ringes erhalten werden. Das Spektrum C (siehe Fig.) zeigt kein Singulett mehr, und das Aromatenintegral entspricht nur noch 5 Indolprotonen (in D_2O).

Somit ist die ^{1}H-NMR.-Spektroskopie ein sicheres und rasches Verfahren für den Nachweis von Benzylschutzgruppen, die an Sauerstoffatomen sitzen.

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38. A New and Convenient Synthesis of Substituted Acylthioacylureas. Reaction of Aryl and Alkyl Thioamides with Acyl Isocyanates

by **Victor Israel Cohen**

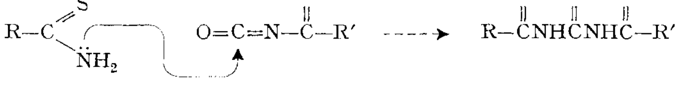
Organic Chemistry Laboratory, Sciences Faculty, Ferdowsi University, Mashhad, Iran

(17. XII. 75)

Summary. The addition of acyl isocyanates to a solution of aryl and alkyl thioamides affords substituted acylthioacylureas. The IR. spectra of substituted acylthioacylureas is described.

The synthesis of thioacylureas from thioamides and aryl isocyanates has been described previously [1]. In the present note we want to describe the preparation of substituted acylthioacylureas from thioamides and acyl isocyanates. When·aliphatic or aromatic thioamides are refluxed with acyl isocyanate in benzene, toluene or xylene, substituted acylthioacylureas are obtained.

The above mentioned reaction provides a satisfactory preparation of acylthioacylureas for which we propose the following scheme:



R, R′ = alkyl or aryl

The spectra of the acylthioacylureas (Table 1) showed a thiocarbonyl absorption at 1274–1235 cm^{-1} (the related 1-alkyl or 1-aryl-3-acylureas show no absorption in this region), carbonyl(urea) absorption at 1705–1660 cm^{-1} and carbonyl(acyl) absorption at 1745–1715 cm^{-1}; the intensity ratio $\nu(C{=}O)/\nu(C{=}S)$ is 1.4:1.0.

The reaction of acyl isocyanates with alkyl and aryl thioamides provides a general method for preparing substituted acylthioacylureas. The previous preparation has involved the addition of amide to thiobenzoyl isocyanate or a less direct method [2].

Substituted Acylthioacylureas: $R\text{—}\overset{S}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}\text{—}R'$

No.	B	R'	C=S (thioacyl)	C=O (urea)	C=O (acyl)	M.p., °C	Cryst. solvent	Reflux time, min	Yield %	Reflux solvent	Color	Formula[a])
1	CH_3	C_6H_5	1251	1675	1715	230	1-Butanol	10	95	Benzene	Yellow	$C_{10}H_{10}N_2O_2S$
2	C_6H_5	C_6H_5	1242	1670	1730	235 [b])	Benzene	2	95	Benzene	Purple	$C_{15}H_{12}N_2O_2S$
3	(*p*-)CH_3—C_6H_4	C_6H_5	1247	1670	1730	250	1-Butanol	5	95	Xylene	Rose-coloured	$C_{16}H_{14}N_2O_2S$
4	(*p*-)Br—C_6H_4	C_6H_4	1248	1670	1733	260	1-Butanol	5	98	Benzene	Rose-coloured	$C_{15}H_{11}BrN_2O_2S$
5	α-$C_{10}H_7$	C_6H_5	1260	1674	1730	206	1-Butanol	10	81	Toluene	Rose-coloured	$C_{19}H_{14}N_2O_2S$
6	CH_3	$C_6H_5CH_2$	1274	1705	1730	130	Benzene	5	80	Xylene	Light yellow	$C_{11}H_{12}N_2O_2S$
7	C_6H_5	$C_6H_5CH_2$	1255	1700	1740	167	Toluene	5	95	Xylene	Violet	$C_{16}H_{14}N_2O_2S$
8	(*p*-)CH_3—C_6H_4	$C_6H_5CH_2$	1255	1700	1740	148	Toluene	5	90	Xylene	Violet	$C_{17}H_{16}N_2O_2S$
9	(*p*-)Br—C_6H_4	$C_6H_5CH_2$	1245	1690	1735	178	Toluene	5	88	Xylene	Violet	$C_{16}H_{13}BrN_2O_2S$
10	CH_3	(*p*-)CH_3—C_6H_4	1265	1683	1718	224	Ethanol	5	53	Benzene	Light yellow	$C_{11}H_{12}N_2O_2S$
11	C_6H_5	(*p*-)CH_3—C_6H_4	1250	1673	1730	212	1-Butanol	5	75	Xylene	Rose-coloured	$C_{16}H_{14}N_2O_2S$
12	(*p*-)CH_3—C_6H_4	(*p*-)CH_3—C_6H_4	1248	1670	1728	260	Benzene	5	70	Benzene	Rose-coloured	$C_{17}H_{16}N_2O_2S$
13	(*p*-)Br—C_6H_4	(*p*-)CH_3—C_6H_4	1250	1670	1730	261	1-Butanol	5	70	Benzene	Rose-coloured	$C_{16}H_{13}BrN_2O_2S$
14	α-$C_{10}H_7$	(*p*-)CH_3—C_6H_4	1258	1670	1725	216	Toluene	5	54	Benzene	Rose-coloured	$C_{20}H_{16}N_2O_2S$
15	CH_3	(*o*-)CH_3—C_6H_4	1240	1690	1730	158	Ethanol	5	85	Xylene	Yellow	$C_{11}H_{12}N_2O_2S$
16	C_6H_5	(*o*-)CH_3—C_6H_4	1245	1680	1730	183	Toluene	5	90	Xylene	Purple	$C_{16}H_{14}N_2O_2S$
17	(*p*-)CH_3—C_6H_4	(*o*-)CH_3—C_6H_4	1247	1675	1745	182	Benzene	5	85	Benzene	Violet	$C_{17}H_{16}N_2O_2S$
18	(*p*-)Br—C_6H_4	(*o*-)CH_3—C_6H_4	1235	1660	1735	215	Anisole	5	95	Xylene	Violet	$C_{16}H_{13}BrN_2O_2S$
19	α-$C_{10}H_7$	(*o*-)CH_3—C_6H_4	1248	1580	1729	174	Benzene	10	92	Toluene	Violet	$C_{20}H_{16}N_2O_2S$
20	C_6H_5	α-$C_{10}H_7$	1252	1675	1745	192	Benzene	5	50	Benzene	Rose-coloured	$C_{19}H_{14}N_2O_2S$
21	(*p*-)CH_3—C_6H_4	α-$C_{10}H_7$	1249	1673	1730	190	Benzene	20	49	Benzene	Purple	$C_{20}H_{16}N_2O_2S$
22	(*p*-)Br—C_6H_4	α-$C_{10}H_7$	1247	1665	1740	224	1-Propanol	5	60	Xylene	Rose-coloured	$C_{19}H_{13}BrN_2O_2S$
23	α-$C_{10}H_7$	α-$C_{10}H_7$	1245	1678	1728	165	1-Butanol	1	25	Xylene	Violet	$C_{23}H_{16}N_2O_2S$

[a]) Satisfactory combustion analytical data C,H,N, and S (±0.4%) were found for these compounds. [b]) *O. Tsuge, M. Tashiro, R. Mizuguchi & S. Kanemasa* [2], report 186°.

Experimental Part

General. – Melting points were measured on a *Köfler* hotbench apparatus. A *Beckman* IR-20A spectrophotometer was used for IR. spectra, which were run in KBr. Microanalyses were performed by CNRS (Service Central de Microanalyse; 2, rue Henry-Dunant, 94–Thiais, France).

Commercially available thioacetamide was used as received. Acyl isocyanates and arylthioamides were prepared by established procedures [3] [4]. Useful solvents for the reaction are benzene, toluene and xylene. To avoid side reaction, dry solvents should be used for reflux and recrystallisation. In a typical example a solution of 0.75 g (0.01 mol) of thioacetamide, 1.61 g (0.01 mol) of phenylacetylisocyanate in 5 ml of anhydrous xylene was heated under reflux for 5 min. The product of reaction was filtered off. Recrystallisation from anhydrous benzene gave 1-thioacetyl-3-phenylacetylurea (80%): m.p. 130°.

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Errata

Helv, *58,* 2529 (1975), Abhandlung von *Schelz, D.,* und *Priester, M.*: Auf der Seite 2633, 20. Zeile von oben: anstatt 676 (erste Zahl in der Zeile) lies 267.

Die gleiche Zeile: anstatt 2,03(*s*, 4H, $OCOCH_3$); 4,56(*s*, (CH_2–CH_2)–N(8)); 26,9
lies: 2,03(*s*, $OCOCH_3$); 4,56(*s*, 4H(CH_2–CH_2)–N(8)); 6,96

Helv. *58,* 2536 (1975), Abhandlung *Schelz, D.,* und *Priester, M.*: 2. Zeile des englischen Titels: anstatt -quinoxalino- lies -isoquinolino-.

Helv. *58* 1913 (1975), Contribution Nr. 210 by *G. Balimann* and *P. S. Pregosin,* p. 1914: in the line 8 of the text, in place of 'propanol' read 'propane'.

Helv. *56,* 1879 (1973), Abhandlung Nr. 194 von *Ohloff et al.,* Tabelle: lies (–)-γ-Jonon (**E-4**) anstelle von (+)-γ-Jonon (**4**).