

REACTION OF BENZOYL AND TRICHLOROACETYL  
ISOCYANATES WITH SCHIFF BASES

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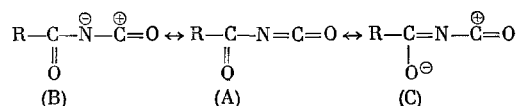
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Benzoyl isocyanate reacts with diene, olefin and acetylene compounds, by the type of 1,2-addition, with the formation of a 4-membered  $\beta$ -lactam ring [1, 2]. It seemed of interest to us to ascertain whether benzoyl and trichloroacetyl isocyanates would also react in this manner with unsaturated compounds, containing a heteroatom, and primarily with Schiff bases. From the literature data it is known that  $\alpha$ -naphthyl and phenyl isocyanates react with Schiff bases either by the type of substitution [3] or with the formation of a 4-member  $\beta$ -lactam ring [4]. Thiobenzoyl and alkyl(aryl)mercaptothiocarbonyl isocyanates react with Schiff bases by the diene synthesis type, with the formation of adducts containing a 6-membered ring, namely thiadiazinone derivatives [5, 6]. Phenyl isocyanate reacts with benzaethylamine with the formation of 6-membered adducts, namely triazinone and triazinedione derivatives in a ratio of 1:2 and 2:1 [7].

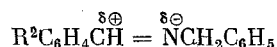
Our study of the reaction of benzoyl and trichloroacetyl isocyanates with benzalbenzylamine and p-benzalbenzylamine derivatives disclosed that the reaction proceeds with the formation of the adducts of the 1,4-addition of benzoyl and trichloroacetyl isocyanates to the indicated Schiff bases, which adducts correspond to oxadiazinone derivatives. The reactions go at room temperature in 75-90% yields. All of the obtained oxadiazinone derivatives are crystalline compounds which are exceedingly sensitive to moisture. The data on the adducts are given in Table 1.

The structure of the obtained compounds is confirmed by the elemental analysis data, the IR spectra, and chemical transformations. In the IR spectra of the obtained compounds are present the intense absorption bands of the C=O group of the oxadiazine ring at 1670-1767  $\text{cm}^{-1}$  for the adducts of benzoyl isocyanate with Schiff bases, and at 1698  $\text{cm}^{-1}$  for the adduct of trichloroacetyl isocyanate with benzalbenzylamine [5]. The IR spectra of compounds (I) and (II) are shown in Fig. 1.

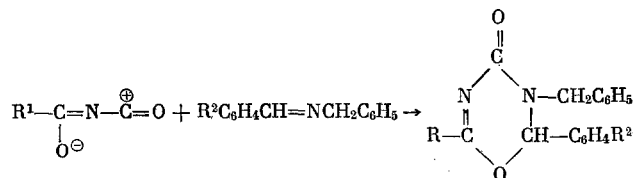
Acyl(aroil) isocyanates are polarized in such a manner [8] that they can behave in addition reactions as either 1,2- or 1,4-dipoles:



Starting with the premise that the reaction of benzoyl and trichloroacetyl isocyanates with Schiff bases, as the IR spectra show, in the given case proceeds by the diene synthesis type, i.e., the starting isocyanate acts as a 1,4-dipole (C), and taking into consideration the polarization of Schiff bases:



the following order of addition can be assigned to the reaction adducts:



(I):  $\text{R}^1=\text{C}_6\text{H}_5$ ;  $\text{R}^2=\text{H}$  (a),  $\text{R}^2=(\text{CH}_3)_2\text{N}-p$  (b),  $\text{R}^2=\text{Cl}-p$  (c),  $\text{R}^2=\text{Br}-p$  (d),  $\text{R}^2=\text{CH}_3\text{O}-p$  (e)

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TABLE 1

Starting Schiff base	Adduct empirical formula	Mp, °C	Yield, %	Found, %				Calculated, %			
				C	H	N	Hal	C	H	N	Hal
$C_8H_5CH_2N=CHC_6H_5$	$C_{22}H_{18}O_2N_2$	1124-124,5	90	77,01	5,38	8,26	—	77,17	5,29	8,19	—
$C_8H_5CH_2N=CHC_6H_4N(CH_3)_{2-p}$	$C_{24}H_{23}O_2N_3$	116-118	80	—	—	10,98 10,82	—	—	—	10,90	—
$C_8H_5CH_2N=CHC_6H_4Cl-p$	$C_{22}H_{17}O_2N_2Cl$	107-108	85	69,61	5,07	7,50	9,10	70,14	4,55	7,43	9,40
$C_8H_5CH_2N=CHC_6H_4Br-p$	$C_{22}H_{17}O_2N_2Br$	110-111	75	33,01	3,95	6,80	17,92	62,72	4,07	6,65	18,09
$C_8H_5CH_2N=CHC_6H_4OCH_3$	$C_{23}H_{20}O_3N_2$	105-107	80	74,56	5,31	7,55	—	74,14	5,41	7,52	—
$C_8H_5CH_2N=CHC_6H_5^*$	$C_{17}H_{13}O_2N_2Cl_3$	151-153	80	53,70	3,25	7,01	28,02	53,24	3,43	7,03	27,72

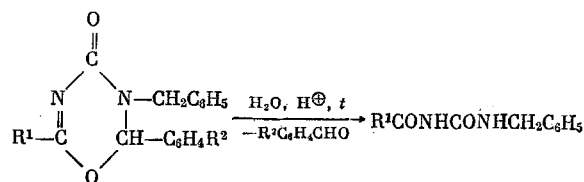
\* Isocyanate -  $CCl_3CONCO$ .

TABLE 2

Schiff base	Empirical formula	Bp, °C (p, mm of Hg)	Yield, %	Found, %				Calculated, %			
				C	H	Hal	Hal	C	H	Hal	Hal
$C_8H_5CH_2N=CHC_6H_5$	$C_{15}H_{13}N$	171-172 (8)	71	85,92	6,94	—	—	86,11	6,71	—	—
$C_8H_5CH_2N=CHC_6H_4N(CH_3)_{2-p}$	$C_{16}H_{13}N_2$	178-180 (1,5) *	63	81,02	7,65	—	—	80,64	7,61	—	—
$C_8H_5CH_2N=CHC_6H_4Cl-p$	$C_{14}H_{12}NCl$	154-155 (1,5)	68	73,34	5,16	15,01	15,01	73,20	5,26	15,43	15,43
$C_8H_5CH_2N=CHC_6H_4Br-p$	$C_{14}H_{12}NBr$	210-212 (12)	74	60,97	4,60	28,91	28,91	61,33	4,41	29,14	29,14
$C_8H_5CH_2N=CHC_6H_4OCH_3-p$	$C_{13}H_{13}ON$	171-173 (13)	79	80,29	6,50	—	—	80,01	6,71	—	—

\* Mp. 70-71°.

This order for the addition of benzoyl and trichloroacetyl isocyanates to the starting Schiff bases was established in the following manner. When the reaction adducts of benzoyl isocyanate with Schiff bases were heated in refluxing aqueous dioxane, acidified with HCl, the corresponding benzaldehydes were obtained and, in all cases, also a compound that proved to be identical with N-benzoyl-N'-benzylurea. As a result, the hydrolysis of the given adducts proved to be analogous to the hydrolysis of the thio analogs, studied in [9],



The adduct of trichloroacetyl isocyanate with benzalbenzylamine (II) has a similar structure. This product when heated in refluxing acetone, acidified with HCl, gives N-trichloroacetyl-N'-benzylurea.

## EXPERIMENTAL

The benzoyl and trichloroacetyl isocyanates were synthesized as described in [10, 11].

The benzalbenzylamines (Table 2) were synthesized by refluxing benzene solutions of benzylamine and the appropriate benzaldehyde, and were purified by vacuum-distillation [12].

The reactions were run in sealed glass tubes, filled with anhydrous  $\text{CO}_2$ , and the reaction products were worked up in a box over  $\text{P}_2\text{O}_5$ ; some of the reactions were also run in a box over  $\text{P}_2\text{O}_5$ .

2,6-Diphenyl-3-benzyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (Ia). In a tube, filled with anhydrous  $\text{CO}_2$ , to a solution of 7.35 g of benzoyl isocyanate in 30 ml of absolute ether was added a solution of 9.75 g of benzalbenzylamine in 50 ml of absolute ether. A white curdy precipitate began to deposit within several minutes. The tube was sealed. After two days the obtained precipitate was filtered in a box, and washed four times with absolute ether; mp 124-124.5°; yield 15.4 g (90%).

A frequency at  $1670 \text{ cm}^{-1}$  (CO) is present in the IR spectrum of the compound (Nujol).

N-Benzoyl-N'-benzylurea. A solution of 2 g of (Ia) in 15 ml of dioxane, acidified with two drops of 2 N HCl solution, was heated at the boil for 15 min. The mixture was diluted with an equal volume of water. White crystals with mp 168° (from ethanol) deposited on standing; yield 1.2 g (80%). The mixed melting point with the product, obtained by the method described below, was not depressed.

In a two-necked flask, to a solution of 1.47 g of benzoyl isocyanate in 15 ml of absolute ether was added in drops a solution of 1.07 g of benzylamine in 10 ml of absolute ether. The mixture was refluxed for 10 min, and the obtained crystals were filtered to give a substance with mp 168°; yield 2.41 g (96%). Found: C 70.59; H 5.59%.  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ . Calculated: C 70.8 8; H 5.51%.

2-(p-Dimethylamino) phenyl-3-benzyl-6-phenyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (Ib). To a solution of 2.94 g of benzoyl isocyanate in 100 ml of absolute ether, cooled in ice and found in a box, was added a solution of 4.76 g of p-dimethylaminobenzalbenzylamine in 75 ml of absolute ether. A precipitate of yellow crystals was obtained. After 20 min the crystals were filtered and washed five times with absolute ether. We obtained 6.15 g (80% yield) of (Ib) with mp 116-118°. Infrared spectrum of (Ib) (Nujol):  $1676 \text{ cm}^{-1}$  (C=O). The hydrolysis of (Ib) also gave N-benzoyl-N'-benzylurea.

2-(p-Chloro) phenyl-3-benzyl-6-phenyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (Ic). To a solution of 2.79 g of p-chlorobenzalbenzylamine in 50 ml of absolute ether, found in a box, was added a solution of 1.8 g of benzoyl isocyanate in 40 ml of absolute ether. White crystals began to deposit after several minutes. After 8 h the obtained precipitate was filtered and washed three times with absolute ether to give 3.9 g (85% yield) of (Ic) with mp 107-180°. Infrared spectrum of (Ic) (Nujol):  $1672 \text{ cm}^{-1}$  (C=O).

2-(p-Bromo)phenyl-3-benzyl-6-phenyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (Id). In a tube, filled with anhydrous  $\text{CO}_2$  and cooled to -20°, to a mixture of 3.72 g of p-bromobenzalbenzylamine in 30 ml of absolute petroleum ether was added a solution of 2.0 g of benzoyl isocyanate in 40 ml of absolute petroleum

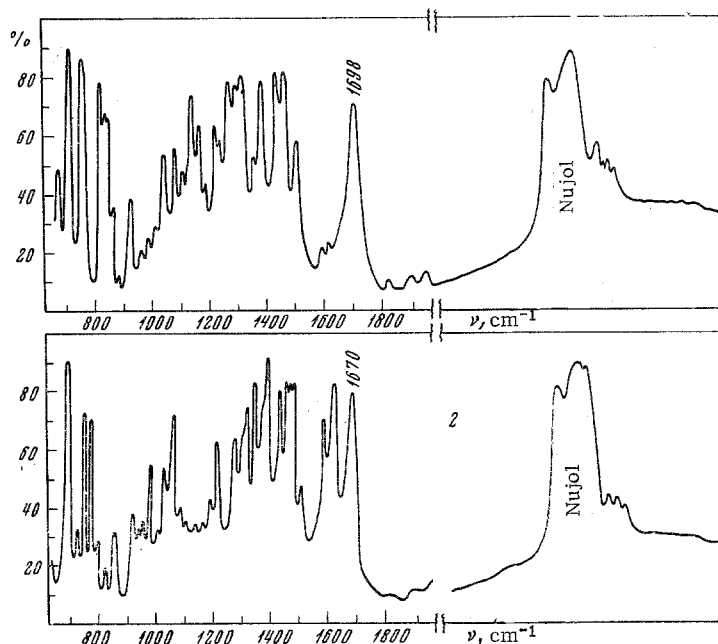


Fig. 1. Infrared spectra (Nujol) of 2-phenyl-3-benzyl-6-trichloromethyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (1) and 2,6-diphenyl-3-benzyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (2).

ether. The tube was sealed. White crystals began to deposit gradually. The tube was allowed to stand for 12 h at room temperature. The obtained precipitate was filtered in a box, washed three times with absolute petroleum ether, and then twice with absolute ether. We obtained 4.17 g (75% yield) of (Id) with mp 110–111°. Infrared spectrum of (Id) (Nujol): 1670  $\text{cm}^{-1}$  (C=O).

2-(p-Methoxy)phenyl-3-benzyl-6-phenyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (Ie). To a solution of 3.77 g of p-methoxybenzalbenzylamine in 50 ml of absolute ether, cooled in ice and found in a box, was added a solution of 2.5 g of benzoyl isocyanate in 50 ml of absolute ether. A white precipitate was obtained. The precipitate was filtered after 3 h, washed twice with absolute ether. We obtained 5.0 g (80% yield) of (Ie) with mp 105–107°. Infrared spectrum of (Ie) (Nujol): 1670  $\text{cm}^{-1}$  (C=O).

2-Phenyl-3-benzyl-6-trichloromethyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one (II). In a tube, filled with anhydrous  $\text{CO}_2$ , to a solution of 12 g of trichloroacetyl isocyanate in 45 ml of ether was added a solution of 12.4 g of benzalbenzylamine in 40 ml of absolute ether. A white precipitate began to deposit immediately. The tube was sealed. After 20 h the obtained precipitate was filtered in a box and washed three times with absolute ether. We obtained 19.5 g (80% yield) of (II) with mp 151–153°. Infrared spectrum of (II) (Nujol): 1698  $\text{cm}^{-1}$  (C=O).

N-Trichloroacetyl-N'-benzylurea. A solution of 2 g of (II) in 20 ml of acetone, acidified with two drops of 2 N HCl solution, was heated at the boil for 10 min. Then the mixture was cooled and diluted with an equal volume of water. White crystals deposited on standing; mp 106° (from ethanol); yield 0.8 g (80%). The mixed melting point with the product, obtained by the method described below, was not depressed.

N-Trichloroacetyl-N'-benzylurea. In a two-necked flask, to a solution of 1.84 g of trichloroacetyl isocyanate in 15 ml of absolute ether was added in drops a solution of 1.07 g of benzylamine in 15 ml of absolute ether. Then the mixture was refluxed for 20 min. The ether was removed using the vacuum of a water-jet pump to give a white solid in the flask; mp 106°; yield 2.6 g (90%). Found: C 40.58; H 3.30; Cl 36.01%.  $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_2\text{Cl}_3$ . Calculated: C 40.64; H 3.07; Cl 35.98%.

## CONCLUSIONS

Benzalbenzylamine and p-substituted benzalbenzylamines react with benzoyl and trichloroacetyl isocyanates by the type of 1,4-addition, with the formation of 2,6-diphenyl-3-benzyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one and 2-phenyl-3-benzyl-6-trichloromethyl-3,4-dihydro-2H-1-oxa-3,5-diazin-4-one derivatives.

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