# The Reaction of Phthalic Anhydride with Cyanoacetic Acid

By Toshio HAYASHI

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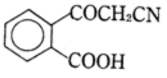
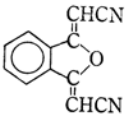
Yale reported that the reaction of phthalic anhydride with malonic acid, in the presence of pyridine, gave *o*-acetophenonecarboxylic acid in a good yield.[1] The present author has attempted a similiar reaction using cyanoacetic acid in place of malonic acid, expecting to obtain *o*-carboxy-$\alpha$-cyanoacetophenone (I). However, the reaction of phthalic anhydride with cyanoacetic acid in pyridine, in addition to unaltered phthalic anhydride and a small quantity of phthalic acid, yielded a new, bright yellow compound (II) (m. p. 221~222°C, $C_{12}H_6ON_2$).



(I)



(II)

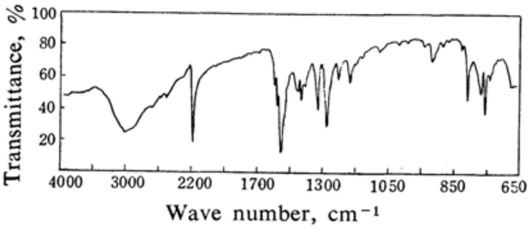


Fig. 1. Infrared spectrum of II in KBr disk.

The infrared spectrum of II (Fig. 1) unexpectedly lacks an absorption band in the C=O stretching region; on the other hand, it does show a sharp and strong band at 2208 cm$^{-1}$ indicating the presence of a conjugated cyano group, and a strong absorption at 1576 cm$^{-1}$, which is regarded as the C=C stretching frequency which is shifted to the lower wave number region by conjugation with the benzene nucleus and with the cyano group. The enhanced intensity of this band is possibly due to the substitution of a hydrogen atom by an oxygen atom on one of the carbon atoms constituting the double bond. It also shows the out-of-plane deformation band of hydrogen atom of the tri-substituted double bond at 821 cm$^{-1}$ and that of hydrogen atoms of the ortho-di-substituted benzene ring at 768 cm$^{-1}$. Biscyanomethylenephthalan (II) is the most probable structure to explain all the facts mentioned above. All attempts to hydrolyze II according to the usual method failed giving further evidence that the cyano groups are conjugated with double bonds.

## Experimental

**Biscyanomethylenephthalan (II).**—A finely-powdered mixture of 26.5 g. (0.18 mol.) of phthalic anhydride and 18.0 g. (0.21 mol.) of cyanoacetic acid was heated with 20 ml. of pyridine on a water bath for 1.5 hr. Carbon dioxide was evolved throughout the heating. The clear red solution, on dilution with 200 ml. of water, results in the separation of a colorless solid (m. p. 124~126°C). When this was filtered and dried, it was identified as unaltered phthalic anhydride by a mixed melting point determination with an authentic sample. After the filtrate had been treated with 20 ml. of concentrated hydrochloic acid and allowed to stand for three days at room temperature, the precipitates which formed were filtered and identified as phthalic acid. To the filtrate 20 ml. of concentrated hydrochloric acid was again added and the mixture allowed to stand for additional three days. Clusters of yellow plates appeared on the sides of the flask. These were filtered off; weight 2.3 g. One crystallization of this sample from aqueous ethanol gave bright yellow plates (m. p. 221~222°C).

Found: C, 74.09; H, 2.88; N, 14.03. Calcd. for $C_{12}H_6ON_2$: C, 74.22; H, 3.11; N, 14.03%.

*The Institute of Physical and*
*Chemical Research*
*Bunkyo-ku, Tokyo*

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[1] H. L. Yale, *J. Am. Chem. Soc.*, **69**, 1547 (1947).