

Reaction of Ketenes with
N,N-Disubstituted α -Aminomethyleneketones. XII. Synthesis of
N,N-Disubstituted 4-Amino-3-chloro-6-(2-methyl-1-propenyl)
 (2-phenylethenyl)-2*H*-pyran-2-ones

Alberto Bargagna, Pietro Schenone*, Francesco Bondavalli and Mario Longobardi

Istituto di Scienze Farmaceutiche dell'Università, Viale Benedetto XV-3, 16132 Genova, Italy
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Cycloaddition of dichloroketene to *N,N*-disubstituted (*E*)-1-amino-5-methyl-1,4-hexadien-3-ones IV and (*E,E*)-1-amino-5-phenyl-1,4-pentadien-3-ones V occurred in moderate to good yield only in the case of aromatic *N*-substitution to give *N,N*-disubstituted 4-amino-3,3-dichloro-3,4-dihydro-6-(2-methyl-1-propenyl)(2-phenylethenyl)-2*H*-pyran-2-ones, which were dehydrochlorinated with DBN to afford in good yield *N,N*-disubstituted 4-amino-3-chloro-6-(2-methyl-1-propenyl)(2-phenylethenyl)-2*H*-pyran-2-ones. In the case of aliphatic *N,N*-disubstitution (dimethylamino group) of enamines IV and V, the cycloaddition led directly in low yield to 3-chloro-4-dimethylamino-6-(2-methyl-1-propenyl)(2-phenylethenyl)-2*H*-pyran-2-ones.

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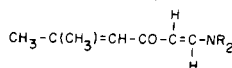
Our continuing interest in the field of 1,4-cycloaddition of dichloroketene to open-chain *N,N*-disubstituted α -aminomethyleneketones I led to the use of a number of such compounds with a wide variation of the substituents R and R' in order to modulate the cycloaddition, which ultimately gave a number of functionalized 2*H*-pyran-2-ones (1).

We wish to report now the cycloaddition of dichloroketene to open-chain enamines such as IV and V, both containing the carbonyl group doubly conjugated with the

usual enamino group and also with a double bond. Whereas R' was hydrogen in both cases, the substituents of the double bond were chosen in order to obtain a full aliphatic substitution in the case of IV and a partial aromatic substitution in the case of V.

Starting *N,N*-disubstituted (*E*)-1-amino-5-methyl-1,4-hexadien-3-ones (IVa-d) (Table I) and (*E,E*)-1-amino-5-phenyl-1,4-pentadien-3-ones (Va-d) (Table II) were prepared in satisfactory yield by reaction of (*Z*)-1-hydroxy-5-methyl-1,4-hexadien-3-one II and (*Z,E*)-1-hydroxy-5-

Table I
N,N-Disubstituted (*E*)-1-Amino-5-methyl-1,4-hexadien-3-ones (IVa-d) (a)



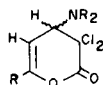
Compound No.	NR ₂	Yield %	Mp, °C (b) or Bp/mm	Molecular Formula	Analyses %		
					C	H	N
IVa	N(CH ₃) ₂	41	104 (c)	C ₉ H ₁₅ NO	70.55	9.87	9.14
					70.75	10.05	9.10
IVb	N(C ₂ H ₅) ₂	86	150/0.1	C ₁₁ H ₁₉ NO	72.88	10.57	7.73
					72.80	10.43	7.79
IVc	N(CH ₃)C ₆ H ₅	70	84	C ₁₄ H ₁₇ NO	78.10	7.96	6.50
					78.22	7.92	6.42
IVd	N(C ₆ H ₅) ₂	48	114	C ₁₉ H ₁₉ NO	82.28	6.91	5.05
					82.36	6.82	5.00

UV, IR and NMR Spectral Data

UV λ max nm (log ϵ)	IR, cm ⁻¹ (Tetrachloromethane)	NMR, δ (Tetrachloromethane)
IVa 251 (3.84) 336 (4.29)	1663, 1643, 1620, 1562	1.81 (d, J = 1.2, CH ₃ C=), 2.10 (d, J = 1.2, CH ₃ C=), 2.92 (s, 2 CH ₃ N), 4.88 (d, J = 13.2, CH-2), 5.82 (mc, CH-4), 7.34 (d, J = 13.2, CH-1)
IVb 253 (3.68) 332 (4.13)	1667, 1655, 1623, 1565	1.18 (t, J = 7.2, 2 CH ₂ -CH ₂), 1.83 (near s, CH ₃ C=), 2.12 (near s, CH ₃ C=), 3.28 (q, J = 7.2, 2 CH ₂ -CH ₃), 5.01 (d, J = 13.2, CH-2), 5.90 (mc, CH-4), 7.45 (d, J = 13.2, CH-1)
IVc 253 (3.96) 352 (4.34)	1668, 1622, 1605, 1562	1.86 (near s, CH ₃ C=), 2.14 (near s, CH ₃ C=), 3.25 (s, CH ₃ N), 5.29 (d, J = 13.2, CH-2), 5.90 (mc, CH-4), 7.0-7.6 (m, C ₆ H ₅), 7.89 (d, J = 13.2, CH-1)
IVd 244 (3.98) 264 (3.99) 361 (4.26)	1667, 1625, 1605, 1555	1.80 (near s, CH ₃ C=), 2.14 (near s, CH ₃ C=), 5.21 (d, J = 13.2, CH-2), 5.79 (mc, CH-4), 6.9-7.7 (m, 2 C ₆ H ₅), 7.97 (d, J = 13.2, CH-1)

(a) Compounds IVa-b were prepared according to the literature (2). Compounds IVc-d were also prepared according to the literature (3). (b) From diethyl ether. (c) Lit (8) mp 104°.

Table III
N,N-Disubstituted 4-Amino-3,3-dichloro-6-(2-methyl-1-propenyl)(2-phenylethenyl)-2H-pyran-2-ones (VIa-d) (a)



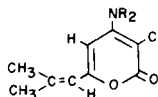
Compound No.	R	NR ₂	Yield %	Mp, °C (b)	Molecular Formula	Analyses %		
						Calcd./Found	C	H
VIa	CH ₃ -C(CH ₃)=CH	N(CH ₃)C ₆ H ₅	45	76	C ₁₆ H ₁₇ Cl ₂ NO ₂	58.91 58.76	5.25 5.28	4.29 4.27
VIb	CH ₃ -C(CH ₃)=CH	N(C ₆ H ₅) ₂	35	98	C ₂₁ H ₁₉ Cl ₂ NO ₂	64.96 65.06	4.93 4.98	3.61 3.59
VIc	C ₆ H ₅ -C ^H =C ^H	N(CH ₃)C ₆ H ₅	82	117	C ₂₀ H ₁₇ Cl ₂ NO ₂	64.19 64.45	4.58 4.70	3.74 3.91
VI d	C ₆ H ₅ -C ^H =C ^H	N(C ₆ H ₅) ₂	80	160	C ₂₅ H ₁₉ Cl ₂ NO ₂	68.82 68.57	4.39 4.55	3.21 3.17

IR and NMR Spectral Data

	IR, cm ⁻¹ (Chloroform)		NMR, δ (Deuteriochloroform)	
	C=O	C=C		
VIa	1775	1670	1.90 (near s, CH ₃ C=), 2.00 (near s, CH ₃ C=), 2.73 (s, CH ₃ N), 5.06 (d, J = 6, CH-5), 5.17 (d, J = 6, CH-4), 5.65 (mc, CH=), 6.85-7.55 (m, C ₆ H ₅)	
VIb	1775	1673	1.76 (s, 2 CH ₃ C=), 5.22 (d, J = 6, CH-5), 5.35 (d, J = 6, CH-4), 5.36 (mc, CH=), 6.85-7.55 (m, 2 C ₆ H ₅)	
VIc	1785	1663	2.76 (s, CH ₃ N), 5.15 (d, J = 6, CH-5), 5.47 (d, J = 6, CH-4), 6.55 (d, J = 15.6, CH=), 6.8-7.6 (m, 2 C ₆ H ₅ + CH=)	
VI d	1785	1663	5.48 (near s, CH-4 + CH-5), 6.34 (d, J = 15.6, CH=), 6.7-7.5 (m, 3 C ₆ H ₅ + CH=)	

(a) All compounds were prepared according to the literature (9). (b) From diethyl ether-acetone 10:1.

Table IV
N,N-Disubstituted 4-Amino-3-chloro-6-(2-methyl-1-propenyl)-2H-pyran-2-ones (VIIa-c) (a)



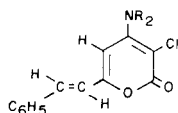
Compound No.	NR ₂	Yield %	Mp, °C (b)	Molecular Formula	Analyses %		
					Calcd./Found	C	H
VIIa	N(CH ₃) ₂	33	163	C ₁₁ H ₁₄ ClNO ₂	58.03 58.13	6.20 6.35	6.15 5.94
VIIb	N(CH ₃)C ₆ H ₅	90	124	C ₁₆ H ₁₆ ClNO ₂	66.32 66.56	5.57 5.60	4.83 4.74
VIIc	N(C ₆ H ₅) ₂	67	150	C ₂₁ H ₁₈ ClNO ₂	71.69 71.81	5.15 5.22	3.98 3.99

UV, IR and NMR Spectral Data

UV λ max nm (log ϵ)	IR, cm ⁻¹ (Chloroform)		NMR, δ (Deuteriochloroform)	
VIIa	253 (4.29) 305 (4.04) 342 (3.83)	1695, 1653, 1618, 1530	1.94 (near s, CH ₃ C=), 2.14 (near s, CH ₃ C=), 3.17 (s, 2 CH ₃ N), 5.77 (near s, CH=C), 5.85 (near s, CH-5)	
VIIb	238 (4.12) 265 (4.18) 324 (4.17)	1690, 1645, 1612, 1510	1.89 (near s, CH ₃ C=), 2.08 (near s, CH ₃ C=), 3.52 (s, CH ₃ N), 5.70 (near s, CH=C), 5.76 (near s, CH-5), 6.95-7.55 (m, C ₆ H ₅)	
VIIc	238.5 (4.23) 269 (4.31) 3.40 (4.24)	1695, 1645, 1610, 1510	1.87 (near s, CH ₃ C=), 2.03 (near s, CH ₃ C=), 5.72 (mc, 2 CH=), 6.9-7.5 (m, 2 C ₆ H ₅)	

(a) Compound VIIa was obtained directly from IVa by reaction with dichloroacetyl chloride and triethylamine according to the literature (9). Compounds VIIb,c were prepared from VIa,b, respectively, by dehydrochlorination with DBN according to the literature (5). (b) From diethyl ether-acetone 5:1.

Table V
N,N-Disubstituted 4-Amino-3-chloro-6-(2-phenylethenyl)-2*H*-pyran-2-ones (VIIIa-c) (a)



Compound No.	NR ₂	Yield %	Mp, °C (b)	Molecular Formula	Analyses %		
					Calcd./Found	C	H
VIIIa	N(CH ₃) ₂	24	185	C ₁₅ H ₁₄ ClNO ₂	65.34	5.12	5.08
					65.35	5.28	5.02
VIIIb	N(CH ₃)C ₆ H ₅	83	193	C ₂₀ H ₁₆ ClNO ₂	71.11	4.77	4.15
					70.98	4.82	4.05
VIIIc	N(C ₆ H ₅) ₂	90	220	C ₂₅ H ₁₈ ClNO ₂	75.09	4.54	3.50
					75.36	4.58	3.40

UV, IR and NMR Spectral Data		
UV λ max nm (log ε)	IR, cm ⁻¹ (Chloroform)	NMR, δ (Deuteriochloroform)
VIIIa 236 (4.09) 241 (4.06) 278 (4.31) 327 (4.27)	1680, 1643, 1617, 1530	3.19 (s, 2 CH ₃ N), 6.03 (near s, CH-5), 6.57 (d, J = 15.6, CH=), 7.20-7.65 (m, C ₆ H ₅ + CH=)
VIIIb 237 (4.02) 243 sh (3.96) 280 (4.19) 344 (4.23)	1700, 1640, 1612, 1515	3.56 (s, CH ₃ N), 5.94 (s, CH-5), 6.49 (d, J = 15.6, CH=), 7.0-7.7 (m, 2 C ₆ H ₅ + CH=)
VIIIc 238 (3.37) 245 (3.35) 277 (3.52) 362 (3.61)	1698, 1638, 1610, 1510	5.88 (s, CH-5), 6.43 (d, J = 15.6, CH=), 7.0-7.7 (m, 3 C ₆ H ₅ + CH=)

(a) Compound VIIIa was obtained directly from Va by reaction with dichloroacetyl chloride and triethylamine according to the literature (9); compounds VIIIb,c were prepared from VIc,d, respectively, by dehydrochlorination with DBN according to the literature (5). (b) From diethyl ether-acetone 5:1.

N,N-disubstituted 4-amino-3-chloro-6-(2-methyl-1-propenyl)-2*H*-pyran-2-ones VIIb,c (Table IV) and 4-amino-3-chloro-6-(2-phenylethenyl)-2*H*-pyran-2-ones VIIIb,c (Table V) in good yield.

In the case of aliphatic *N,N*-disubstitution, the cycloaddition of dichloroketene to enaminones IVa and Va [NR₂ = N(CH₃)₂] led directly in low yield to the dehydrochlorinated products VIIa and VIIIa, respectively, whereas we were unable to isolate any reaction product from IVb and Vb [NR₂ = N(C₂H₅)₂]. Thus, the cycloaddition of dichloroketene to enaminones IV and V basically confirmed the general trends already found in the case of other open-chain enaminones (1).

We have also unsuccessfully attempted the cycloaddition of sulfene (prepared *in situ* from methanesulfonyl chloride and triethylamine) to enaminones IV and V. In all cases we were unable to isolate any product from the reaction mixture. This result is in agreement with the well established fact that sulfene does not react with open-chain enaminones lacking substituents on C-2, as is the case of IV and V [cf. (1)].

EXPERIMENTAL

The uv spectra were measured in 95% ethanol with a Hitachi-Perkin-Elmer Model EPS-3T spectrophotometer. The ir spectra were taken on a Perkin-Elmer Model 398 spectrophotometer, and the nmr spectra were recorded on a Perkin-Elmer Model R12 instrument (60 MHz; TMS as the internal standard; J in Hz).

(Z)-1-Hydroxy-5-methyl-1,4-hexadien-3-one (II)

This compound was prepared from 4-methyl-3-penten-2-one (0.20 mole), ethyl formate (0.22 mole) and sodium (0.22 mole) according to the procedure of Ainsworth (6). As it was shown by its nmr spectrum, II contained about 10% of an isomeric product which could not be separated even by repeated distillations *in vacuo*; 68% yield, bp 65°/0.1 mm; ir (tetrachloromethane): μ max 1733, 1610 (broad), 1452 cm⁻¹; nmr (tetrachloromethane): δ 1.92 (d, J = 1.2, CH₃C=), 2.20 (d, J = 1.2, CH₃C=), 5.42 (d, J = 3.6, CH-2), 5.73 (mc, CH-4), 8.14 (d, J = 3.6, CH-1), 14.42 (broad s, OH; disappears with deuterium oxide). These data were obtained by extrapolating the signals due to the impurity.

Anal. Calcd. for C₇H₁₀O₂: C, 66.64; H, 7.99. Found: C, 66.38; H, 7.91.

(Z,E)-1-Hydroxy-5-phenyl-1,4-pentadien-3-one (III)

This compound was obtained by the usual acidification and ether extraction procedure from its sodium salt, prepared from (*E*)-4-phenyl-3-buten-2-one (0.20 moles), ethyl formate (0.22 moles) and sodium methoxide (0.22 moles) in anhydrous diethyl ether (500 ml) according to the

literature (7), yield, 32%, bp 125°/0.1 mm, mp 43°; ir (tetrachloromethane): μ max 1645, 1615, 1583, 1450 cm^{-1} ; nmr (tetrachloromethane): δ 5.57 (d, J = 3, CH-2), 6.42 (d, J = 15.6, CH-4), 6.9-7.7 (m, C₆H₅), 7.61 (d, J = 15.6, CH-5), 8.65 (d, J = 3, CH-1), 14.27 (broad s, OH; disappears with deuterium oxide).

Anal. Calcd. for C₁₁H₁₀O₂: C, 75.84; H, 5.79. Found: C, 76.11; H, 6.08.

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