol) of ethyl cyanoacetate, 0.62 g (0.0005 mol) of tetrakis(triphenylphosphine)platinum(0) and 20 m*l* of benzene was stirred at 80°C for 20 hr. The reaction mixture was fractionally distilled to give 1.8 g (15.8% yield) of 1-cyano-1, 3-diethoxycarbonyl-2-amino-1-propene (II); bp 153—155°C/0.02 mmHg, mp 54—55°C; IR(KBr): 3420, 3300, 3230, 2990, 2200, 1740, 1680, 1630, 1528, 1270, 1185, 1095, 1020, and 785 cm^{-1}; NMR (in carbon tetrachloride): τ 8.69 (t, 6H, J= 7.0 Hz), 6.43 (s, 2H), 5.80 and 5.77 (two quartet, J=7.0 Hz), 2.55 (broad, 1H), and 0.68 (broad, 1H); UV (in ethanol): λ_{max} 277 mμ (ε 17600). Found: C, 53.01; H, 6.22; N, 12.37%; mol wt, 227.3. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.37; mol wt, 226.2.