REACTION OF N,N-DIMETHYLCARBAMOYL BROMIDE WITH 1,2,4-TRIAZINES

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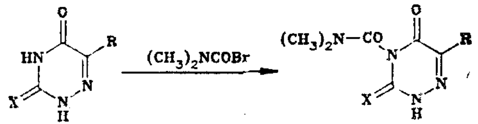
The acylation of substituted 1,2,4-triazines with N,N-dimethylcarbamoyl bromide was studied. 4,5-Dihydro-4-(N,N-dimethylcarbamoyl)-3-thioxo(oxo)-5-oxo-6-R-1,2,4-triazines were synthesized. The spectral characteristics of the synthesized compounds are discussed.

The acylation of 1,2,4-triazines in the nucleus with several acid anhydrides and acids is described in [1]. In order to obtain biologically active compounds, we wished to acylate 1,2,4-triazines with derivatives of carbamic acid, allowing the introduction of an $R^1R^2-C(O)-$ type substituent into the triazine nucleus. Syntheses of this kind have not been described in the literature for 1,2,4-triazines.

As the acylating agent, we used N,N-dimethylcarbamoyl bromide, by the action of which on 6-tert-butyl- (Ia), 6-phenyl-1,2,4-triazine-3(2H)-thione-5(4H)-one (Ib), 6-phenyl- (Ic), and 6-tert-butyl-1,2,4-triazine-3(2H),5(4H)-dione (Id) in dimethylformamide at 25-40°C for 2.5-3 h, the 4,5-dihydro-4-(N,N-dimethylcarbamoyl)-3-thioxo(oxo)-5-oxo-6-R-1,2,4-triazines (IIa-d) were obtained.



Ia-d IIa-d

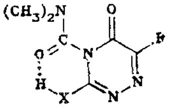
I, II a,b X=S; d,k X=O; a,d $R=C(CH_3)_3$; b,c $R=C_6H_5$

Acylation occurs at the $N_{(4)}$ atom of the triazine ring. This is obviously due to the greater electron density localized on it than on $N_{(2)}H$ [2]. In view of the high reactivity of the acylating agent, it is not necessary to use a catalyst.

The structures of the synthesized compounds, IIa-d, were established by an accumulation of elementary analyses and IR, UV, and PMR spectroscopic data.

Absorption bands at 1660-1690 ($\nu_{C=O}$), 1165 ($\nu_{C=S}$), and 3429-3458 cm^{-1} ($\nu_{N_{(2)}H}$) were preserved in the IR spectra of all of the compounds synthesized, IIa-d. A new absorption band, at 1710-1750 cm^{-1}, is attributable to the stretching vibration of the carbonyl group of the N,N-dimethylcarbamoyl residue. An intense, broad absorption band in the 2800-2880 cm^{-1} range is attributable to the C—H stretching vibration in the dimethylamino group. As a whole, the lines in the IR spectra are broadened and the intensity of absorption increased, which could be evidence of greater association of compounds IIa-d compared with starting compounds Ia-d.

In the PMR spectra of compound IIa-d, there is a singlet at 3.38-3.41 ppm that is assigned to protons of groups of the N,N-dimethylcarbamoyl residue. In a weak field, at 12.06-13.68 ppm, a doublet is observed from protons of the $N_{(2)}H$ and OH (SH) groups. In fact, stabilization of the thermodynamically less stable enol (enthiol) form by the formation of an intramolecular hydrogen bond is possible (III):



III

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TABLE 1. Spectral Characteristics of Compounds IIa-d

Compound	Empirical formula	T_{mp}, °C	IR spectra, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm	Yield, %
IIa	$C_{10}H_{16}N_4O_2S$	308 . . . 309	3429 ($\nu_{N_{(2)}H}$); 1710 ($\nu_{C=O}$, carbonyl gr.); 1690 ($\nu_{C=O}$, tr. ring); 2830, 2870 (ν_{C-H}); 1210 ($\nu_{C=S}$)	282,5 (3,63), 258,3 (3,46), 252,3 (3,41), 246,7 (3,42), 240,8 (3,42), 235,8 (3,35)	1,25 s [$C(CH_3)_3$], 3,41 s [$(CH_3)_2N$], 13,24 s (NH)	69
IIb	$C_{12}H_{12}N_4O_2S$	265 . . . 266*	3468 ($\nu_{N_{(2)}H}$; 1745 ($\nu_{C=O}$, carbonyl gr.); 1690 ($\nu_{C=O}$, tr. ring); 1165 ($\nu_{C=S}$)	362,5 (3,67), 281,7 (3,64), 258,3 (3,48), 251,7 (3,43), 245,8 (3,44), 240,8 (3,44), 235,8 (3,38)	3,41 s [$(CH_3)_2N$], 7,49 . . . 7,91 m (C_6H_5), 13,24 . . . 13,68 s [SH (0,5), NH (0,5H)]	62
IIc	$C_{12}H_{12}N_4O_3$	263 . . . 265	3458 ($\nu_{N_{(2)}H}$; 1740 ($\nu_{C=O}$, carbonyl gr.); 1690 ($\nu_{C=O}$, tr. ring); 2800, 2880 (ν_{C-H})	320,8 (3,55), 281,7 (3,64), 258,3 (3,48), 251,7 (3,43), 245,8 (3,44), 240,8 (3,44), 235,8 (3,38)	3,38 s [$(CH_3)_2$], 7,44 . . . 7,86 m (C_6H_5), 12,06 . . . 12,49 d (NH)	73
IId	$C_{10}H_{16}N_4O_3$	279	3420 ($\nu_{N_{(2)}H}$); 1750 ($\nu_{C=O}$, carbonyl gr.); 1670 ($\nu_{C=O}$, tr. ring); 2815, 2880 (ν_{C-H})	273,3 (3,58), 258,3 (3,41), 252,5 (3,36), 245,8 (3,37), 240,8 (3,37), 235,8 (3,30)	—	68

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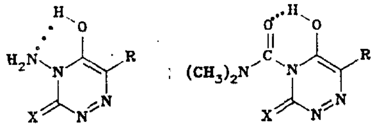
*From tar.

When D_2O is added, the rate of proton exchange is increased, and the doublet in the PMR spectrum of 4,5-dihydro-4-(N,N-dimethylcarbamoyl)-3-thioxo-5-hydroxo-6-phenyl-1,2,4-triazine (IIb), for example, changes to a singlet.

In the 240.8-258.3 nm region of the UV spectra of compounds Ia-d and IIa-d, there are four absorption bands similar to the absorption bands in the spectra of other nitrogen-containing heterocycles [3]. The difference from the starting compounds lies in the appearance of a new band with λ_{max} 235.8 nm (log ε 1.98-2.38) attributed to an n-π* electronic transition of the carbonyl group of a carbamoyl radical. The position and intensity of this band agree with the literature data [4]. The spectra of compounds IIb,c preserve absorption bands at 320 and 365.5 nm arising from π-π* electronic transitions in the $-C(O)-NH-N{=}C(C_6H_5)-$ and $-C(S)-NH-N{=}C(C_6H_5)-$ chromophores, respectively. At the same time, the absorption band at 293 nm in, for example, the spectrum of compound Ib, undergoes a hypsochromic shift to 281.7 nm without a decrease in the intensity of the absorption. It can be hypothesized that we are dealing with an absorption band arising not from a $-N{=}C(C_6H_5)-$ chromophore, as in the starting compound, but from another one. The band at 293 nm observed in the electronic absorption spectrum of 3-thio-4-amino-6-R-1,2,4-triazine-5-ones [5] arising from the $-C(S)-N{=}N-C(R){=}C(OH)$ chromophore is close. The realization of this structure is facilitated, obviously, by a hydrogen bond of type IV. The formation of an analogous bond is not precluded in synthesized compounds IIa-d.

The 273.3-285.5 nm absorption bands in the spectra of compounds IIa-d are probably due to similar chromophores.



IV

Starting from the different chemical shifts of the protons of the $N_{(2)}H$ groups in the PMR spectra of compounds IIb and IIc, one obviously has to consider the basic structure to be structure III with the hydrogen bond in position 3 on the ring.

The compounds synthesized may find use as intermediates in the syntheses of pesticides.

EXPERIMENTAL

The IR spectra, in KBr pellets, were taken on a UR-10 instrument; the electronic absorption spectra, in dioxane ($c = 10^{-3}$ M), on a Beckman YB/BUC instrument. The PMR spectra were obtained in D_6-DMSO on a Tesla BS-487B spectrometer with a frequency of 80 MHz and TMS as an internal standard. The purity of the products was checked by TLC on Silufol UV-254 plates in a 9:1 chloroform–acetone system. The characteristics of the synthesized compounds are presented in Table 1. The data from elementary analyses agreed with the calculated values.

Compounds Ia-d were synthesized according to [6, 7].

4,5-Dihydro-4-(N,N-dimethylcarbamoyl)-3-thioxo(oxo)-5-oxo-6-R-1,2,4-triazines (IIa-d). A solution of 7.6 g (0.05 mole) of N,N-dimethylcarbamoyl bromide in 15 ml of DMFA is added dropwise with vigorous stirring to a solution of 0.05 mole of the 6-R-1,2,4-triazone-3(2H)-one(tione)-5(4H)-one (Ia-d) in 50 ml of DMFA at 20-25°C. The reaction mixture is stirred for 2.5-3 hours at 25-40°C. After it has cooled to 20-25°C, 150 ml of water are added. The precipitate that forms is filtered off, washed with isopropyl alcohol to remove water until the medium is neutral, dried in air, and recrystallized from isopropyl alcohol.

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FEATURES OF THE (2 + 3)-CYCLOADDITION OF TRIFLUOROACETONITRILE OXIDE

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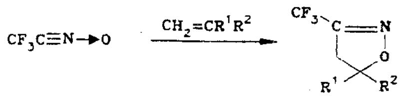
The (2 + 3)-cycloaddition of trifluoroacetonitrile oxide is a function of the donor and steric properties of dipolarophiles and usually proceeds regiospecifically. A significant temperature effect was found for the cycloaddition of trifluoroacetonitrile oxide to dipolarophiles with low donor capacity.

Trifluoroacetonitrile oxide [1] has high reactivity toward donor alkenes and extremely low activity in reactions with acceptor dipolarophiles. In the present communication, results are given for a more detailed study of the reactions of oxide I with donor dipolarophiles, cyclic alkenes, and dipolarophiles with low donor capacity.

The cycloaddition of oxide I to unconjugated monosubstituted alkenes is a function of the donor properties of these substrates. The yields of the cycloadducts, which are greatest using ethyl vinyl ether, decrease with decreasing donor properties in the cases of vinyl acetate and allyl bromide.

These reactions are regiospecific. The orientation of the substituents occurs only at $C_{(5)}$ of the ring formed as indicated by NMR spectral analysis. Complete regiospecificity is also found for reaction with other mono- and disubstituted alkenes.



III–VI

III $R^1=OC_2H_5$, $R^2=H$ (65%); IV $R^1=OAc$, $R^2=H$; V $R^1=CH_2Br$, $R^2=H$; VI $R^1=CH_3$, $R^2=CH_3$

The presence of two geminal methyl groups in isobutylene produces steric hindrance in the transition state and the yield of oxazoline VI is low.*

The reactivity of oxide I relative to cyclohexene and cyclopentene increases significantly with the calculated ring strain (2.61 and 6.93 kcal/mole, respectively [3]).

The reaction of oxide I with cyclopentadiene as a representative of conjugated cyclic alkenes proceeds rather readily but the reaction is nonregioselective. ^{19}F NMR spectroscopy indicated the formation of a 2:3 mixture of cycloadducts. However, the isomers could not be assigned using ^1H NMR spectroscopy.

Other conjugated alkenes such as styrene and ethyl acrylate as well as N-methylbenzalimine react smoothly with oxide I. Styrene, which is a good donor, proved the most active and phenyloxazoline X is formed in this case in 80% yield. N-Methylbenzalimine, which is a

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*An opposite effect is found in the analogous reactions of nonfluorinated nitrile oxides. Isobutylene is a more active dipolarophile than, for example, allyl bromide [2].

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