

Reaction of Ketenes with *N,N*-Disubstituted 2-Aminomethylenecycloalkanones.
 V. Synthesis of *N,N*-Disubstituted 4'-Aminospiro [1,3-dithiane-2,3'-(5',6'-polymethylene-3',4'-dihydro- α -pyrones)].

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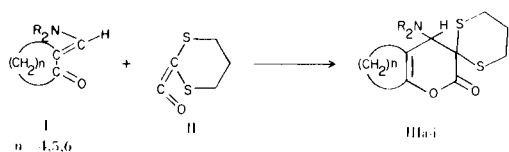
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The reaction of 2-carbonyl-1,3-dithiane, a sulfene prepared *in situ* from 2-chlorocarbonyl-1,3-dithiane and triethylamine, with *N,N*-disubstituted 2-aminomethylenecycloalkanones gave the 1,4-cycloadducts, namely *N,N*-disubstituted 4'-aminospiro[1,3-dithiane-2,3'-(5',6'-polymethylene-3',4'-dihydro- α -pyrones)].

J. Heterocyclic Chem., 13, 1105 (1976).

In the course of our work on 1,4-cycloaddition of ketenes to *N,N*-disubstituted 2-aminomethyleneketones (1), we reported the characteristic reactivity of dichloroketene caused by the electron-withdrawing substituents.

On the other hand we were also interested in the search of new sulphur antiradiation agents with 1,3-dithiolane structure (2). The availability of a new *in situ* prepared ketene bearing thioalkyl groups as electronegative substituents, namely 2-carbonyl-1,3-dithiane (II) (3), prompted us to react it with a number of *N,N*-disubstituted 2-aminomethylenecycloalkanones I, in order to obtain *N,N*-disubstituted 4'-aminospiro[1,3-dithiane-2,3'-(5',6'-polymethylene-3',4'-dihydro- α -pyrones)] (IIIa-i).



The structure of the cycloadducts III (see Table) was proven as follows. The ir spectra show, in agreement with similar structures (4), a strong CO stretching at 1718-1750 cm^{-1} , indicative of a δ -lactone; the double bond absorption at about 1700 cm^{-1} is often covered by the carbonyl stretching. The nmr spectra show the C-4 protons as near singlets at δ 3.21-4.56, according to the amine substitutions.

The lowered nucleophilicity of II, in comparison with dichloroketene, allows the formation in fair yield of adducts even in the case of aliphatic amine substituents

(diethylamine, piperidine, morpholine). Thus in this respect II behaves rather like diphenylketene (compare (4)). The size of the cycloalkane moiety is also important, because we were unable to obtain any adduct in the case of 2-methylphenylamino, 2-diethylamino and 2-piperidino-methylenecycloheptanone.

EXPERIMENTAL

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

Compounds I were prepared according to (4), (5) and (6).

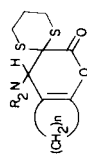
General Procedure for *N,N*-Disubstituted 4'-Aminospiro[1,3-dithiane-2,3'-(5',6'-polymethylene-3',4'-dihydro- α -pyrones)].

A solution of 2-chlorocarbonyl-1,3-dithiane (3) (3.65 g., 20 mmoles) in anhydrous benzene (30 ml.) was added dropwise with stirring to an ice-cooled solution of *N,N*-disubstituted 2-aminomethylenecycloalkanone (20 mmoles) and triethylamine (2.02 g., 20 mmoles) in anhydrous benzene (50 ml.). After the addition was complete the reaction mixture was refluxed for 3 hours, cooled and filtered. The filtrate was evaporated and the residue was chromatographed on a Florisil $\text{\textcircled{R}}$ column (100-200 mesh, 5 g.), using benzene-petroleum ether (b.p. 40-70 $^{\circ}$) 1:1 as eluent.

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N,N-Disubstituted 4'-Aminospiro[1,3-dithiane-2,3'-(5',6'-polymethylene-3',4'-dihydro- α -pyrones)] (IIIa-i)



Formula Number	n	NR ₂	Yield %	M.p. °C	Molecular Formula	Analyses % -Calcd. / Found	Ir C=O	(cm ⁻¹) C=C	Nmr (δ) CHNR ₂ , s	Notes
						C H N				
IIIa	4	-N(C ₂ H ₅) ₂	63	91-92 (a)	C ₁₆ H ₂₅ NO ₂ S ₂	58.68 58.92	7.69 7.58	4.28 4.02	3.40	
IIIb	4	-N	45	145 (b)	C ₁₇ H ₂₅ NO ₂ S ₂	60.14 60.37	7.42 7.73	4.13 4.25	3.21	1700 (d)
IIIc	4	-N	30	149-150 (c)	C ₁₆ H ₂₃ NO ₃ S ₂	56.28 56.44	6.79 6.49	4.10 4.29	3.22	1704
III d	4	-N(CH ₃)C ₆ H ₅	75	177-178 (a)	C ₁₉ H ₂₃ NO ₂ S ₂	63.13 63.20	6.41 6.22	3.87 3.88	4.48	1726
III e	5	-N	70	155-156 (a)	C ₁₈ H ₂₇ NO ₂ S ₂	61.15 60.90	7.70 7.60	3.96 3.98	3.22	1720
III f	6	-N(C ₂ H ₅) ₂	52	91-92 (a)	C ₁₈ H ₂₉ NO ₂ S ₂	60.81 60.66	8.22 8.28	3.94 3.72	3.48	1718
III g	6	-N	40	127-128 (a)	C ₁₉ H ₂₉ NO ₂ S ₂	62.09 61.93	7.95 7.99	3.81 4.04	3.38	1720
III h	6	-N	27	175 (e)	C ₁₈ H ₂₇ NO ₃ S ₂	58.50 58.49	7.36 7.17	3.76 4.05	3.21	1750
III i	6	-N(CH ₃)C ₆ H ₅	37	193-194 (a)	C ₂₁ H ₂₇ NO ₂ S ₂	64.75 64.58	6.99 6.91	3.60 3.84	4.56	1732

(a) From benzene-petroleum ether. (b) From benzene. (c) From diethyl ether. (d) In carbon tetrachloride.

REFERENCES AND NOTES

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