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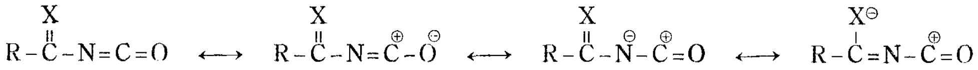
Dipolar Cycloaddition Reaction of Benzoyl and Thiobenzoyl Isocyanates[*1]

In the previous papers[1,2] in which the di- or trimerization reaction of benzoyl isocyanates were investigated under the influence of various catalysts, it was shown that 1,2- and 1,4-dipolar cycloaddition products were formed. Consequently, the formation of a new heterocyclic compound by the cycloaddition with an unsaturated substance was expected due to the contribution of the following resonance structures of acyl and thioacyl isocyanates.



$$R-\overset{\overset{X}{\|}}{C}-N=C=O \longleftrightarrow R-\overset{\overset{X}{\|}}{C}-N=\overset{\oplus}{C}-\overset{\ominus}{O} \longleftrightarrow R-\overset{\overset{X}{\|}}{C}-\overset{\ominus}{N}-\overset{\oplus}{C}=O \longleftrightarrow R-\overset{\overset{X^{\ominus}}{|}}{C}=N-\overset{\oplus}{C}=O$$

X=O or S

We planned to develop the dipolar cycloaddition reactions of acyl and thioacyl isocyanates with various compounds of a wider range. In this communication we report the reactions of benzoyl (Ia~d) and thiobenzoyl isocyanates (IIa~c)[3] with benzylideneaniline (III), benzylidenebenzylamine (IV), N-phenyl- (V) and N-benzylbenzaldoxime (VI). In addition, this paper deals with the reaction of II with triethylamine.

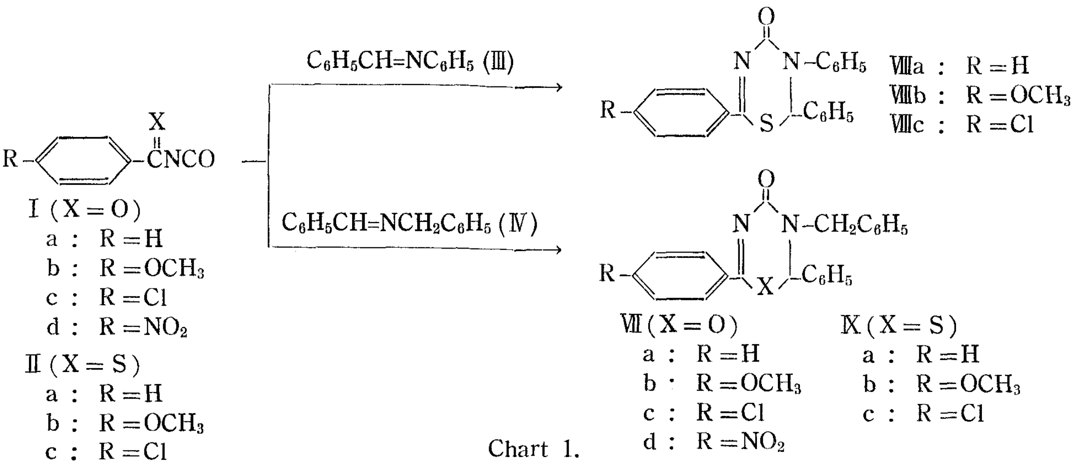


Chart 1.

[*1] Presented at the 18th Annual Meeting (Osaka, April, 1965) and the 19th Annual Meeting of the Chem. Soc. Japan (Yokohama, March, 1966).

1) O. Tsuge, R. Mizuguchi: J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi), **86**, 325 (1965).

2) *Idem*: J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi), **69**, 939 (1966).

3) J. Goerdeler, H. Schenk: Chem. Ber., **98**, 2954 (1965). In the present work, 2-arylthiazoline-4,5-dione which was prepared by the reaction of the corresponding thiobenzamide with oxalyl chloride, was decomposed in xylene by heating to yield II, and II was used *in situ*.

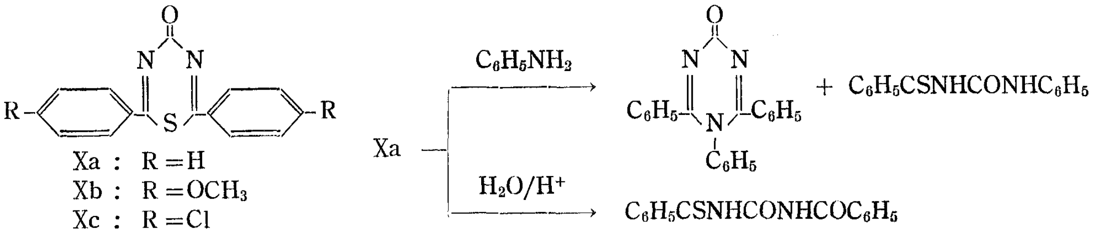
Although the addition of Ⅰ to Ⅲ was not found take place,[*2] Ⅰ reacted with Ⅳ in benzene at room temperature to give the new heterocycle, 2*H*-1,3,5-oxadiazin-4(3*H*)-one (Ⅶa~d) in a quantitative yield. On the other hand, Ⅱ reacted with Ⅲ as well as with Ⅳ at room temperature, affording the corresponding 2*H*-1,3,5-thiadiazin-4(3*H*)-one Ⅷa~c,[4] and Ⅸa~c respectively in a good yield.

As is shown in Chart 1, the compounds (Ⅶ, Ⅷ and Ⅸ) correspond to the 1,4-dipolar cycloaddition compound of Ⅰ or Ⅱ with Ⅲ or Ⅳ in the respective case. These reaction products were confirmed by the infrared spectra, in which they exhibited characteristic bands due to the C=O and C=N bond, and also by elemental analyses. The physical properties and yields are shown in Table Ⅰ.

Table Ⅰ. 2*H*-1,3,5-Oxa(and thia)diazin-4(3*H*)-ones

Compound	Yield (%)	m.p. (°C) (decomp.)	Appearance
Ⅶa	100	118	white needles
Ⅶb	100	92	〃
Ⅶc	100	100	〃
Ⅶd	100	102	〃
Ⅷa	100	193 ~194	〃
Ⅷb	100	191.5~192	〃
Ⅷc	100	185 ~186	yellow needles
Ⅸa	88	180 ~181	white needles
Ⅸb	80	155 ~157	〃
Ⅸc	100	167 ~168	〃

The reaction of Ⅱ with triethylamine at room temperature afforded the 4*H*-1,3,5-thiadiazin-4-one (Xa~c), which was equivalent to the structure derived from the dimer of Ⅱ under the elimination of carbonyl sulfide, in a fairly good yield. In the treatment of Xa with aniline in benzene, 1,2,6-triphenyl-1,3,5-triazin-4(1*H*)-one, m.p. 295~296°, and 1-phenyl-3-thiobenzoylurea, m.p. 203~205°, were obtained in 41 and 26% yield respectively. Also, Xa hydrolyzed with 10% hydrochloric acid, affording rose-colored needles, m.p. 186°, in 84% yield. This compound was proved by the admixed melting point and the infrared spectrum to be identical with 1-benzoyl-3-thiobenzoylurea which was prepared from benzamide and Ⅱa. The structure of X was confirmed on the basis of above observations as well as by infrared spectra and elemental analyses. The physical properties and yields of X are shown in Table Ⅱ. Recently, Goerdeler, *et al.*[3] reported that Xa, m.p. 184°, was obtained by heating the dimer of Ⅱa.



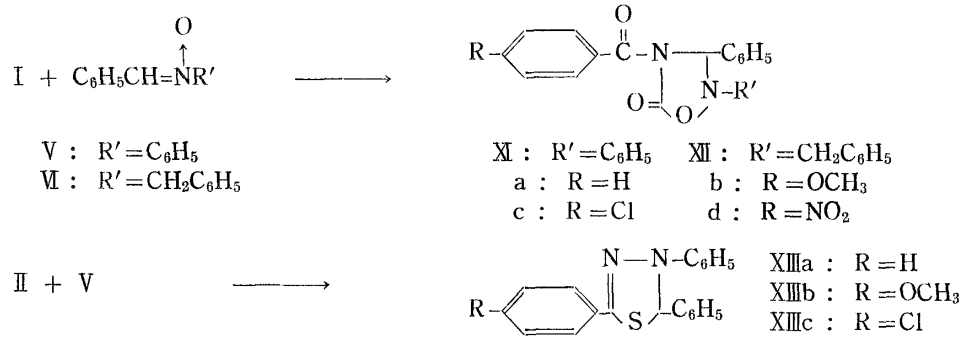
[*2] When a mixture of phenylacetyl isocyanate and Ⅲ in benzene was refluxed for 4 hr., 6-benzyl-2,3-diphenyl-2*H*-1,3,5-oxadiazin-4(3*H*)-one, m.p. 285°(decomp.), which was the isomer of Ⅶa, was obtained in 70% yield.

4) After the completion of this work, we learned that Ⅷa, m.p. 185~190°(decomp.) and Ⅷb, m.p. 186~190°(decomp.) were independently prepared by J. Goerdeler and H. Schenk: Chem. Ber., **98**, 3831(1965).

Table Ⅱ.

Compound	Yield (%)	m.p. (°C)	Appearance
Xa	86	148	white needles
Xb	88	203	yellow needles
Xc	86	216.5	white needles
Ⅺa	100	141 (decomp.)	〃
Ⅺb	100	125 (〃)	〃
Ⅺc	100	125 (〃)	〃
Ⅺd	100	129 (〃)	yellow needles
Ⅻa	100	127	white needles
Ⅻb	100	108	〃
Ⅻc	100	113	〃
Ⅻd	100	137	yellow needles
XⅢa	35	147 ~147.5 (decomp.)	red prisms
XⅢb	70	156.5~157 (〃)	〃
XⅢc	22	155 (〃)	〃

Furthermore, I reacted with the nitrone compounds (Ⅴ and Ⅵ), giving the corresponding 1,2-dipolar cycloaddition compounds, 1,2,4-oxadiazoline, Ⅺa~d and Ⅻa~d in a quantitative yield respectively. However, Ⅱ showed a different behavior from Ⅰ toward the nitrone compound. In the reaction of Ⅱ with Ⅴ the 1,3,4-thiadiazole (XⅢa~c), whose structure was equivalent to the compound derived from the 1,4-cycloaddition compound under the elimination of carbon dioxide, was obtained. The compounds (Ⅺ, Ⅻ and XⅢ) were confirmed by the infrared spectra as well as by elemental analyses. The physical properties and yields are also shown in Table Ⅱ.



Ⅴ : $R'=C_6H_5$
Ⅵ : $R'=CH_2C_6H_5$

Ⅺ : $R'=C_6H_5$ Ⅻ : $R'=CH_2C_6H_5$
a : R=H b : $R=OCH_3$
c : R=Cl d : $R=NO_2$

XⅢa : R=H
XⅢb : $R=OCH_3$
XⅢc : R=Cl

All melting points were not corrected, but the results of elemental analyses were satisfactorily obtained for all compounds reported here.

Further investigation is in progress in this laboratory, and the details of this work will be published in the near future.

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