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Studies of Acyl and Thioacyl Isocyanates. IX.[1] The Cycloaddition Reactions of Benzoyl and Thiobenzoyl Isocyanates with Anils

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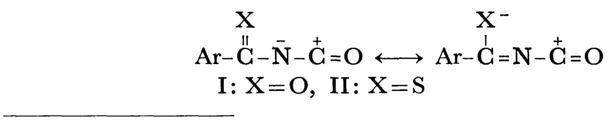
Thiobenzoyl isocyanates react with benzylidenanilines, benzylidenalkylamines and dianils to yield the corresponding mono- and bis(4+2) cycloadducts. Benzoyl isocyanates do not react with benzylidenanilines, but they are easily added to benzylidenebenzylamine to give the (4+2) cycloadducts in good yields. Cycloaddition of these isocyanates to anils is dependent upon the basicity of the nitrogen atom of C=N bond. Neither benzoyl isocyanates nor thiobenzoyl isocyanates are added to the C=C bond of cinnamylidenanilines, but they react with the C=N bond to afford the (4+2) cycloadducts.

The 1,4-dipolar contribution of benzoyl (I) and thiobenzoyl isocyanates (II) is manifest in cycloaddition reactions as evidenced by their dimerization[2] and reactions of carbodiimides.[3]



$$\mathrm{Ar{-}\overset{\overset{X}{\|}}{C}{-}N{=}C{=}O \longleftrightarrow Ar{-}\overset{\overset{X}{\|}}{C}{-}\overset{+}{N}{=}\overset{-}{C}{-}O \longleftrightarrow Ar{-}\overset{\overset{X}{\|}}{C}{-}\overset{-}{N}{-}\overset{+}{C}{=}O \longleftrightarrow Ar{-}\overset{\overset{X^-}{|}}{C}{=}N{-}\overset{+}{C}{=}O}$$

I: X=O, II: X=S

We have therefore undertaken to expand the cycloaddition reactions of these isocyanates with various compounds having a C=N bond. A preliminary report was given on the cycloaddition reaction of I and II with some benzylidenamines.[4]

Investigation was made to prepare new heterocycles, and obtain information on the differences between the reactivities of I and II in cycloaddition reactions. This paper deals with the cycloaddition to benzylidenamines, dianils and cinnamylidenanilines.

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[1] Part VIII of this series: O. Tsuge and K. Sakai, This Bulletin, **45**, 1534 (1972).

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

[3] O. Tsuge and K. Sakai, This Bulletin, **45**, 1534 (1972).

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

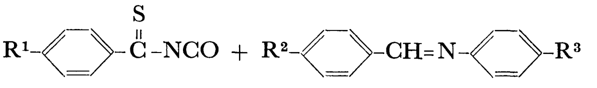
Table 1. 2,3,6-Triaryl-2*H*-1,3,5-thiadiazin-4(3*H*)-ones IV[a)]

	IV			Yield	Mp[b)]	Appearance (recryst. solvent)	IR, cm^{-1}		Microanalysis (%) Found (Calcd)		
	R^1	R^2	R^3	(%)	(°C)		$\nu_{C=O}$	$\nu_{C=N}$	C	H	N
a	H	H	H	100	193—194	colorless needles (benzene)	1675	1650	73.59 (73.24)	4.68 (4.68)	7.83 (8.14)
b	OMe	H	H	100	191.5—192	colorless needles (benzene)	1655	1640	70.79 (70.58)	4.78 (4.85)	7.09 (7.48)
c	Cl	H	H	100	185—186	pale yellow needles (benzene-petr. ether)	1680	1650	66.81 (66.60)	3.85 (3.97)	7.68 (7.40)
d[c)]	H	OMe	H	88	185	colorless needles (benzene-petr. ether)	1685	1650	70.88 (70.58)	4.97 (4.85)	7.67 (7.48)
e[d)]	H	H	OMe	94	168—169	colorless needles (benzene-petr. ether)	1670	1640	70.86 (70.58)	4.55 (4.85)	7.58 (7.48)
f	H	NO$_2$	H	89	184.5	pale yellow needles (benzene)	1685	1650	65.82 (65.83)	3.42 (3.77)	10.61 (10.47)
g	H	H	NO$_2$	70[e)]	203—204	pale yellow needles (benzene)	1680 1660	1645	65.68 (65.83)	3.51 (3.77)	10.51 (10.47)

a) Reaction conditions: at room temperature for 5 min. b) All the compounds melted with decomposition. c) NMR (CDCl$_3$) δ ppm: 3.78 (3H, singlet, OCH$_3$), 6.18 (1H, singlet, >CH), 6.78—8.20 (14H, multiplet, aromatic protons). d) NMR (CDCl$_3$) δ ppm: 3.79 (3H, singlet, OCH$_3$), 6.16 (1H, singlet, >CH), 6.78—8.18 (14H, multiplet, aromatic protons). e) Reaction conditions: at room temperature for 5 hr.

Results and Discussion

Reactions with Benzylidenamines. No reaction of benzoyl isocyanates (I) with benzylidenanilines (III) took place even in xylene under reflux, but thiobenzoyl isocyanates (II) reacted easily with anils IIIa—IIIg at room temperature to afford the corresponding 1:1 adducts IVa—IVg in good yields.

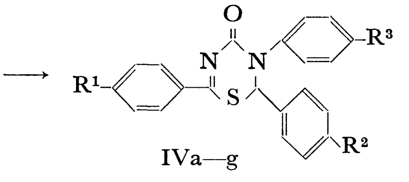


II

a: R^1=H
b: R^1=OMe
c: R^1=Cl

III

a: R^2=R^3=H
b: R^2=OMe, R^3=H
c: R^2=H, R^3=OMe
d: R^2=NO$_2$, R^3=H
e: R^2=H, R^3=NO$_2$
f: R^2=R^3=NO$_2$



IVa—g

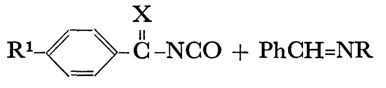
The structures of IV were deduced to be the (4+2) cycloadducts, 2*H*-1,3,5-thiadiazin-4(3*H*)-ones, on the basis of their spectral data. The yields, physical properties and results of elemental analyses of IV are given in Table 1.

IVe was easily hydrolyzed with hydrochloric acid to *N*-(*p*-methoxyphenyl)-*N'*-thiobenzoylurea (V), identical with an authentic sample prepared from IIa and *p*-anisidine. This supports the proposed structure for IV.[5)]

V

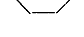
As shown in Table 1, the yield of IV is affected by the nature of substituent R^3 but hardly at all by that of R^2, from the fact that IIa reacted easily with *p*-nitrobenzylidenaniline (IIId) to give IVf while it took 5 hr for IIa to disappear with benzylidene-*p*-nitroaniline (IIIe). Addition of IIa to *p*-nitrobenzylidene-*p*-nitroaniline (IIIf) did not take place even under forced conditions (90—100°C, 1 hr).

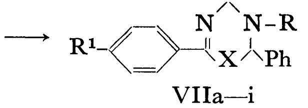
On the other hand, benzoyl isocyanates (I) as well as II reacted easily with benzylidenebenzylamine (VIa) at room temperature, forming (4+2) cycloadducts VII in excellent yields. Similarly, the (4+2) cycloadduct was obtained from IIa and benzylidene-*n*-propylamine (VIb) and -cyclohexylamine (VIc). The structures of VII were confirmed by their spectral data and elemental analyses. The yields, physical properties and results of elemental analyses of VII are given in Table 2.



I (X=O)
a: R^1=H, b: R^1=OMe
c: R^1=Cl, d: R^1=NO$_2$
II (X=S)

VI
a: R=CH$_2$Ph
b: R=*n*-Pr
c: R=





VIIa—i
X=O or S

Reactions with Dianils. Benzoyl isocyanate (Ia) reacted easily with dibenzylidenethylenediamine (VIIIa) at room temperature to afford colorless crystals, whose IR spectrum indicated that the product is a

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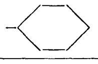
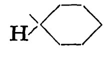
[5)] After completion of this work, we learned that IVa, mp 185—190°C (decomp.), and IVb, mp 190°C (decomp.), were independently prepared by J. Goerdeler and H. Schenk (*Chem. Ber.*, **98**, 3831 (1965)).

Table 2. 3-Alkyl-2,6-diaryl-2H-1,3,5-oxa(thia)diazin-4(3H)-ones VII[a]

	VII[b]			Yield (%)	Mp[c] (°C)	IR, cm^{-1}		Microanalysis (%)					
								Found			Calcd		
	X	R′	R			$\nu_{C=O}$	$\nu_{C=N}$	C	H	N	C	H	N
a	O	H	$\mathrm{CH_2Ph}$	100	118	1680, 1660	1600	77.07	5.60	8.40	77.17	5.30	8.18
b	O	OMe	$\mathrm{CH_2Ph}$	100	92	1660	1600	74.29	5.69	7.25	74.14	5.41	7.52
c	O	Cl	$\mathrm{CH_2Ph}$	100	100	1660	1605	69.91	4.24	7.79	70.12	4.55	7.43
d	O	$\mathrm{NO_2}$	$\mathrm{CH_2Ph}$	100	102	1680	1620, 1600	68.32	4.75	10.63	68.21	4.42	10.85
e	S	H	$\mathrm{CH_2Ph}$	88	180—181	1660	1640	73.75	5.13	8.17	73.73	5.06	7.82
f	S	OMe	$\mathrm{CH_2Ph}$	80	155—157	1690, 1660	1645	70.89	5.06	6.92	71.12	5.19	7.21
g	S	Cl	$\mathrm{CH_2Ph}$	100	167—168	1680, 1665	1640	67.25	4.37	6.84	67.26	4.33	7.13
h[d]	S	H	n-Pr	73	160—161	1660	1642	69.80	5.73	8.94	69.66	5.85	9.03
i[e]	S	H		74	216—216.5	1660	1637	72.05	6.48	8.10	71.98	6.33	8.00

a) Reaction conditions: at room temperature for 5 min. b) All the compounds are colorless needles. c) All the compounds melted with decomposition. d) NMR ($\mathrm{CDCl_3}$) δ ppm: 0.92 (3H, triplet, $-(\mathrm{CH_2})_2-\mathrm{C\underline{H}_3}$), 1.4—2.0 (2H, multiplet, $-\mathrm{CH_2}-\mathrm{C\underline{H}_2}-$Me), 3.11, 4.05 (each 1H, double triplet, $-\mathrm{C\underline{H}_2}-$Et), 5.85 (1H, singlet, ⋟CH), 7.15—8.1 (10H, multiplet, aromatic protons). e) NMR ($\mathrm{CDCl_3}$) δ ppm: 0.9—2.2 (10H, multiplet, $\mathrm{CH_2}$), 4.4—5.0 (1H, broad signal, ), 5.97 (1H, singlet, ⋟CH), 7.2—8.1 (10H, multiplet, aromatic protons).

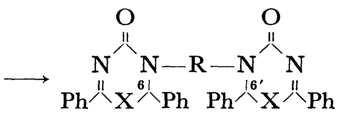
mixture of bis(4+2) cycloadduct IXa and N,N'-dibenzoylcarbamoylethylenediamine X. As bis(4+2) cycloadduct IXa was rather unstable and decomposed during recrystallization to give X, the crystals were washed with benzene and then diethyl ether to obtain almost pure IXa, mp 131—132.5°C (decomp.), whose IR spectrum showed that the bands are due to $\nu_{C=O}$ and $\nu_{C=N}$ at 1680, 1665, and 1615 cm^{-1}. However, the NMR spectrum could not be determined because of decomposition of IXa in solution. Signals appeared at δ 3.78, 4.0 (each $\mathrm{CH_2}$), 6.2 (NH), 6.9 (CH), 7.2—8.05 (aromatic protons), 8.32 (NH), and 10.05 ppm (CHO) in the NMR spectrum in deuteriochloroform ($\mathrm{CDCl_3}$); this indicates that IXa was partially hydrolyzed to X and benzaldehyde. Hydrolysis of IXa with hydrochloric acid in ethanol afforded Xa, mp 270.5°C (decomp.), in a good yield.

Ia or IIa + PhCH=N-R-N=CHPh

VIII

a: R=$(\mathrm{CH_2})_2$

b: R=PhCH



IX

a: X=O, R=$(\mathrm{CH_2})_2$

b: X=S, R=$(\mathrm{CH_2})_2$

c: X=S, R=PhCH

$$\mathrm{IXa} \xrightarrow[\text{in EtOH}]{\text{HCl}} \underset{\mathrm{X}}{(\mathrm{PhCONHCONHCH_2})_2} + \mathrm{PhCHO}$$

The reactions of IIa with VIIIa and with hydrobenzamide (VIIIb) afforded the corresponding bis-(4+2) cycloadducts IXb and IXc, even when equimolar amounts of IIa and VIII were used. The yields for the 2: 1 molar ratio (Ia or IIa to VIII), physical properties and results of elemental analyses of IX are given in Table 3.

In the reaction with VIIIb, two isomers IXc-1 (high melting) and IXc-2 (low melting) were formed. Their IR spectra were very similar and the NMR spectra supported the (4+2) cycloadduct structures.[6]

Table 3. Bis-2H-1,3,5-thia (oxa) diazin-4(3H)-ones IX[a]

	X	R	Yield (%)	Mp (°C)	IR, cm^{-1}		Microanalysis (%)					
							Found			Calcd		
					$\nu_{C=O}$	$\nu_{C=N}$	C	H	N	C	H	N
IXa	O	$(\mathrm{CH_2})_2$	82	131—132.5 (decomp.)	1680 1660	1615	72.02	5.00	10.63	72.44	4.94	10.56
IXb	S	$(\mathrm{CH_2})_2$	75	230—231 (decomp.)	1660	1640	68.32	4.66	9.95	68.27	4.40	9.58
IXc-1	S	PhCH	30	208—209 (decomp.)	1660	1636	71.32	4.25	8.59	71.14	4.52	8.97
IXc-2	S	PhCH	67	186	1660	1637	71.39	4.38	8.52	71.14	4.52	8.97

a) Reaction conditions: I or II/VIII (2/1 molar ratio), at room temperature for a few minutes. All the compounds are colorless needles.

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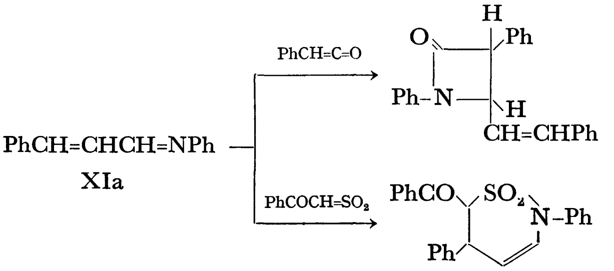
[6] Although it is conceivable that IXc-1 and IXc-2 are stereoisomers resulting from the configurations of 6- and 6′-phenyl groups in the 1,3,5-thiadiazine rings and from the conformation of the methine carbon atom between both rings, their stereochemistry is not clear.

Reaction with Cinnamylidenanilines. Very few investigations of cycloaddition to cinnamylidenaniline (XIa) have been reported. Pfleger and Jäger[7] proposed an addition reaction of phenylketene to XIa of the Diels-Alder type, but Sakamoto and Tomimatsu[8] analyzed the structure of the same reaction product and showed that it is the (2+2) cycloadduct, β-lactam. Recently,[9] we found that the reaction of benzoylsulfene with XIa gives an adduct of the Diels-Alder type. It thus seemed of interest to investigate the reaction of I or II with cinnamylidenanilines.



Under various conditions, the reaction of Ia with XIa gave resinous materials exclusively. However, IIa reacted easily with XIa at room temperature to afford a good yield of crystalline 1: 1 adduct XIIa.

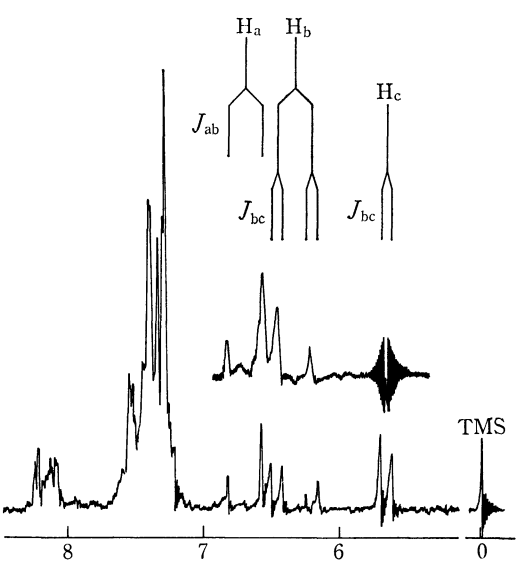
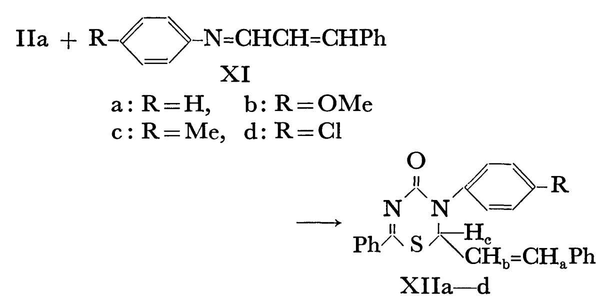
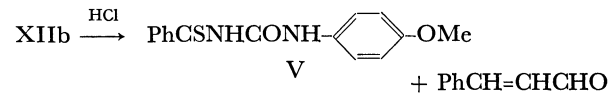


Fig. 1. NMR spectrum of XIIa.

The IR spectrum of XIIa was very similar to that of IVa and showed the characteristic band assignable to the CH=CH (*trans*) linkage at 976 cm^{-1}. The NMR spectrum (Fig. 1) exhibited two olefinic protons H_a and H_b, and methine proton H_c at δ 6.76 (1H, doublet with $J_{ab}=15.8$ Hz), 6.38 (1H, double doublet with $J_{ab}=15.8$ and $J_{bc}=5.2$ Hz, changed to a doublet with $J_{ab}=15.8$ Hz when irradiated at δ 5.70 ppm) and 5.70 ppm (1H, doublet with $J_{bc}=5.2$ Hz), besides aromatic protons.

The value of the ethylenic coupling constant of the β-lactam obtained from phenylketene and XIa has been reported to be 17 Hz,[8] and that of *trans*-cinnamaldehyde, the starting material of XIa, is 16.2 Hz.[10] Thus it is apparent that XIIa is the (4+2) cycloadduct of IIa to the C=N bond in XIa, 3,6-diphenyl-2-*trans*-styryl-2*H*-1,3,5-thiadiazin-4(3*H*)-one.





Similar reactions of IIa with cinnamylidenanilines XIb—XId gave the corresponding (4+2) cycloadducts XIIb—XIId. Finally, XIIb was easily hydrolyzed with hydrochloric acid to urea V and cinnamaldehyde, providing additional support for the proposed structure. The yields, physical properties, results of elemental analyses, and spectral data of XII are given in Tables 4 and 5, respectively.

TABLE 4. 3,6-DIARYL-2-*trans*-STYRYL-2*H*-1,3,5-THIADIAZIN-4(3H)-ONES XII

XII	R	Yield (%)	Mp$^{a)}$ (°C)	Appearance (recryst. solvent)	Microanalysis (%) Found C	Found H	Found N	Calcd C	Calcd H	Calcd N
a	H	88	175	pale yellow prisms (benzene-petr. ether)	74.98	5.01	7.36	74.58	4.90	7.56
b	OMe	86	147—148	colorless needles (benzene-petr. ether)	71.83	5.00	6.96	71.98	5.03	7.00
c	Me	73	169—170	yellow needles (benzene)	75.26	5.06	7.27	74.98	5.24	7.29
d	Cl	71	170—171	yellow needles (benzene-diethyl ether)	68.50	4.19	6.81	68.34	4.21	6.93

a) All the compounds melted with decomposition.

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[7] R. Pfleger and A. Jäger, *Chem. Ber.*, **90**, 2460 (1957).

[8] M. Sakamoto and Y. Tomimatsu, *Yakugaku Zasshi*, **90**, 1386 (1970).

[9] O. Tsuge and S. Iwanami, This Bulletin, **44**, 2750 (1971).

[10] The olefinic coupling constant of XIa could not be measured as the olefinic protons appeared at the same position as the aromatic protons. The olefinic coupling constant of cinnamylidene-*n*-propylamine was 16 Hz.

Table 5. IR and NMR spectral data

	IR, cm^{-1}			NMR ($CDCl_3$) δ ppm				J (Hz)	
	$\nu_{C=O}$	$\nu_{C=N}$	$\delta_{CH=CH}$ (trans)	H_a	H_b	H_c	CH_3	J_{ab}	J_{bc}
XIIa	1680	1662	976	6.76	6.38	5.70		15.8	5.2
XIIb	1680	1645	975	6.70	6.33	5.60	3.77	15.8	5.3
XIIc	1670	1657	968	6.66	6.31	5.59	2.32	15.0	5.3
XIId	1670	1655	968	6.72	6.37	5.65		15.2	5.0

Experimental

All melting points are uncorrected. The IR spectra were measured as KBr pellets on a Nippon Bunko IR-S spectrophotometer; the NMR spectra were determined at 60 MHz on a Hitachi R-20 NMR spectrometer with TMS as an internal reference.

Materials. Benzoyl isocyanates (Ia—Id) were prepared by the method reported previously.[2] Thiobenzoyl isocyanates (IIa—IIc):[11] A solution of 1.0 g of 2-phenyl-,[12] 2-*p*-methoxyphenyl-[12] or 2-*p*-chlorophenylthiazoline-2,4-dione[12] in 10 m*l* of xylene was heated at 120°C, giving a reddish violet solution of II which was used *in situ*. This solution is referred to as the standard solution of II.

Anils were prepared from the corresponding aldehyde and amine. Benzylidenaniline (IIIa), mp 54°C (lit,[13] mp 53.5°C); *p*-methoxybenzylidenaniline (IIIb), mp 61°C (lit,[14] mp 58—59°C); benzylidene-*p*-anisidine (IIIc), mp 73—74°C (lit,[15] mp 72°C); *p*-nitrobenzylidenaniline (IIId), mp 93°C (lit,[16] mp 93°C); benzylidene-*p*-nitroaniline (IIIe), mp 118°C (lit,[17] mp 117—118°C); *p*-nitrobenzylidene-*p*-nitroaniline (IIIf), mp 199°C (lit,[18] mp 198.5°C); benzylidenebenzylamine (VIa), bp 200—201°C/18 mmHg (lit,[19] bp 205°C/20 mmHg); -*n*-propylamine (VIb), bp 101—102°C/16 mmHg (lit,[20] bp 208—210°C/744 mmHg); -cyclohexylamine (VIc), bp 154°C/18 mmHg (lit,[21] bp 136°C/16 mmHg). Dibenzylidenethylenediamine (VIIIa), mp 54°C (lit,[22] mp 53—54°C); hydrobenzamide (VIIIb), mp 110°C (lit,[23] mp 110°C). Cinnamylidenaniline (XIa), mp 109°C (lit,[22] mp 109°C); -*p*-anisidine (XIb), mp 118—119°C (lit,[24] mp 119°C); -*p*-toluidine (XIc), mp 82°C (lit,[25] mp 83°C); -*p*-chloroaniline (XId), mp 106—107°C (lit,[24] mp 107°C).

General Procedure for the Reaction of I or II with III and/or VI. A solution of equimolar amounts of I or II and III or IV in xylene was stirred at room temperature for a few minutes, during which time the reaction was completed. Filtration and recrystallization of crystals gave the corresponding (4+2) cycloadducts. The yields, physical properties, and results of elemental analyses of (4+2) cycloadducts IV and VII are given in Tables 1 and 2, respectively.

Hydrolysis of (4+2) Cycloadduct IVe. A solution of 0.3 g of IVe in 20 m*l* of methanol containing 2 m*l* of concentrated hydrochloric acid was stirred at 50°C for 5 min during which time it turned into a clear yellow solution. The solution was evaporated *in vacuo* to leave a residue which was washed with diethyl ether. Recrystallization of the ether-insoluble yellow crystals from ethanol gave 0.13 g (57%) of *N*-(*p*-methoxyphenyl)-*N'*-thiobenzoylurea (V), mp 178—179°C (decomp.) (lit,[26] mp 179°C (decomp.)), which was identical with the authentic sample prepared from IIa and *p*-anisidine. From the ether-washings, benzaldehyde was identified as its 2,4-dinitrophenylhydrazone.

Reaction of Ia with Dibenzylidenethylenediamine (VIIIa). A solution of 1.25 g of Ia and 1.0 g of VIIIa in 20 m*l* of dry benzene was stirred at room temperature for 10 min, and then filtered to give 1.85 g of solid whose IR spectrum indicated it to be a mixture of bis(4+2) cycloadduct IXa and *N,N'*-dibenzoylcarbamoylethylenediamine (X). The crystals were washed with benzene and then diethyl ether to leave colorless crystals, mp 131—132.5°C (decomp.), which were subjected to microanalysis without further purification.

The washings were evaporated *in vacuo* to leave X which corresponds to the hydrolyzed product of IXa.

A solution of 0.5 g of IXa in 20 m*l* of ethanol containing 2 m*l* of concentrated hydrochloric acid was stirred at 50°C for a few minutes, and the colorless crystals were filtered. Recrystallization from acetic acid afforded 0.28 g (84%) of X, mp 270.5°C (decomp.), as colorless prisms.

Found: C, 61.32; H, 4.96; N, 15.80%. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12; N, 15.81%.

IR cm^{-1}: 3290 (NH), 1697, 1665 (C=O).

NMR (trifluoroacetic acid (CF_3COOH)) δ ppm: 3.88 (4H, broad signal, CH_2), 7.4—8.1 (10 H, multiplet, phenyl protons), 9.5, 10.0 (each 2H, broad signal, NH).

Reaction of IIa with Hydrobenzamide (VIIIb). When 0.8 g of VIIIb was added to the standard solution of IIa at room temperature, colorless crystals deposited immediately. Filtration gave 0.5 g (30%) of (4+2) cycloadduct IXc-l, which was washed with hot benzene and then subjected to microanalysis because of its insolubility in ordinary organic solvents.

NMR (CF_3COOH) δ ppm: 6.62 (1H, singlet, CH), 6.9—8.3 (22H, multiplet, two methine and 20 aromatic protons).

The xylene filtrate was evaporated *in vacuo* to leave a viscous oily substance, which solidified on trituration with petroleum ether. Recrystallization from benzene–petroleum ether (bp 45—65°C) gave 1.12 g (67%) of isomeric (4+2) cycloadduct IXc-2 as colorless needles.

NMR (carbon tetrachloride) δ ppm: 6.28 (1H, singlet, CH), 6.8—7.8 (22H, multiplet, two methine and 20 aromatic protons).

Similarly, the reaction of the standard solution of IIa with 0.62 g of VIIIa at room temperature for 5 min gave (4+2) cycloadduct IXb, which on recrystallization from

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ethanol afforded 1.2 g (75%) of colorless needles.

NMR (CF_3COOH) δ ppm: 3.6—4.3 (4H, multiplet, CH_2), 6.63 (2H, singlet, CH), 7.5—8.2 (20H, multiplet, aromatic protons).

The physical properties and results of elemental analyses of IX are given in Table 3.

Reaction of IIa with Cinnamylidenanilines (XI). When an equimolar amount of XI was added to the standard solution of IIa, crystals were formed immediately. Filtration and recrystallization afforded the corresponding (4+2) cycloadduct XII.

Hydrolysis of (4+2) Cycloadduct XIIb. A solution of 0.3 g of XIIb in 20 m*l* of methanol containing 4 m*l* of concentrated hydrochloric acid was stirred at 50°C for 5 min during which time it turned into a clear yellow solution. The solution was evaporated *in vacuo* to leave a residue which was washed with diethyl ether and then ethanol. Recrystallization from ethanol afforded 0.11 g (52%) of urea V, mp 178—179°C (decomp.).

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