

X. Synthesis of *N,N*-Disubstituted 6-Alkyl-4-amino-3,3-dichloro-3,4-dihydro-2*H*-pyran-2-ones and of 6-Alkyl-4-amino-3-chloro-2*H*-pyran-2-ones

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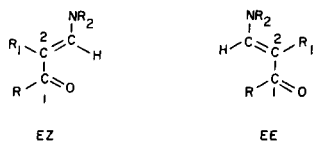
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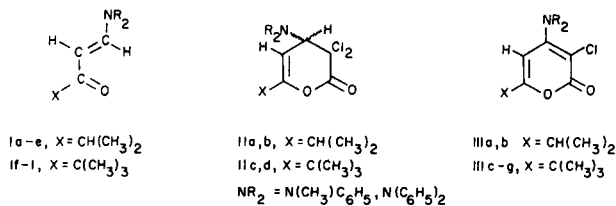
Cycloaddition of dichloroketene to *N,N*-disubstituted 1-amino-4-methyl-1-penten-3-ones and 1-amino-4,4-dimethyl-1-penten-3-ones occurred in moderate to fair yield only in the case of aromatic *N*-substitution to give *N,N*-disubstituted 6-alkyl-4-amino-3,3-dichloro-3,4-dihydro-2*H*-pyran-2-ones, which were dehydrochlorinated with DBN to afford in good yield *N,N*-disubstituted 6-alkyl-4-amino-3-chloro-2*H*-pyran-2-ones. In the case of aliphatic *N,N*-disubstitution, cycloaddition led directly to 6-alkyl-4-dialkylamino-3-chloro-2*H*-pyran-2-ones only for *N,N*-disubstituted 1-amino-4,4-dimethyl-1-penten-3-ones. The reaction between 1-dimethylamino-4-methyl-1-penten-3-one and dichloroketene gave 3-chloro-4-dimethylamino-3,6-dihydro-6-isopropylidene-2*H*-pyran-2-one in low yield.

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In previous work (1,2) we have shown that the dipolar 1,4-cycloaddition of dichloroketene to open-chain  $\alpha$ -aminomethyleneketones is only dependent on the *N*-substituent of the enaminone, irrespective of the substituent  $R_1$  on C-2 of the *EZ* rotamer.



In order to gain more evidence for this finding, we have extended this reaction to other open-chain enaminones such as I, where  $R_1 = \text{H}$  and R is an alkyl group providing increased steric hindrance, namely isopropyl and *t*-butyl. The nitrogen atom bears both aliphatic and aromatic disubstitution.



*N,N*-Disubstituted 1-amino-4-methyl-1-penten-3-ones (Ia-e) and 1-amino-4,4-dimethyl-1-penten-3-ones (If-l) (Table I) are easily available from 1-hydroxy-4-methyl-1-penten-3-one and 1-hydroxy-4,4-dimethyl-1-penten-3-one, respectively, by reaction with secondary amines following previously described procedures (3,4). The ir and nmr spectra of these enaminones (Table II) demonstrate that compounds Ia-e occur as a mixture of both *EE* and *EZ* isomers, and that compounds If-l occur as *EZ* rotamers only (*cf.* 5).

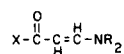
The reaction of I with dichloroketene (prepared *in situ* from dichloroacetyl chloride and triethylamine) gave the expected *N,N*-disubstituted 6-alkyl-4-amino-3,3-dichloro-3,4-dihydro-2*H*-pyran-2-ones IIa-d (Table III) only in the case of aromatic *N*-substitution. Yields seem to depend on the degree of aromatic substitution found in the NR<sub>2</sub> group rather than on the bulkiness of the X group. Thus, in this reaction enaminones I behave like *N,N*-disubstituted 3-amino-1-phenyl-2-propene-1-ones (I, X = C<sub>6</sub>H<sub>5</sub>) (1).

Refluxing IIIa-d in benzene with DBN (6) afforded the corresponding dehydrochlorinated products, namely 6-alkyl-3-chloro-4-methylphenylamino- and 6-alkyl-3-chloro-4-diphenylamino-2*H*-pyran-2-ones IIIa,b, and IIIf,g, respectively in good yield (Tables IV and V).

In the case of aliphatic *N,N*-disubstitution, the cycloaddition of dichloroketene to enaminones If,g,h [X = C(CH<sub>3</sub>)<sub>3</sub>] led directly to the dehydrochlorinated products IIIc,d,e in low to moderate yield (Tables IV and V), whereas we were unable to isolate any reaction product from Ib,c [X = CH(CH<sub>3</sub>)<sub>2</sub>]. Therefore this reaction seems to occur only with those enaminones which are predominantly found as *EZ* rotamers.

Apparently, this reaction also occurred with 1-dimethylamino-4-methyl-1-penten-3-one (Ia), wherein a solid product was isolated in low yield. This product had an elemental analysis corresponding to the molecular formula C<sub>10</sub>H<sub>14</sub>ClNO<sub>2</sub> and therefore in agreement with structure III [X = CH(CH<sub>3</sub>)<sub>2</sub>, NR<sub>2</sub> = N(CH<sub>3</sub>)<sub>2</sub>]. However, spectral evidence indicated a structure isomeric with III. Besides the differences occurring in the uv spectra, a striking difference was found between the nmr spectrum of the product and those of IIIa,b. The former showed only four peaks: a singlet at  $\delta$  3.07 (6H), which is due to a

Table I

*N,N*-Disubstituted 1-Amino-4-methyl-1-penten-3-ones (Ia-e) and 1-Amino-4,4-dimethyl-1-penten-3-ones (If-l) (a)

Compound No.	X	NR <sub>2</sub>	Yield %	B.p./mm Hg or M.p., °C	Molecular Formula	Analyses %		
						C	H	N
Ia	CH(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	55	110-12/0.1 (b)	C <sub>8</sub> H <sub>15</sub> NO			
Ib	CH(CH <sub>3</sub> ) <sub>2</sub>	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	48	100/0.01 (c)	C <sub>10</sub> H <sub>19</sub> NO			
Ic	CH(CH <sub>3</sub> ) <sub>2</sub>	morpholino	30	131-132/0.1	C <sub>10</sub> H <sub>17</sub> NO <sub>2</sub>	65.54	9.35	7.64
						65.66	9.25	7.38
Id	CH(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	40	130-131/0.1	C <sub>13</sub> H <sub>17</sub> NO	76.81	8.43	6.89
						76.89	8.73	6.96
Ie	CH(CH <sub>3</sub> ) <sub>2</sub>	N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	62	91 (d)	C <sub>18</sub> H <sub>19</sub> NO	81.47	7.22	5.28
						81.39	7.30	5.29
If	C(CH <sub>3</sub> ) <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	40	38 (d) (e)	C <sub>9</sub> H <sub>17</sub> NO			
Ig	C(CH <sub>3</sub> ) <sub>3</sub>	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	70	95-96/0.3 (f)	C <sub>11</sub> H <sub>21</sub> NO			
Ih	C(CH <sub>3</sub> ) <sub>3</sub>	morpholino	66	57 (g)	C <sub>11</sub> H <sub>19</sub> NO <sub>2</sub>	66.97	9.71	7.10
						67.22	9.91	6.98
Ii	C(CH <sub>3</sub> ) <sub>3</sub>	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	31	50 (g)	C <sub>14</sub> H <sub>19</sub> NO	77.38	8.81	6.45
						77.36	8.94	6.51
Il	C(CH <sub>3</sub> ) <sub>3</sub>	N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	50	121 (g)	C <sub>19</sub> H <sub>21</sub> NO	81.68	7.58	5.01
						81.71	7.86	5.08

(a) Compounds Ia,b,c,f,g,h were prepared according to (3), and Id,e,i,l according to (4). (b) Lit. (10) b.p. 132-134/16 mm. (c) Lit. (11) b.p. 102-103/2 mm. (d) From diethyl ether. (e) Lit. (10) b.p. 132-135/15 mm. (f) Lit. (12) b.p. 138/11 mm. (g) From *n*-hexane.

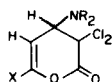
Table II

Uv, Ir and Nmr Spectral Data of Compounds Ia-l

Compound No.	Uv λ max Nm (log ε)	Ir, Cm <sup>-1</sup> (Tetrachloromethane)		Nmr, δ (Tetrachloromethane)	
		C=O	C=C		
Ia	(a)	(b)		1.02 (d, J = 7.2, C(CH <sub>3</sub> ) <sub>2</sub> ), 2.27-2.74 (m, CHMe <sub>2</sub> ), 2.98 (s, 2NCH <sub>3</sub> ), 4.99 (d, J = 12.6, =CHCO), 7.49 (d, J = 12.6, =CHN) (c)	
Ib	(a)	(b)		1.01 (d, J = 7.2, C(CH <sub>3</sub> ) <sub>2</sub> ), 1.18 (t, J = 7.2, 2CH <sub>2</sub> -CH <sub>2</sub> ), 2.25-2.70 (m, CHMe <sub>2</sub> ), 3.26 (q, J = 7.2, 2CH <sub>2</sub> -CH <sub>3</sub> ), 5.02 (d, J = 12.6, =CHCO), 7.47 (d, J = 12.6, =CHN)	
Ic	307 (4.37)	1665	1615	1575	1.09 (d, J = 7.2, C(CH <sub>3</sub> ) <sub>2</sub> ), 2.35-2.82 (m, CHMe <sub>2</sub> ), 3.31 (m, 2NCH <sub>2</sub> ), 3.75 (m, 2OCH <sub>2</sub> ), 5.25 (d, J = 12.6, =CHCO), 7.50 (d, J = 12.6, =CHN) (d)
Id	228 (3.61) 324 (4.21)	1670	1618	1562	1.16 (d, J = 7.2, C(CH <sub>3</sub> ) <sub>2</sub> ), 2.2-3.0 (m, CHMe <sub>2</sub> ), 3.19 (s, NCH <sub>3</sub> ), 5.49 (d, J = 12.6, =CHCO), 6.90-7.55 (m, NC <sub>6</sub> H <sub>5</sub> ), 8.03 (d, J = 12.6, =CHN) (d)
Ie	228.5 (3.87) 278 sh (3.75) 333 (4.33)	1670	1620	1560	1.00 (d, J = 7.2, C(CH <sub>3</sub> ) <sub>2</sub> ), 2.0-2.8 (m, CHMe <sub>2</sub> ), 5.22 (d, J = 12.6, =CHCO), 6.85-7.55 (m, 2NC <sub>6</sub> H <sub>5</sub> ), 8.05 (d, J = 12.6, =CHN)
If	(a)	(b)			1.08 (s, C(CH <sub>3</sub> ) <sub>3</sub> ), 2.99 (s, 2NCH <sub>3</sub> ), 5.18 (d, J = 12.6, =CHCO), 7.48 (d, J = 12.6, =CHN)
Ig	(a)	(b)			1.07 (s, C(CH <sub>3</sub> ) <sub>3</sub> ), 1.20 (t, J = 7.2, 2CH <sub>2</sub> -CH <sub>2</sub> ), 3.29 (q, J = 7.2, 2CH <sub>2</sub> -CH <sub>2</sub> ), 5.21 (d, J = 12.6, =CHCO), 7.45 (d, J = 12.6, =CHN)
Ih	310 (4.31)	1658		1562	1.06 (s, C(CH <sub>3</sub> ) <sub>3</sub> ), 3.24 (m, 2NCH <sub>3</sub> ), 3.74 (m, 2OCH <sub>2</sub> ), 5.26 (d, J = 12.6, =CHCO), 7.36 (d, J = 12.6, =CHN)
Ii	230 (4.15) 325 (4.63)	1664		1557	1.14 (s, C(CH <sub>3</sub> ) <sub>3</sub> ), 3.27 (s, NCH <sub>3</sub> ), 5.56 (d, J = 12.6, =CHCO), 6.90-7.35 (m, NC <sub>6</sub> H <sub>5</sub> ), 7.89 (d, J = 12.6, =CHN)
Il	230 (3.94) 280 sh (3.84) 335 (4.35)	1662		1550	1.01 (s, C(CH <sub>3</sub> ) <sub>3</sub> ), 5.46 (d, J = 12.6, =CHCO), 6.8-7.6 (m, 2NC <sub>6</sub> H <sub>5</sub> ), 8.08 (d, J = 12.6, =CHN)

(a) Reference (13). (b) Reference (11). (c) Reference (14). (d) In deuteriochloroform.

Table III

*N,N*-Disubstituted 6-Alkyl-4-amino-3,3-dichloro-3,4-dihydro-2*H*-pyran-2-ones (IIa-d) (a)

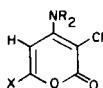
Compound No.	X	NR <sub>2</sub>	Yield %	M.p., °C	Molecular Formula	Analyses %		
						Calcd./Found	C	H
IIa	CH(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	25	73 (b)	C <sub>15</sub> H <sub>17</sub> Cl <sub>2</sub> NO <sub>2</sub>	57.34	5.45	4.46
						57.31	5.69	4.29
IIb	CH(CH <sub>3</sub> ) <sub>2</sub>	N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	60	125 (c)	C <sub>20</sub> H <sub>19</sub> Cl <sub>2</sub> NO <sub>2</sub>	63.84	5.09	3.72
						63.58	5.23	3.96
IIc	C(CH <sub>3</sub> ) <sub>3</sub>	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	29	84 (b)	C <sub>16</sub> H <sub>19</sub> Cl <sub>2</sub> NO <sub>2</sub>	58.55	5.83	4.27
						58.57	5.88	4.12
IId	C(CH <sub>3</sub> ) <sub>3</sub>	N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	54	152 (c)	C <sub>21</sub> H <sub>21</sub> Cl <sub>2</sub> NO <sub>2</sub>	64.62	5.42	3.59
						64.40	5.65	3.49

## Ir and Nmr Spectral Data

Compound No.	Ir, Cm <sup>-1</sup> (Tetrachloromethane)		Nmr, $\delta$ (Tetrachloromethane)
	C=O	C=C	
IIa	1788	1692	1.21 (d, J = 7.2, C(CH <sub>3</sub> ) <sub>2</sub> ), 2.2-2.9 (m, CHMe <sub>2</sub> ), 2.67 (s, NCH <sub>3</sub> ), 4.94 and 5.12 (2d, J = 6, CH-5 + CH-4), 6.60-7.45 (m, NC <sub>6</sub> H <sub>5</sub> )
IIb	1781	1692	0.91 (d, J = 7.2, C(CH <sub>3</sub> ) <sub>2</sub> ), 1.85-2.65 (m, CHMe <sub>2</sub> ), 5.17 and 5.30 (2d, J = 6.6, CH-5 + CH-4), 6.8-7.6 (m, 2NC <sub>6</sub> H <sub>5</sub> )
IIc	1781	1667	1.25 (s, C(CH <sub>3</sub> ) <sub>3</sub> ), 2.67 (s, NCH <sub>3</sub> ), 4.94 and 5.15 (2d, J = 6.6, CH-5 + CH-4), 6.70-7.35 (m, NC <sub>6</sub> H <sub>5</sub> )
IId	1778	1682	0.94 (s, C(CH <sub>3</sub> ) <sub>3</sub> ), 5.16 and 5.26 (2d, J = 6.6 CH-5 + CH-4), 6.75-7.50 (m, 2NC <sub>6</sub> H <sub>5</sub> )

(a) All compounds were prepared according to (9). (b) From petroleum ether (b.p. 40-70°). (c) From anhydrous diethyl ether-petroleum ether.

Table IV

*N,N*-Disubstituted 6-Alkyl-4-amino-3-chloro-2*H*-pyran-2-ones (IIIa-g) (a)

Compound No.	X	NR <sub>2</sub>	Yield %	M.p., °C	Molecular Formula	Analyses %		
						Calcd./Found	C	H
IIIa	CH(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	68	84 (b)	C <sub>15</sub> H <sub>16</sub> ClNO <sub>2</sub>	64.87	5.81	5.04
						64.73	5.88	5.11
IIIb	CH(CH <sub>3</sub> ) <sub>2</sub>	N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	68	122 (b)	C <sub>20</sub> H <sub>18</sub> ClNO <sub>2</sub>	70.69	5.34	4.12
						70.90	5.40	4.20
IIIc	C(CH <sub>3</sub> ) <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	37	91 (b)	C <sub>11</sub> H <sub>16</sub> ClNO <sub>2</sub>	57.51	7.02	6.10
						57.60	6.99	6.07
IIId	C(CH <sub>3</sub> ) <sub>3</sub>	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	65	125 (b)	C <sub>13</sub> H <sub>20</sub> ClNO <sub>2</sub>	60.58	7.82	5.43
						60.69	7.80	5.47
IIIe	C(CH <sub>3</sub> ) <sub>3</sub>	morpholino	20	132 (b)	C <sub>13</sub> H <sub>18</sub> ClNO <sub>2</sub>	57.46	6.68	5.15
						57.20	6.58	4.94
IIIff	C(CH <sub>3</sub> ) <sub>3</sub>	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	67	70 (b)	C <sub>16</sub> H <sub>18</sub> ClNO <sub>2</sub>	65.87	6.22	4.80
						66.13	6.29	4.78
IIIg	C(CH <sub>3</sub> ) <sub>3</sub>	N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	98	147 (c)	C <sub>21</sub> H <sub>20</sub> ClNO <sub>2</sub>	71.28	5.70	3.96
						71.02	5.93	3.87

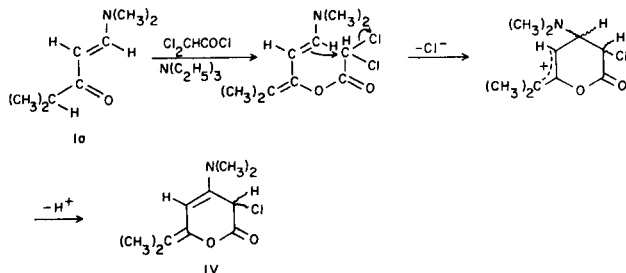
(a) Compounds IIIa,b,f,g were prepared from IIa,b,c,d, respectively, by dehydrochlorination with DBN according to (6). Compounds IIIc,d,e were obtained directly from If,g,h, respectively, by reaction with dichloroacetyl chloride and triethylamine according to (9). (b) From anhydrous diethyl ether-petroleum ether. (c) From diethyl ether.

Table V  
Uv, Ir and Nmr Spectral Data of Compounds IIIa-g

Compound No.	Uv $\lambda$ max Nm (log $\epsilon$ )	Ir, $\text{Cm}^{-1}$		Nmr, $\delta$	
		C=O	C=C	C=O	C=C
IIIa	213 (4.09), 238 (4.04), 250 sh (4.01), 280 (3.88), 328.5 (4.02)	1680	1640	1510	1.19 (d, J = 7.2, $\text{C}(\text{CH}_3)_2$ ), 2.35-2.95 (m, $\text{CHMe}_2$ ), 3.57 (s, $\text{NCH}_3$ ), 5.82 (near s, CH-5), 7.0-7.6 (m, $\text{NC}_6\text{H}_5$ ) (b)
IIIb	250.5 (4.14), 273 (4.15), 347.5 (4.07)	1692	1640	1515	1.16 (d, J = 7.2, $\text{C}(\text{CH}_3)_2$ ), 2.40-2.95 (m, $\text{CHMe}_2$ ), 5.72 (near s, CH-5), 6.85-7.55 (m, $\text{NC}_6\text{H}_5$ ) (b)
IIIc	235.5 (4.26), 270 (3.80), 319 (4.02)	1693	1640	1527	1.29 (s, $\text{C}(\text{CH}_3)_3$ ), 3.20 (s, $2\text{NCH}_3$ ), 5.90 (near s, CH-5) (c)
IIId	236 (4.29), 270 (3.91), 317 (4.04)	1713	1643	1525	1.28 (s, $\text{C}(\text{CH}_3)_3$ ), 1.28 (t, J = 7.2, $2\text{CH}_3\text{-CH}_2$ ), 3.55 (q, J = 7.2, $2\text{CH}_2\text{-CH}_3$ ), 5.82 (near s, CH-5) (c)
IIIe	237 (4.20), 275.5 (3.96), 322 (4.06)	1724	1638	1525	1.28 (s, $\text{C}(\text{CH}_3)_3$ ), 3.40 (m, $2\text{NCH}_2$ ), 3.76 (m, $2\text{OCH}_2$ ), 5.83 (near s, CH-5) (c)
III f	239.5 (4.07), 251 (4.07), 277.5 (3.99), 328 (4.03)	1718	1637	1522	1.22 (s, $\text{C}(\text{CH}_3)_3$ ), 3.52 (s, $\text{NCH}_3$ ), 5.71 (near s, CH-5), 6.9-7.5 (m, $\text{NC}_6\text{H}_5$ ) (c)
IIIg	250 (4.23), 273.5 (4.20), 347 (4.14)	1720	1635	1522	1.19 (s, $\text{C}(\text{CH}_3)_3$ ), 5.63 (near s, CH-5), 6.9-7.5 (m, $2\text{NC}_6\text{H}_5$ ) (c)

(a) In chloroform. (b) In deuteriochloroform. (c) In tetrachloromethane.

dimethylamino group; a singlet at  $\delta$  1.90 (6H), which can evidently not be assigned to two isopropyl methyl groups but rather to two methyl groups on an unsaturated carbon atom; and two peaks at  $\delta$  5.01 and 6.35 (1H each), which are split by allylic coupling ( $J \sim 2.5$  Hz). On this basis we propose the structure 3-chloro-4-dimethylamino-3,6-dihydro-6-isopropylidene-2H-pyran-2-one IV for the reaction product. This compound could arise from acylation of the enolic form of Ia with dichloroacetyl chloride and triethylamine, followed by ring closure with elimination of hydrogen chloride as shown in the accompanying scheme.



We have also unsuccessfully attempted the cycloaddition of sulfene (prepared *in situ* from methanesulfonyl chloride and triethylamine) to all enaminones I. In all cases the starting enaminones were recovered unchanged from the reaction mixture. This result is in agreement with the chemistry of I, since I contains no substituents on C-2 in all cases (*cf.* 2).

#### 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, and nmr spectra were recorded

on a Perkin-Elmer Model R12 instrument (60 MHz; TMS as internal standard; J in Hz).

#### 1-Hydroxy-4-methyl-1-penten-3-one.

This compound was prepared from 3-methylbutanone, ethyl formate and sodium according to the procedure of Ainsworth (7) in 46% yield, b.p.  $73^\circ/15$  mm; ir (tetrachloromethane):  $\nu$  max 1710, 1630, 1590  $\text{cm}^{-1}$ ; nmr (tetrachloromethane):  $\delta$  1.15 (d, J = 7.2,  $\text{C}(\text{CH}_3)_2$ ), 2.30-2.75 (m,  $\text{CHMe}_2$ ), 5.56 (d, J = 4.2, =CHCO), 7.92 (d, J = 4.2, =CH-O-), 11.10 (m, OH; disappears with deuterium oxide).

#### 1-Hydroxy-4,4-dimethyl-1-penten-3-one.

This compound was prepared from 3,3-dimethylbutanone, ethyl formate and sodium according to the procedure of Ainsworth (7) in 50% yield, b.p.  $73^\circ/55$  mm [lit. (8)  $80\text{-}83^\circ/75$  mm]; ir (tetrachloromethane):  $\nu$  max 1690, 1615, 1585,  $\text{cm}^{-1}$ ; nmr (tetrachloromethane):  $\delta$  1.17 (s,  $\text{C}(\text{CH}_3)_3$ ), 5.69 (d, J = 4.2, =CHCO), 8.01 (d, J = 4.2, =CH-O-), 11.35 (m, OH; disappears with deuterium oxide).

#### 3-Chloro-4-dimethylamino-3,6-dihydro-6-isopropylidene-2H-pyran-2-one (IV).

This compound was obtained from Ia, dichloroacetyl chloride and triethylamine according to the literature (9) in 10-15% yield, m.p.  $137^\circ$  from acetone-diethyl ether; uv:  $\lambda$  max nm (log  $\epsilon$ ) 230 (4.02), 263.5 (3.62), 304.5 (3.73); ir (chloroform):  $\nu$  max 1680, 1643, 1548  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  1.90 (s, = $\text{C}(\text{CH}_3)_2$ ), 3.07 (s,  $2\text{NCH}_3$ ), 5.01 (d, J = 2.4, CH-3), 6.33 (d, J = 2.4, CH-5).

Anal. Calcd. for  $\text{C}_{10}\text{H}_{14}\text{ClNO}_2$ : C, 55.69; H, 6.54; N, 6.49. Found: C, 55.91; H, 6.48; N, 6.32.

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