

Alberto Bargagna (a), Filippo Evangelisti (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 Chimica Farmaceutica e Tossicologica dell'Università, Genova, Italy

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The dipolar 1,4-cycloaddition of dichloroketene to *N,N*-disubstituted 3-amino-1-phenyl-2-propene-1-ones led directly to *N,N*-disubstituted 4-amino-3-chloro-6-phenyl-2*H*-pyran-2-ones only in the case of an usual aliphatic *N,N*-disubstitution. In the case of partial or full aromatic *N*-substitution, *N,N*-disubstituted 4-amino-3,3-dichloro-3,4-dihydro-6-phenyl-2*H*-pyran-2-ones were instead obtained, which were dehydrochlorinated with DBN to the corresponding 4-amino-3-chloro-6-phenyl-2*H*-pyran-2-ones.

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The synthetic utility of the polar 1,4-cycloaddition of dichloroketene to *N,N*-disubstituted 2-aminomethylene ketones to give 2-pyrone derivatives has already been shown (1). We have now extended this reaction to a series of *N,N*-disubstituted 3-amino-1-phenyl-2-propene-1-ones (I) bearing fully aliphatic [NR₂ = N(CH₃)₂,

N(C₂H₅)₂, , strong hindering aliphatic (NR₂

= N[CH(CH₃)₂]₂) and aromatic disubstituted amino groups [NR₂ = N(CH₃)C₆H₅, N(C₆H₅)₂].

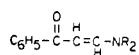
Enaminoketones (I) are mostly known, excepting [I, NR₂ = N[CH(CH₃)₂]₂, N(C₆H₅)₂] (Table I), which were prepared from the corresponding secondary amines

and 3-hydroxy-1-phenyl-2-propene-1-one (2) by a previously described procedure (3). They are E isomers, as can be argued from the J value of 12.6 Hz concerning the C-2 and C-3 protons [compare (4)].

The reaction of I with dichloroacetyl chloride and triethylamine (dichloroketene prepared *in situ*) gave the expected *N,N*-disubstituted 4-amino-3,3-dichloro-3,4-dihydro-6-phenyl-2*H*-pyran-2-ones (IIIa, b) (Table II) only in the case of aromatic *N*-substitution [I, NR₂ = N(CH₃)-C₆H₅, N(C₆H₅)₂].

Refluxing IIIa, b in benzene with DBN (5) afforded the dehydrochlorinated products, namely 4-methylphenyl- and 4-diphenylamino-3-chloro-6-phenyl-2*H*-pyran-2-ones (IVd, e) (Table III). The structures of IIIa, b and IVd, e

Table I
N,N-Disubstituted 3-Amino-1-phenyl-2-propene-1-ones (Ia, b)



Compound No.	NR ₂	Yield %	M.p., °	Molecular Formula	Anal. C	Calcd./Found	
						H	N
Ia	N[CH(CH ₃) ₂] ₂	44	78 (a)	C ₁₅ H ₂₁ NO	77.88	9.15	6.05
					78.16	9.28	6.21
Ib (6)	N(C ₆ H ₅) ₂	95	125 (a)	C ₂₁ H ₁₇ NO	84.25	5.72	4.68
					84.26	5.92	4.79

Uv, Ir and Nmr Spectral Data

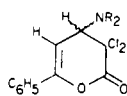
Uv	λ max	nm (log ϵ)	Ir, cm ⁻¹		Nmr, δ
			C=O	(tetrachloromethane) C=C	
Ia	246.5	(4.04)	1643	1543	1.25 (d, J = 6.6, 4CH ₃), 3.78 (mc, 2NCH), 5.90 (d, J = 12.6, CH-2), 7.96 (d, J = 12.6, CH-3), 7.30-8.15 (m, C ₆ H ₅)
	347	(4.38)			
Ib	255.5	(4.24)	1657	1545	5.96 (d, J = 12.6, CH-2), 7.0-7.9 (m, 3C ₆ H ₅), 8.29 (d, J = 12.6, CH-3) (b)
	362	(4.46)			

(a) From anhydrous diethyl ether. (b) In tetrachloromethane.

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Table II

N,N-Disubstituted 4-Amino-3,3-dichloro-3,4-dihydro-6-phenyl-2*H*-pyran-2-ones (IIIa, b)

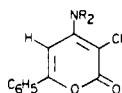
Compound No.	NR ₂	Yield %	M.p., °	Molecular Formula	Anal. C	Calcd./Found	
						H	N
IIIa	N(CH ₃)C ₆ H ₅	76	122 (a)	C ₁₈ H ₁₅ Cl ₂ NO ₂	62.09 62.13	4.34 4.41	4.02 3.82
IIIb	N(C ₆ H ₅) ₂	45	118 (a)	C ₂₃ H ₁₇ Cl ₂ NO ₂	67.33 67.43	4.18 4.15	3.41 3.55


Ir and Nmr Spectral Data

Ir,	cm ⁻¹ C=O	(tetrachloromethane) C=C	Nmr, δ
IIIa	1785	1670	2.75 (s, NCH ₃), 5.18 (d, J = 6.6, CH-4), 5.86 (d, J = 6.6, CH-5), 6.7-7.8 (m, 2C ₆ H ₅)
IIIb	1792	1673	5.55 (d, J = 6.6, CH-4), 5.93 (d, J = 6.6, CH-5), 6.9-7.7 (m, 3C ₆ H ₅)

(a) From anhydrous diethyl ether-petroleum ether.

Table III

N,N-Disubstituted 4-Amino-3-chloro-6-phenyl-2*H*-pyran-2-ones (IVa-e)

Compound No.	NR ₂	Yield %	M.p., °	Molecular Formula	Anal. Calcd./Found		
					C	H	N
IVa	N(CH ₃) ₂	37	144 (a)	C ₁₃ H ₁₂ ClNO ₂	62.54	4.84	5.61
					62.48	4.91	5.34
IVb	N(C ₂ H ₅) ₂	32	129 (a)	C ₁₅ H ₁₆ ClNO ₂	64.87	5.81	5.04
					65.03	5.99	4.93
IVc		50	125 (a)	C ₁₆ H ₁₆ ClNO ₂	66.32	5.57	4.83
					66.56	5.67	4.90
IVd	N(CH ₃)C ₆ H ₅	76	186 (b)	C ₁₈ H ₁₄ ClNO ₂	69.35	4.53	4.49
					69.12	4.68	4.70
IVe	N(C ₆ H ₅) ₂	72	180 (b)	C ₂₃ H ₁₆ ClNO ₂	73.90	4.31	3.75
					73.62	4.32	3.85

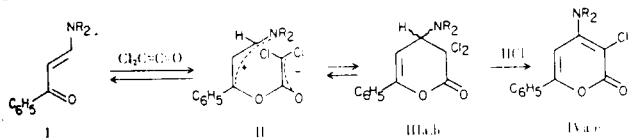
(a) From anhydrous diethyl ether-petroleum ether. (b) From anhydrous diethyl ether-acetone.

Table IV
Uv, Ir and Nmr Spectral Data of Compounds IVa-c

	Uv λ max nm (log ϵ)	Ir, cm^{-1} (chloroform)			Nmr, δ
		C=O	C=C		
IVa	229 (3.98), 261 (4.46), 300 (4.18), 346 (3.99)	1690	1642	1532	3.26 (s, 2NCH ₃), 6.52 (s, CH-5), 7.3-8.0 (m, C ₆ H ₅)
IVb	229 (3.87), 262 (4.41), 303 (4.09), 341 sh (3.91)	1675	1641	1518	1.32 (t, J = 7.2, 2CH ₃), 3.64 (q, J = 7.2, 2NCH ₂), 6.51 (s, CH-5), 7.3-8.0 (m, C ₆ H ₅)
IVc	235 (4.00), 264 (4.51), 305 (4.25), 350 sh (4.02)	1685	1638	1520	1.74 (m, 3CH ₂), 3.54 (m, 2NCH ₂), 6.50 (s, CH-5), 7.3-8.0 (m, C ₆ H ₅)
IVd	229 (4.12), 272 (4.26), 319 (4.22)	1695	1635	1515	3.60 (s, NCH ₃), 6.43 (s, CH-5), 7.0-7.9 (m, 2C ₆ H ₅)
IVe	236 sh (4.54), 274 (4.62), 298 sh (4.48), 335 (4.60)	1700	1632	1514	6.38 (s, CH-5), 6.9-7.9 (m, 3C ₆ H ₅)

were supported by uv, ir and nmr spectral data (Tables II and IV). Compounds IVd, e show a shielding effect of the phenylamino group on CH-5 of about 0.1 ppm in comparison with IVa-c.

In the case of usual aliphatic *N,N*-disubstitution, the reaction between compounds I and dichloroketene led directly to *N,N*-disubstituted 4-amino-3-chloro-6-phenyl-2*H*-pyran-2-ones (IVa-c) (Table III), whereas in the reaction with the derivative bearing the strong hindering diisopropylamino group we were unable to isolate any adduct III or IV, although the presence of the former in the reaction mixture could be inferred from an ir absorption at 1780 cm^{-1} .



We believe that the apparent failure of (I, NR₂ = N[CH(CH₃)₂]₂) to react with dichloroketene could be due to inability of the relative intermediate III to be dehydrochlorinated by some base (triethylamine and/or starting enaminoketone) present in the reaction mixture, and therefore to give the near-aromatic, more stable α -pyrone IV. We have indeed already found that other 3,3-dichloro-3,4-dihydro-4-diisopropylamino-2*H*-pyran-2-ones cannot eliminate hydrogen chloride owing to steric hindrance (5). It may be well that the equilibrium reactions leading to dipolar intermediates II and to cycloadducts III lie towards dissociation, and therefore the reaction is reversed in the case of the diisopropylamino derivative.

Compounds IVa-c, whose structures were confirmed by uv, ir and nmr spectral data (Table IV), were isolated in yields never exceeding 50%. Actually, the precipitate

which separated from the solvent at the end of reaction was formed by a mixture of triethylamine and I hydrochlorides, as could be inferred by comparison of ir spectra (potassium bromide) with those of authentic samples of I hydrochlorides ($\sim 1650, 1565 \text{ cm}^{-1}$). On the other hand, the α -pyrones IV were unable to react in benzene solution with dry hydrogen chloride gas to afford the corresponding hydrochlorides, and therefore they cannot act as dehydrochlorination agents.

In conclusion, the 1,4-cycloaddition described appears to occur irrespective of the nature of amino group substituents, provided they are not too bulky.

EXPERIMENTAL

Uv spectra were measured in 95% ethanol with a Hitachi-Perkin-Elmer Model EPS-3T spectrophotometer. Ir spectra were taken on a Perkin-Elmer Model 257 spectrometer; nmr spectra were recorded in deuteriochloroform on a Perkin-Elmer Model R12 instrument (60 MHz; TMS as internal standard; J in Hz). Melting points were determined with a Fisher-Johns apparatus. Compounds Ia,b were prepared according to reference 3 and were purified by chromatography on Florisil $\text{\textcircled{R}}$ eluting with diethyl ether. Compounds IVd,e were prepared from IIIa, b, respectively, by dehydrochlorination with DBN according to reference 5.

General Procedure for Compounds IIIa, b and IVa,c.

These compounds were obtained starting from I (20 mmoles), dichloroacetyl chloride (20 mmoles) and triethylamine (40 mmoles) in anhydrous benzene, by a previously described procedure (7). Purification before recrystallisation was achieved by chromatography on Florisil $\text{\textcircled{R}}$ eluting with anhydrous diethyl ether-petroleum ether (b.p. 40-70 $^{\circ}$) in various ratios (from 10:1 in the case of IIIa to 1:1 in most other cases).

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