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Studies of Acyl and Thioacyl Isocyanates. VIII.[1] Cycloaddition Reactions of Benzoyl and Thiobenzoyl Isocyanates with Carbodiimides

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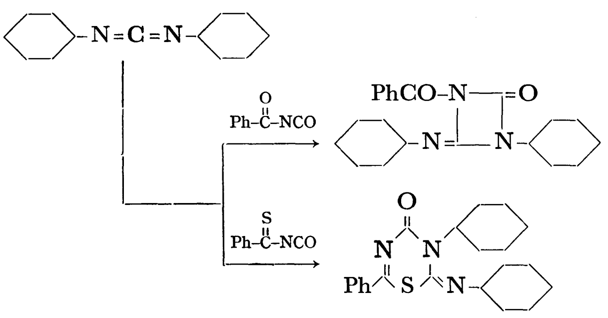
The investigations of cycloaddition reactions of benzoyl and thiobenzoyl isocyanates with carbodiimides have shown that the adducts formed from benzoyl isocyanates and *N*,*N*′-dicyclohexylcarbodiimide are the corresponding (4+2) cycloadducts, and not the (2+2) cycloadducts proposed by Neidlein. The reaction of isocyanates with *N*,*N*′-diphenylcarbodiimide at 0°C gave (2+2) cycloadducts, which were thermally isomerized into the corresponding (4+2) cycloadducts. Benzoyl isocyanates reacted with *N*-cyclohexyl-*N*′-phenylcarbodiimide to give (4+2) cycloadducts of isocyanates to the cyclohexyl-N=C bond in the carbodiimide. On treatment with neutral alumina, (4+2) cycloadducts were easily isomerized into 1,3,5-triazines. Thiobenzoyl isocyanate reacted with both the N=C bonds of the carbodiimide to afford two isomeric (4+2) cycloadducts. It has been found that benzoyl isocyanates reacted with *N*-phenyl-*N*′-*o*-tolylcarbodiimide to yield the corresponding (4+2) cycloadducts of isocyanates to the *o*-tolyl-N=C bond and/or the isomeric 1,3,5-oxadiazin-6-ones, depending on the nature of the substituent in the isocyanate. Reaction paths for the formation of the product are also discussed.

During the last few years, cycloaddition reactions of carbodiimides with various reagents have been extensively investigated.[2]

Neidlein[3] reported that benzoyl isocyanate reacts with *N*,*N*′-dicyclohexylcarbodiimide to form a (2+2) cycloadduct, while Goerdeler and Schenk[4] reported that the cycloaddition of thiobenzoyl isocyanate to the same carbodiimide gave a (4+2) cycloadduct.



In the dimerization[5] and cycloaddition to anils,[6] benzoyl isocyanates gave (4+2) cycloadducts but no (2+2) cycloadducts. Formation of the (2+2) cycloadduct reported by Neidlein[3] would be the first example of (2+2) cycloaddition of benzoyl isocyanate to a C=N bond.

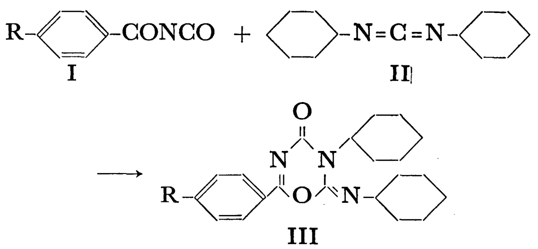
Acoordingly, the cycloaddition reactions of benzoyl isocyanates with carbodiimides were of special interest to us. This paper deals with the cycloaddition reactions of benzoyl and thiobenzoyl isocyanates with symmetrical and asymmetrical carbodiimides.

Results and Discussion

Cycloadditions to Symmetrical Carbodiimides. The reaction of benzoyl isocyanate (Ia) with an equimolar amount of *N*,*N*′-dicyclohexylcarbodiimide (II) in a benzene–diethyl ether solution at 0°C or at room temperature gave the 1:1 adduct IIIa of Ia and II. From a comparison of the melting point and UV spectrum of IIIa with those of the adduct reported by Neidlein,[3] the adduct IIIa obtained here was found to be the same one obtained by Neidlein.

The absorption bands in the range 1300—1750 cm^{-1} in the IR spectrum of IIIa are very similar to those in the spectra of 3-benzyl-2,6-diphenyl-2*H*-1,3,5-oxadiazin-4(3*H*)-one[6] and of the (4+2) cycloadduct[4] of thiobenzoyl isocyanate to II. The correlation between the intensities and the wave numbers of $\nu_{C=O}$ and $\nu_{C=N}$ in the three compounds is similar to that between the intensity and the wave number of $\nu_{C=O}$ and $\nu_{C=C}$ in γ-pyrone.[5]

Consequently, it can be assumed that IIIa is the (4+2) cycloadduct, 3-cyclohexyl-2-cyclohexylimino-6-phenyl-2*H*-1,3,5-oxadiazin-4(3*H*)-one, rather than the (2+2) cycloadduct proposed by Neidlein.[3]



a: R=H, b; R=Cl, c: R=NO$_2$, d: R=OMe

Similar reactions of *p*-substituted benzoyl isocyanates (Ib—Id) with II gave the corresponding (4+2) cycloadducts (IIIb—IIId). The yields, physical properties and elemental analyses of III are summarized in Table 1.

On the other hand, with *N*,*N*′-diphenylcarbodiimide (IV) at 0°C, benzoyl isocyanate (Ia) gave the corre-

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[1] Part VII of this series; O. Tsuge, T. Itoh, and K. Sakai, *Nippon Kagaku Zasshi*, **90**, 1031 (1969).

[2] H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, London 1967, p. 254.

[3] R. Neidlein, *Arch. Pharm.* (Weinheim), **297**, 623 (1964).

[4] J. Goerdeler and H. Schenk, *Chem. Ber.*, **98**, 3831 (1965).

[5] O. Tsuge and R. Mizuguchi, *Kogyo Kagaku Zasshi*, **69**, 939 (1966).

[6] O. Tsuge, M. Tashiro, R. Mizuguchi, and S. Kanemasa, *Chem. Pharm. Bull.* (Tokyo), **14**, 1055 (1966).

Table 1. Reaction of I with II[1)]

	R	Yield (%)	Mp (°C)	λ_{max}^{EtOH} nm(log ε)	$\nu_{C=O}$[2)] cm^{-1}	$\nu_{C=N}$[3)] cm^{-1}	Analysis (%) Found (Calcd) C	H	N
IIIa	H	54	142—143	260 (4.27)	1745	1670 1630	71.52	7.85	11.75
		(82)[4)]	(138—139)[5)]	(256)[5)]			(71.36)	(7.70)	(11.89)
IIIb	Cl	76	122—123	271 (4.32)	1740	1690 1630	64.89	6.94	10.85
							(65.10)	(6.68)	(10.85)
IIIc	NO$_2$	87	139—140	271 (4.44)	1740	1680 1640	63.34	6.45	14.22
							(63.30)	(6.54)	(14.07)
IIId	OMe	64	157—158		1730	1675 1630	68.68	7.91	10.71
							(68.90)	(7.62)	(10.96)

1) At room temperature for a few minutes.
2) Weak bands.
3) Very strong bands.
4) At 0°C for 15 hr.
5) Mp and λ_{max}^{EtOH} nm reported by R. Neidlein (lit.3).

Table 2. Reaction of I with IV at 0°C for 24 hr

	R	Yield (%)	Mp (°C)	λ_{max}^{EtOH} nm(log ε)	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	Analysis (%) Found (Calcd) C	H	N
Va	H	55	112—113 (decomp.)	238 (4.62)	1880 1695	1740	74.05	4.41	12.34
							(73.89)	(4.43)	(12.31)
Vb	Cl	72	115—116 (decomp.)	242 (4.65)	1880 1695	1735	66.92	3.58	11.04
							(67.20)	(3.72)	(11.18)
Vc	NO$_2$	50	102—103 (decomp.)	250 (4.65)	1880 1695	1740	65.12	3.51	14.55
							(65.28)	(3.65)	(14.50)

Table 3. Isomerization of V at 120°C for 1 hr

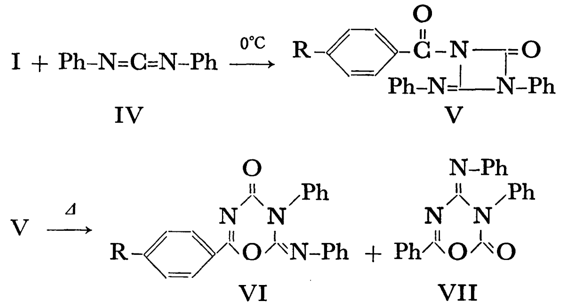
	R	Yield (%)	Mp (°C)	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	Analysis (%) Found (Calcd) C	H	N
VIa	H	59	179—179.5	1745	1690 1630	73.95	4.33	12.17
						(73.89)	(4.43)	(12.31)
VIb	Cl	81	173—174	1745	1690 1630	67.40	3.48	11.33
						(67.20)	(3.72)	(11.18)
VIc	NO$_2$	72	150—151	1740	1690 1635	65.04	3.93	14.67
						(65.28)	(3.65)	(14.50)

sponding 1:1 adduct Va. From the characteristic $\nu_{C=O}$ at 1880 cm^{-1} in the IR spectrum as well as from the result of thermal isomerization, the structure of Va was established to be the (2+2) cycloadduct, 1-benzoyl-3-phenyl-2-phenylimino-1,3-diazetidin-4-one.

The (2+2) cycloadduct Va was thermally isomerized into the (4+2) cycloadduct, 3,6-diphenyl-2-phenylimino-2*H*-1,3,5-oxadiazin-4(3*H*)-one (VIa); a small amount of isomeric 1,3,5-oxadiazin-6-one VII was also formed.

Similar reactions of *p*-substituted benzoyl isocyanates (Ib—Ic) with IV at 0°C gave the corresponding (2+2) cycloadducts Vb and Vc, which on thermal isomerization afforded good yields of the corresponding (4+2) cycloadducts, VIb and VIc respectively.

The reaction of Ia with IV in a refluxing benzene-ether solution gave VIa and VII, but Va was not formed.



a: R=H, b: R=Cl, c: R=NO$_2$

The proposed structures VI and VII were confirmed by spectral studies. The IR spectrum of VIa is similar to that of (4+2) cycloadducts III, while the absorption bands in VII is similar to those of 2,4-diphenyl-1,3,5-oxadiazin-6-one.[5)] Correlation between the intensity and wave number of $\nu_{C=O}$ and $\nu_{C=N}$ in the spectrum of VII is also similar to that between the intensity and wave number of $\nu_{C=O}$ and $\nu_{C=C}$ in α-pyrone.[5)]

The physical properties and results of elemental analyses of V, VI, and VII are given in Tables 2 and 3 respectively.

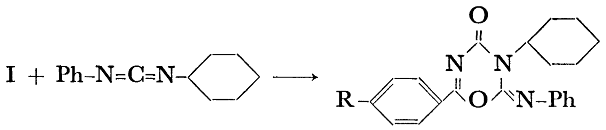
TABLE 4. REACTION OF I WITH VIII AT 70°C

	R	Reaction time (hr)	Yield (%)	Mp (°C)	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	Analysis (%) Found (Calcd) C	H	N	MW (*m*/*e*)
IXa	H	1.5	75	128—129	1740	1685 1635	72.58 (72.60)	6.14 (6.09)	11.98 (12.10)	347
IXb	Cl	1.5	71	117—118	1740	1690 1630	66.25 (66.05)	5.30 (5.24)	11.04 (11.01)	381
IXc	NO_2	1.5	75	125—126	1740	1685 1640	64.45 (64.27)	5.07 (5.14)	14.37 (14.28)	392
IXd	OMe	5	66.5	123—124	1735	1680 1635	70.14 (70.01)	6.35 (6.14)	10.85 (11.13)	377

Cycloaddition to Asymmetrical Carbodiimides. The isocyanates would be expected to attack competitively both C=N bonds of asymmetrical carbodiimides.

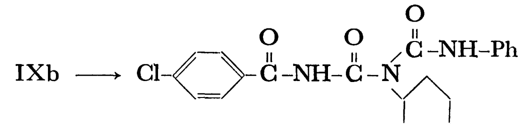
The reactions of benzoyl isocyanates (I) with *N*-cyclohexyl-*N*′-phenylcarbodiimide (VIII) gave the corresponding 1 : 1 adducts IX of I and VIII in good yields.

From the similarity between the IR spectra of IX and the (4+2) cycloadducts III and VI, the structures of the adducts IX were assumed to be (4+2) cycloadducts.



VIII IX

a: R=H, b: R=Cl, c: R=NO_2, d: R=OMe



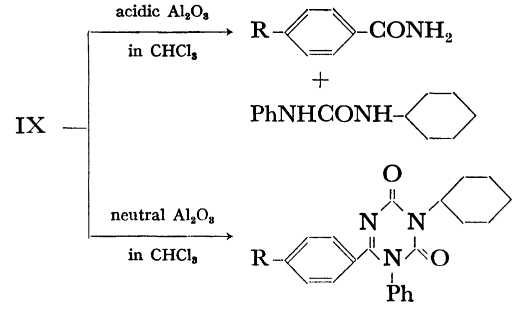
X

Hydrolysis of IXb with dilute hydrochloric acid gave 1-cyclohexyl-1-phenylcarbamoyl-3-*p*-chlorobenzoylurea (X). This indicates that the adduct IXb is 6-*p*-chlorophenyl-3-cyclohexyl-2-phenylimino-2*H*-1,3,5-oxadiazin-4(3*H*)-one, whose structure corresponds to the (4+2) cycloadduct of the isocyanate Ib to the cyclohexyl-N=C bond in VIII.

Thus, it could be concluded that all the adducts of IX are (4+2) cycloadducts of the isocyanates to the cyclohexyl-N=C bond of carbodiimide VIII.

The yields, physical properties and results of elemental analyses of IX are summarized in Table 4.

Treatment of the adducts IX with acidic alumina in chloroform gave the corresponding benzamide and 1-cyclohexyl-3-phenylurea, while similar treatment with neutral alumina afforded the isomeric 1,3,5-triazine-2,6-diones XI.



XI

a: R=H, b: R=Cl, c: R=NO_2, d: R=OMe

The yields, physical properties, and results of elemental analyses of XI are given in Table 5.

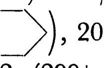
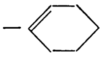
Further confirmation of these assignments was provided by the mass spectral studies. The mass spectrum of IXb showed the parent peak (M$^+$) at *m*/*e* 381 and other peaks at *m*/*e* 299 (M$^+$− ), 200 (M$^+$−ArCONCO), 181 (ArCONCO$^+$), 162 (299$^+$−ArCN), 139 (ArCO$^+$), 119 (PhNCO$^+$), and 118 (PhN=C=NH$^+$, base peak). In the mass spectrum of XIb, the parent peak (M$^+$) appeared at *m*/*e* 381, together with major peaks at *m*/*e* 300, 299 (M$^+$− , base peak), 257 (300$^+$−HCNO), 256 (299$^+$−HCNO), 215 (ArC=$\overset{+}{N}$HPh), 214 (Ar–C≡$\overset{+}{N}$–Ph), 163 (300$^+$−ArCN),

TABLE 5. ISOMERIZATION OF IX

	R	Yield (%)	Mp (°C)	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	Analysis (%) Found (Calcd) C	H	N	MW (*m*/*e*)
XIa	H	32.4	225.5—226	1745 1690	1620	72.84 (72.60)	6.18 (6.09)	12.17 (12.10)	347
XIb	Cl	33	182 —183	1740 1680	1610	66.03 (66.05)	5.35 (5.24)	10.76 (11.01)	381
XIc	NO_2	44	142 —143	1745 1685	1620	66.91 (66.80)	5.52 (5.33)	12.99 (12.99)	392
XId	OMe	30	213	1740 1680	1610	70.52 (70.14)	6.25 (6.14)	10.91 (11.13)	377

TABLE 6. REACTION OF I WITH XV

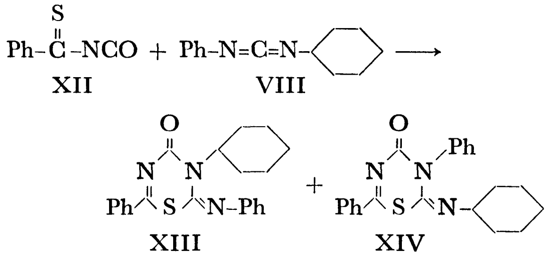
	R	Yield (%)	Mp (°C)	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	Analysis (%) Found (Calcd) C	H	N	MW (m/e)
XVIa	H	70[1]	154—155	1740[2]	1690 1640	74.07 (74.35)	4.92 (4.82)	11.49 (11.84)	355
XVIb	Cl	56	141—142	1740[2]	1690 1635	67.79 (67.80)	4.34 (4.12)	10.52 (10.78)	389
XVIc	NO_2	51	137—138	1740[2] 1720	1690 1640	66.31 (66.00)	4.04 (4.03)	13.64 (13.99)	400
XVIIa	H		194—195	1770[3]	1665 1640	74.54 (74.35)	4.81 (4.82)	11.85 (11.84)	355
XVIId	OMe	67.5[4]	151—152	1780[3]	1660 1640	71.54 (71.67)	5.19 (4.97)	10.66 (10.90)	385

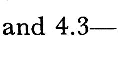
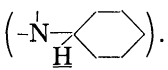
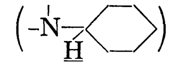
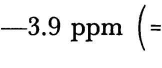
1) Total yield of XVIa and XVIIa. 2) Weak bands. 3) Very strong bands. 4) Total yield of XVId and XVIId.

138 ($ArC{\equiv}\overset{+}{N}H$), and 119 ($PhNCO^+$).[7]

Thiobenzoyl isocyanate (XII) reacted with VIII to give two isomeric cycloadducts, XIII (mp 146.5—147.5°C) and XIV (mp 160°C), in 23 and 20% yields, respectively.

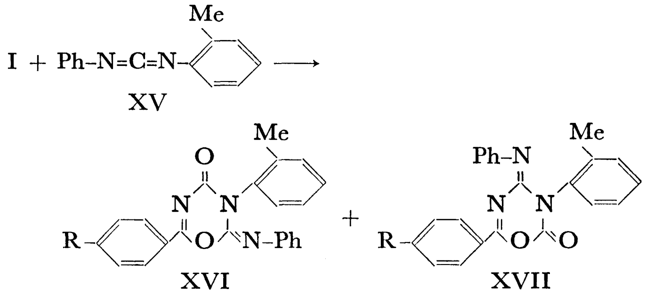
On the basis of IR and NMR spectra, structures XIII and XIV were assigned to (4+2) cycloadducts of the isocyanate to the cyclohexyl–N=C bond and to the phenyl–N=C bond of VIII, respectively.



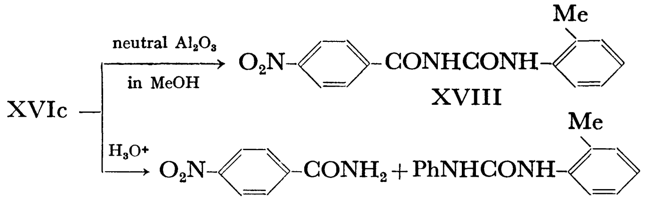
In the NMR spectrum of (4+2) cycloadduct IXb the methine-proton of *N*-cyclohexyl ring appears at δ 4.4—5.0 ppm as a multiplet, and the spectrum of (4+2) cycloadduct IIIa gives two methine-protons at δ 3.4—4.0  and 4.3—5.0 ppm . The spectra of XIII and XIV show a multiplet at δ 4.8—5.2 ppm  and one at δ 3.2—3.9 ppm .

Cycloadditions of benzoyl isocyanates (I) to *N*-phenyl-*N'*-*o*-tolylcarbodiimide (XV) were investigated; the results are given in Table 6. The products XVI and/or XVII were formed, depending on the nature of the substituents in the isocyanate. Crystals obtained from the reaction of Id with XV were found to be a mixture of XVId and XVIId by the IR spectrum. An attempt to separate XVId from the crystals by recrystallization was unsuccessful.

On the basis of the IR spectra, the adducts XVI were confirmed to be the corresponding (4+2)cycloadducts. It is evident from the results of chemical conversions that compounds XVI are the 6-aryl-2-phenylimino-3-*o*-tolyl-2*H*-1,3,5-oxadiazin-4(3*H*)-ones, whose structures correspond to the (4+2) cycloadducts of the isocyanates to the *o*-tolyl-N=C bond in XV.



a: R=H, b: R=Cl, c: R=NO_2, d: R=OMe



Treatment of the adduct XVIc with neutral alumina in methanol gave 1-*p*-nitrobenzoyl-3-*o*-tolylurea (XVIII), while XVIc was hydrolyzed with dilute hydrochloric acid to afford *p*-nitrobenzamide and 1-phenyl-3-*o*-tolylurea.

Isomeric adducts XVIIa and XVIId were assumed from the similarity between the IR spectra of XVII and VII, to be the corresponding 1,3,5-oxadiazin-6-ones.

Formation Pathways of the Products. The reaction pathways of the isocyanates and carbodiimides can be considered as follows.

As shown in Scheme 1, the isocyanate reacts with the carbodiimide to give first (2+2) cycloadduct (**A**). In fact, (2+2) cycloadducts V were obtained in the reaction of isocyanates I with carbodiimide IV at 0°C. Since (2+2) cycloadduct (**A**) is thermally unstable, it is converted to (4+2) cycloadduct (**B**) through either isomerization (path a) or 1,4-cycloaddition after dissociation into its components (path b).

On the other hand, 1,3,5-oxadiazin-6-one (**C**) obtained by the thermal isomerization of (2+2) cycloadduct Va or from the reaction of isocyanates I with carbodiimide XV, might be formed through either

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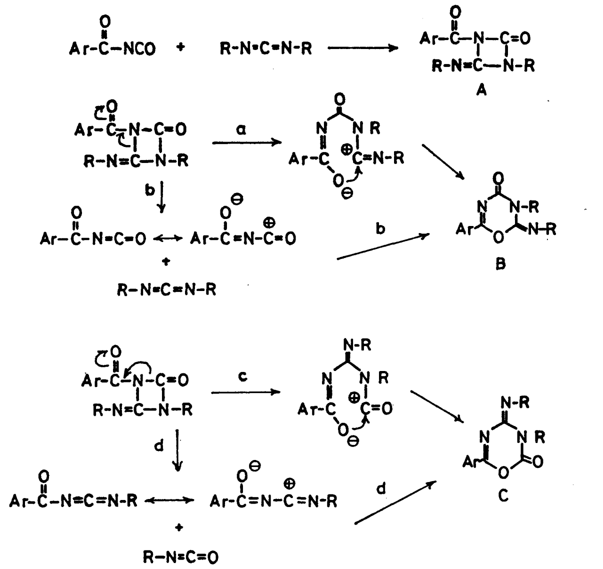
[7] Ar represents the *p*-chlorophenyl group.

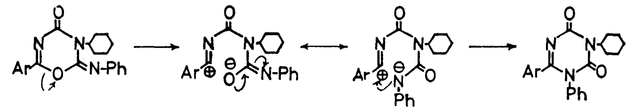


Scheme 1

isomerization (path c) or 1,4-cycloaddition after dissociation into aryl isocyanate and asymmetrical aroyl carbodiimide (path d).

However, isomerization paths a and c would seem to be more reasonable than the dissociation routes b and d. Indeed, no cross-over products, which would be expected from the reactions of isocyanate (Ar–$\underset{\underset{O}{\|}}{C}$–NCO) with carbodiimide (Ar–$\underset{\underset{O}{\|}}{C}$–N=C=N–R) and of isocyanate (RNCO) with carbodiimide (R–N=C=N–R), were formed in all the reactions.

Although the exact course of the formation of 1,3,5-triazine-2,6-diones XI from (4+2) cycloadducts IX and neutral alumina is not clear, we proposed the following sequence: if the ring opening of IX occurs, it would then recyclize to 1,3,5-triazine XI.



IX XI

A similar ring opening followed by recyclization was observed in the isomerization of the adduct of benzoylsulfene to carbodiimide.[8]

Experimental

All the melting points are uncorrected. The IR spectra were recorded on a Nippon Bunko IR-S spectrometer, and the UV spectra were measured with a Shimadzu SV-50A spectrophotometer. The NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as the internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV.

Materials. *p*-Substitued benzoyl isocyanates (Ia—Id)[5] and thiobenzoyl isocyanate (XII)[9] were prepared by the methods reported previously.

N,*N*′-Dicyclohexylcarbodiimide (II), bp 155—156°C/10 mmHg (lit,[10] bp 148—152°C/11 mmHg), and *N*,*N*′-diphenylcarbodiimide (IV), bp 119—120°C/0.2—0.3 mmHg (lit,[11] bp 110—112°C/0.2 mmHg), were prepared according to the reported methods.

N-Cyclohexyl-*N*′-phenylcarbodiimide (VIII). The carbodiimide was obtained from *N*-cyclohexyl-*N*′-phenylthiourea by a method similar to that described by Iwakura and Noguchi.[12] A mixture of *N*-cyclohexyl-*N*′-phenylthiourea (38 g), commercial sodium hypochlorite (650 g), 40% aqueous sodium hydroxide solution (180 m*l*) and toluene (200 m*l*) was stirred at 70°C for 2 hr. After the reaction mixture was cooled, the aqueous layer was separated and then extracted with toluene. The combined toluene solution was washed with water and dried over anhydrous sodium sulfate. After evaporation of the toluene, the residue was distilled over active copper powder,[13] affording VIII (16 g), bp 139—140°C/4 mmHg. $\nu_{N=C=N}$: 2180 cm^{-1}. M$^+$: *m*/*e* 200.

N-Phenyl-*N*′-*o*-tolylcarbodiimide (XV). The carbodiimide was prepared according to a method similar to that described by Meakins and Moss.[14] Yellow mercuric oxide (35.6 g) was added in portions to a refluxing solution of *N*-phenyl-*N*′-*o*-tolylthiourea (20 g) and sulfur (0.2 g) in acetone (400 m*l*). After the reaction mixture was boiled for 20 min, the precipitate was collected and washed with acetone (100 m*l*). The combined acetone solution was dried over anhydrous sodium sulfate and concentrated *in vacuo*, leaving a residue. Since the residue was transformed into *N*,*N*′-diphenyl- and -di-*o*-tolylcarbodiimide on distillation, the residue was purified by chromatography on neutral alumina using petroleum benzine as an eluent. $\nu_{N=C=N}$ 2180 cm^{-1}. M$^+$: *m*/*e* 208.

Reaction of I with II. A solution of 0.7 g of II in 5 m*l* of benzene–diethyl ether mixture (1:1) was added dropwise to a solution of 0.5 g of Ia in 2 m*l* of benzene at 0°C. The reaction mixture was stirred at room temperature for a few minutes, during which time crystals were formed. Filtration gave colorless crystals, which on recrystallization from benzene–petroleum benzine (bp 45—60°C) mixture afforded (4+2) cycloadduct IIIa, mp 142—143°C, as colorless prisms. Yield, 0.6 g (54%).

Similar reactions of Ib—Id with II afforded the corresponding (4+2) cycloadducts IIIb—IIId. The results are given in Table 1.

Reaction of I with IV. *i)*: To a solution of 1.2 g of Ia in 10 m*l* of benzene was added dropwise a solution of 1.6 g of IV in 10 m*l* of benzene–diethyl ether mixture (1:1) at 0°C. After the reaction mixture was stirred at the same temperature for 24 hr, filtration gave colorless crystals. Recrystallization from dichloromethane–petroleum benzine (bp 35—45°C) mixture afforded 1.5 g (55%) of (2+2) cycloadduct Va, mp 112—113°C (decomp.), as colorless needles.

Similar reactions of Ib and Ic with IV gave the corresponding (2+2) cycloadducts Vb and Vc. The results are summarized in Table 2.

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ii): A solution of 1.0 g of Ia and 1.32 g of IV in a mixture of 15 m*l* of benzene and 5 m*l* of diethyl ether was stirred at room temperature for 2 hr, and then at 70°C for 5 hr. The reaction mixture was concentrated *in vacuo* to leave a residue, which crystallized on trituration with petroleum benzine (bp 40—50°C). The crystals were separated into more soluble and less soluble parts by fractional crystallization. The former was recrystallized from ethanol to give 0.69 g (30%) of 3,6-diphenyl-4-phenylimino-2*H*-1,3,5-oxadiazin-2-(3*H*)-one (VII), mp 204—205°C (decomp.), as yellow needles.

Found: C, 73.82; H, 4.43; N, 12.29%. Calcd for $C_{21}H_{15}O_2N_3$: C, 73.89; H, 4.43; N, 12.31%.

Recrystallization of the latter from ethanol afforded 0.29 g (12%) of (4+2) cycloadduct VIa, mp 179—179.5°C, as yellow prisms.

Thermal Isomerization of (2+2) Cycloadduct V. Thermal isomerization of V in the solid state was carried out in a test tube at 120°C (oil bath) for 2 hr. After cooling, the product was triturated with petroleum benzine (bp 40—50°C) to yield crystals. Recrystallization from ethanol afforded isomeric (4+2) cycloadduct VI. The results are given in Table 3.

Reaction of I with VIII. A solution of 0.7 g of Ia and 1.0 g of VIII in a mixture of 18 m*l* of benzene and 8 m*l* of diethyl ether was stirred at 70°C for 1.5 hr. The reaction mixture was then concentrated *in vacuo* to leave a residue, which crystallized on trituration with petroleum benzine (bp 35—50°C). Recrystallization from *n*-pentane afforded 1.3 g (75%) of (4+2) cycloadduct IXa, mp 128—129°C, as colorless needles.

Similar reactions of Ib—Id with VIII gave the corresponding (4+2) cycloadducts IXb—IXd. The results are summarized in Table 4.

Hydrolysis of IXb with Hydrochloric Acid. A suspension of 0.5 g of IXb in 5 m*l* of 1N hydrochloric acid was stirred at room temperature for 3 hr. The solution was filtered to give crystals. Recrystallization from methanol gave 0.36 g (69%) of 1-cyclohexyl-1-phenylcarbamoyl-3-*p*-chlorobenzoylurea (X), mp 131—132°C, as colorless needles.

Found: C, 63.12; H, 5.60; N, 10.62%. Calcd for $C_{21}H_{22}O_3N_3Cl$: C, 63.08; H, 5.51; N, 10.52%.

IR (KBr) cm^{-1}: ν_{NH} 3245, 3230. ν_{CO} 1715, 1680, 1660.

Isomerization of IX with Neutral Alumina. After a mixture of 0.65 g of IXa and 20 g of neutral alumina in 35 m*l* of chloroform was stirred at room temperature for 1 hr, the alumina was collected and washed with chloroform. The combined chloroform solution was concentrated *in vacuo* to leave crystals. Recrystallization from petroleum benzine (bp 60—90°C) gave 0.21 g (32.4%) of the 1,3,5-triazine-2,6-dione XIa, mp 255.5—256°C, as colorless prisms.

The results of similar isomerizations of IXb—IXd with neutral alumina are summarized in Table 5.

Reaction of XII with VIII. To a solution of XII generated *in situ* from 0.93 g of 2-phenylthiazoline-4,5-dione[15] in 20 m*l* of xylene was added 0.97 g of VIII. After the reaction mixture was stirred at room temperature for 3 hr, the xylene was evaporated *in vacuo* to leave crystals. Recrystallization from diethyl ether gave 0.36 g (20%) of the (4+2) cycloadduct XIV, mp 160°C, as colorless needles.

Found: C, 69.65; H, 5.68; N, 11.51%. Calcd for $C_{21}H_{21}ON_3S$: C, 69.40; H, 5.83; N, 11.56%. M^+: *m/e* 363.

IR (KBr) cm^{-1}: $\nu_{C=O}$ 1700 (sh), $\nu_{C=N}$ 1690, 1610.

The mother liquor was concentrated to leave a residue, which on chromatography on neutral alumina using chloroform as an eluent afforded crystals. Recrystallization from petroleum benzine (bp 60—90°C) gave 0.41 g (23%) of the isomeric (4+2) cycloadduct XIII, mp 146.5—147.5°C, as yellow prisms.

Found: C, 69.66; H, 5.65; N, 11.25%. Calcd for $C_{21}H_{21}ON_3S$: C, 69.40; H, 5.83; N, 11.56%. M^+: *m/e* 363.

IR (KBr) cm^{-1}: $\nu_{C=O}$ 1720 (sh), $\nu_{C=N}$ 1700, 1610.

Reaction of I with XV. A solution of 0.7 g of Ib and 0.8 g of XV in a mixture of 18 m*l* of benzene and 8 m*l* of diethyl ether was stirred at 70°C for 4 hr. The reaction mixture was then concentrated to leave a residue which was triturated with petroleum benzine (bp 35—50°C) to form crystals. Recrystallization from *n*-pentane gave 0.85 g (57%) of (4+2) cycloadduct XVI, mp 141—142°C, as yellow prisms.

Similar reactions of Ia and Id with XV gave a mixture of the corresponding (4+2) cycloadducts XVIa and XVId, and isomers XVIIa and XVIId. By repeated fractional recrystallization from *n*-pentane, XVIa, XVIIa, and XVIId were isolated in pure form but not XVId. The results are given in Table 6.

Hydrolysis of XVIc. A mixture of 0.5 g of XVIc and 15 g of neutral alumina in 30 m*l* of methanol was stirred at room temperature for 1.5 hr. The alumina was then collected and washed with methanol and the combined methanol solution concentrated *in vacuo* to leave a residue. Several recrystallizations from methanol gave 0.16 g (42.5%) of 1-*p*-nitrobenzoyl-3-*o*-tolylurea (XVIII), mp 232—233°C, which was identical with the authentic sample prepared from *p*-nitrobenzoyl isocyanate and *o*-toluidine.

Found: C, 60.45; H, 4.30; N, 14.34%. Calcd for $C_{15}H_{13}O_4N_3$: C, 60.19; H, 4.38; N, 14.04%.

IR (KBr) cm^{-1}: ν_{NH} 3240, 3170. $\nu_{C=O}$ 1720, 1690 (sh), 1670 (sh).

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