

Reaction of Ketenes with *N,N*-Disubstituted 2-Aminomethylenecycloalkanonones VI. Synthesis of *N,N*-Disubstituted 4-Amino-3,4-dihydro-3,3-dithioethyl-5,6-polymethylene- α -pyrones

Alberto Bargagna (a), Sergio Cafaggi (b) and Pietro Schenone* (a)

(a) Cattedra di Chimica Organica, Facoltà di Farmacia dell'Università, Viale Benedetto XV-3, 16132 Genova, Italy; (b) Istituto di Tecnica Farmaceutica

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The reaction of dithioethylketene, a new dithioalkylketene prepared *in situ* from dithioethylacetyl chloride and triethylamine, with *N,N*-disubstituted 2-aminomethylenecycloalkanonones gave the 1,4-cycloadducts, namely *N,N*-disubstituted 4-amino-3,4-dihydro-3,3-dithioethyl-5,6-polymethylene- α -pyrones.

J. Heterocyclic Chem., **14**, 249 (1977).

In the course of our work on 1,4-cycloaddition of ketenes to *N,N*-disubstituted 2-aminomethyleneketones, we reported the reaction of 2-carbonyl-1,3-dithiane with a number of *N,N*-disubstituted 2-aminomethylenecycloalkanonones I to give *N,N*-disubstituted 4'-aminospiro[1,3-dithiane-2,3'-(5',6'-polymethylene-3',4'-dihydro- α -pyrones)] (1). This facile 1,4-cycloaddition, which we ascribed to the lowered nucleophilicity of the employed ketene in comparison with dichloroketene, prompted us to extend the research to open chain analogues of 2-carbonyl-1,3-dithiane.

The reaction of dithioethylketene II (a new dithioalkylketene prepared *in situ* from dithioethylacetyl chloride and triethylamine) with I gave in high to fair yield *N,N*-disubstituted 4-amino-3,4-dihydro-3,3-dithioethyl-5,6-polymethylene- α -pyrones IIIa-i (Table I). The structure of the cycloadducts III was proven as follows. The ir spectra (Table II) showed, in agreement with similar structures (1), a strong CO stretching at 1745-1752 cm^{-1} , indicative of a δ -lactone; the double bond absorption was at 1690-1713 cm^{-1} . The nmr spectra (Table II) showed the C-4 protons as near singlets at δ 2.76-4.54, according to the amine substitutions.

The *gem*-dithioethyl groups showed the methyl group triplets clearly splitted, according to their nonequivalence. This effect was stronger in the case of adducts with

aromatic amine substitutions (Compound III d,e,g,i), where the shielding effect of the phenyl group shifted strongly upfield one of the methyl group signals.

The formation of cycloadducts took place with aliphatic (dimethylamine, piperidine, morpholine) and aromatic (*N*-methylaniline, diphenylamine) amine substituents only in the case of *N,N*-disubstituted 2-aminomethylenecyclohexanonones (I, $n = 4$).

The size of the cycloalkane moiety is therefore important, because in the case of *N,N*-disubstituted 2-aminomethylenecycloheptanonones and cyclooctanonones (I, $n = 5$ and 6, respectively) the reaction was successful only in the case of dimethyl and methylphenylamino substituents.

EXPERIMENTAL

The ir spectra were taken on a Perkin-Elmer Model 257 spectrophotometer in carbon tetrachloride solution unless otherwise stated. The nmr spectra were recorded on a Perkin-Elmer Model R12 instrument (60 Mc/s) in carbon tetrachloride solution. Chemical shifts are reported as δ (ppm) relative to TMS as an internal standard. Melting points were determined with a Mettler FP1 apparatus and are uncorrected.

Compounds I were prepared according to (1).

General Procedure for *N,N*-Disubstituted 4-Amino-3,4-dihydro-3,3-dithioethyl-5,6-polymethylene- α -pyrones.

Dithioethylacetyl chloride was prepared from dithioethylacetic acid (2) (3.6 g., 20 mmoles) and thionyl chloride (2.62 g., 22 mmoles) at 80-90° for 2 hours, followed by elimination *in vacuo* of excess thionyl chloride and chromatography on neutral alumina grade I, eluent benzene; yield 3.36 g., 84%; ir (carbon tetrachloride): 1786, 1770, 1711 cm^{-1} .

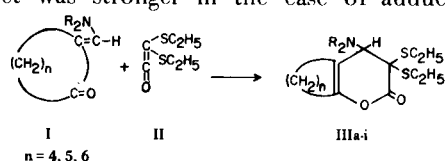
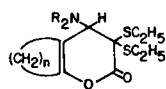


Table I

N,N-Disubstituted 4-Amino-3,4-dihydro-3,3-dithioethyl-5,6-polymethylene- α -pyrones (IIIa-i)



Formula Number	n	NR ₂	Yield %	M.p. °C	Molecular Formula	Analyses % - Calcd./Found		
						C	H	N
IIIa	4	N(CH ₃) ₂	81	58-59	C ₁₅ H ₂₅ NO ₂ S ₂	57.11 56.99	7.99 8.01	4.44 4.70
IIIb	4		38	48-49	C ₁₈ H ₂₉ NO ₂ S ₂	60.80 60.71	8.22 7.94	3.94 4.05
IIIc	4		40	62-63	C ₁₇ H ₂₇ NO ₃ S ₂	57.11 57.31	7.61 7.29	3.92 4.15
III d	4	N(CH ₃)C ₆ H ₅	35	81-82	C ₂₀ H ₂₇ NO ₂ S ₂	63.62 63.55	7.21 6.89	3.71 3.97
IIIe	4	N(C ₆ H ₅) ₂	15	129-130	C ₂₅ H ₂₉ NO ₂ S ₂	68.30 68.20	6.65 6.36	3.19 3.45
III f	5	N(CH ₃) ₂	42	84-85	C ₁₆ H ₂₇ NO ₂ S ₂	58.32 58.62	8.26 7.91	4.25 4.58
III g	5	N(CH ₃)C ₆ H ₅	33	91-92	C ₂₁ H ₂₉ NO ₂ S ₂	64.41 64.21	7.46 7.45	3.57 3.70
III h	6	N(CH ₃) ₂	23	54-55	C ₁₇ H ₂₉ NO ₂ S ₂	59.43 59.32	8.51 8.47	4.08 4.18
III i	6	N(CH ₃)C ₆ H ₅	43	82-83	C ₂₂ H ₃₁ NO ₂ S ₂	65.14 64.87	7.70 7.89	3.45 3.78

Table II

Ir and Nmr Spectral Data of Compounds IIIa-i

Compound Number	Ir (cm ⁻¹)		C $\begin{matrix} \diagup \text{NR}_2 \\ \diagdown \text{H} \end{matrix}$	Nmr (δ) (SCH ₂ CH ₃) ₂	(SCH ₂ CH ₃) ₂
	C=O	C=C			
IIIa	1748	1700	2.86 near s	2.60 q, J ~ 7	1.21; 1.26 2t, J ~ 7
IIIb	1745	1705 (a)	2.76 near s	2.53 mc	1.19; 1.25 2t, J ~ 7
IIIc	1748	1700	2.80 near s	2.54 mc	1.21; 1.27 2t, J = 7.3
III d	1752	1713	4.08 near s	2.15; 2.64 2m	0.85; 1.23 2t, J = 7.3
IIIe	1752	1710	4.54 near s	2.75 near q, J ~ 7	1.01; 1.23 2t, J ~ 7
III f	1748	1690	2.96 near s	2.60 near q, J = 7.5	1.23; 1.26 2t, J = 7.5
III g	1750	1700	4.17 near s	2.03-2.95 m	0.83; 1.23 2t, J = 7.5
III h	1748	1692	3.01 near s	2.64 q, J = 7.3	1.23; 1.27 2t, J = 7.3
III i	1748	1700	4.22 near s	2.47-3.18 m	0.84; 1.24 2t, J = 7.5

(a) Film

A solution of dithioethylacetyl chloride (3.97 g., 20 mmoles), *N,N*-disubstituted 2-aminomethylenecycloalkanone (20 mmoles) and triethylamine (2.02 g., 20 mmoles) in anhydrous benzene (50 ml.) was heated to reflux for 3 hours, cooled and filtered (in the case of the dimethylamino derivatives the reaction was carried out at room temperature). The filtrate was evaporated and the residue was chromatographed on a Florisil[®] column (60-100 mesh, 20 g.), using petroleum ether (b.p. 40-70°) as eluent. All compounds were recrystallized from petroleum ether.

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REFERENCES AND NOTES

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