

THE REACTION OF ISOCYANATE WITH PHTHALALDEHYDE

Iwao Yamamoto, Yoshizo Tabo, and Haruo Gotoh

Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano, Japan.

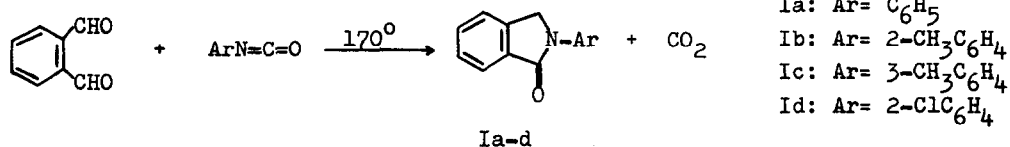
Toru Minami, Yoshiki Ohshiro, and Toshio Agawa

Department of Petroleum Chemistry, Osaka University, Yamada-ka, Suita, Japan.

(Received in Japan 13 May 1971; received in UK for publication 17 May 1971)

Isocyanates(1), N-sulfinylamine(2), and sulfurdiimide(3) react with aldehyde to give Schiff base. We have studied recently that aromatic monoaldehyde reacts with carbodiimide to give Schiff base and isocyanate(4). In the present paper we'll report the reaction of isocyanate with aromatic di-aldehyde.

When the equimolar mixture of phenyl isocyanate and phthalaldehyde was heated at 170°C for 4hr, N-phenylphthalimidine (Ia) was obtained quantitatively: mp. 163-163.5° (lit.(5) 162-162.5),  $\nu$ (Nujol mull) 1690  $\text{cm}^{-1}$  (C=O), and carbon-dioxide which was detected by bariumhydroxide was evolved.

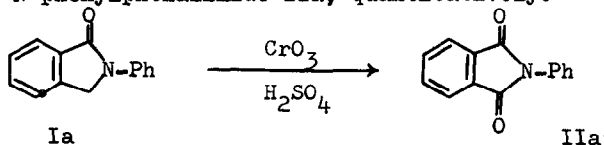


The nmr spectrum( $\text{CDCl}_3$ ) of Ia showed the signals at  $\delta$  4.75(singlet) and 7.3-7.8(multiplet) in the ratio of 2:9 which were assigned to methylene and aromatic protons, respectively. Further the mass spectrum(70eV) contained  $m/e$  209( $M^+$ ) and fragment  $m/e$  181( $M^+ - \text{CO}$ ), 104( $M^+ - \text{PhN}=\text{CH}$ ), and 90( $M^+ - \text{PhNCO}$ ).

Anal. Calc'd for  $\text{C}_{14}\text{H}_{11}\text{ON}$  : C, 80.36; H, 5.30; N, 6.69.

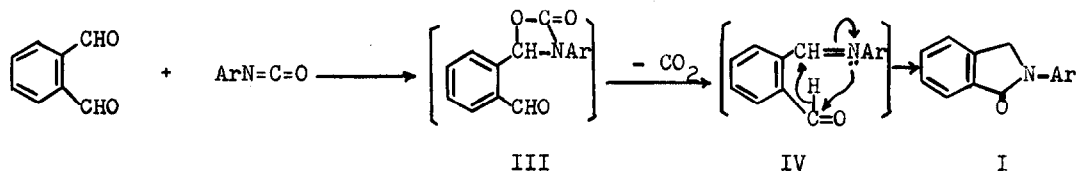
Found : C, 80.70; H, 5.37; N, 6.82.

The oxidation of Ia with chromic anhydride and concentrated sulfuric acid gave N-phenylphthalimide IIa, quantitatively.



No depression of mixed melting point of N-phenylphthalimide with authentic sample(6) was observed.

We assumed the reaction mechanism as follows;



The reaction would probably proceed by initial formation of imino-aldehyde IV, followed by nucleophilic attack of nitrogen to carbonyl carbon. Graebe et al. reported the formation of phthalimidine in the reaction of phthalaldehyde and aniline. In their case, the reaction mechanism may be similar to ours.

The results are summarised in Table I.

Table I. The reaction of isocyanates with phthalaldehyde.

products	reaction <sup>a)</sup>		mp(°C)	ir(C=O) <sup>c)</sup> (cm <sup>-1</sup> )	nmr(δ)		
	time(hr)	yield(%)			CH <sub>2</sub>	Aromatic	CH <sub>3</sub>
Ia	4	99	163-163.5	1690	4.75	7.3-7.8	--
Ib	1	31	98-98.5	1700	4.67	7.1-8.1	2.25
Ic	6	99	142-142.5	1695	4.68	6.7-8.1	2.33
Id	3	57	108-109	1675	4.67	7.2-7.7	--

a) The reaction was stopped when CO<sub>2</sub> was not evolved. b) Based on phthalaldehyde

c) Nujol mull

In the reaction of phthalaldehyde with diphenylcarbodiimide, N-phenylphthalimidine was also obtained in 71% yield. We have presumed that the reaction proceeds in the same course as isocyanate does.

#### REFERENCES

- (1) H. Staudinger and R. Endle, *Ber.*, 50, 1042(1917).
- (2) G. Kresze and R. Albrecht, *Angew. Chem.*, 74, 781(1962).
- (3) D. H. Clemens, A. J. Bell, and J. L. O'Brien, *Tetrahedron Letters*, 1491(1965).
- (4) T. Minami, I. Yamamoto, Y. Ohshiro, and T. Agawa, unpublished results.
- (5) G. Graebe and A. Pictet, *Ann.*, 247, 302(1888).
- (6) K. Kjeldgaard, *Chem. Abstr.* 61, 11928h(1964).