

Reaction of Dichloroketene and Sulfene with  
*N,N*-Disubstituted 2-Aminomethylene-1-indanones.  
 Synthesis of Indeno[1,2-*b*]pyran and Indeno[2,1-*e*]-1,2-oxathiin Derivatives

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The 1,4-cycloaddition of dichloroketene to *N,N*-disubstituted 2-aminomethylene-1-indanones afforded *N,N*-disubstituted 4-amino-3,3-dichloro-3,4-dihydro-2-oxoindeno[1,2-*b*]pyrans only in the case of full or partial aromatic *N*-substitution. The diphenylamino adduct gave 3-chloro-4-diphenylamino-2-oxoindeno[1,2-*b*]pyran by dehydrochlorination with DBN. The 1,4-cycloaddition with sulfene occurred only in the case of 2-diethylaminomethylene-1-indanone to give 4-diethylamino-3,4-dihydroindeno[2,1-*e*]-1,2-oxathiin 2,2-dioxide, a derivative of a new heterocyclic system.

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We have previously reported the characteristic reactivity of dichloroketene and sulfene toward *N,N*-disubstituted 2-aminomethylene-1-tetralones (1,2). With the purpose to synthesize heterocyclic linear structures with proposed CNS activity, we extended these 1,4-cycloadditions to a series of *N,N*-disubstituted 2-aminomethylene-1-indanones (I). The starting compounds Ia-f (Table I) were prepared from secondary amines and 2-hydroxymethylene-1-indanone by previously described procedures (3,4) and their structure was confirmed by uv, ir and nmr spectral data (Table II). They are probably *E* isomers, at least as can be argued from the strong upfield shift of the methylene protons ( $\sim 0.9$  ppm) caused by the phenyl group in compound If. The reaction of I with dichloroacetyl chloride and triethylamine (*in situ* prepared dichloroketene) gave the same results as in the case of *N,N*-disubstituted 2-aminomethylene-1-tetralones (1), namely no reaction in the case of aliphatic *N,N*-disubstitution (Ia-d) and formation of *N,N*-disubstituted 4-amino-3,3-dichloro-3,4-dihydro-2-oxoindeno[1,2-*b*]pyrans (IIIe-f) in the case of full or partial aromatic *N*-substitution. The structure of IIIe-f was supported by ir and nmr spectral data (see Experimental). The dipolar intermediate I seems therefore to explain the dependence of the reaction on  $\text{NR}_2$  from an electronic viewpoint [see (1)]. Treatment of IIIf with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) resulted in the formation of the dehydrochlorinated product, 3-chloro-4-diphenylamino-2-oxoindeno[1,2-*b*]pyran (IV). Its nmr spectrum shows a strong upfield shift of the

methylene protons in comparison with IIIf. This fact could be caused by a phenyl shielding of the adjacent diphenylamino group, now lying in the same plane of the whole ring system. On the other hand, reaction of I with methanesulfonyl chloride and triethylamine (*in situ* prepared sulfene) which occurred readily in the case of aliphatic *N,N*-disubstituted 2-aminomethylene-1-tetralones (2), took place only in the case of Ia to give, in a low yield, 4-diethylamino-3,4-dihydroindeno[2,1-*e*]-1,2-oxathiin 2,2-dioxide (V), a derivative of an hitherto unknown heterocyclic system indeno[2,1-*e*]-1,2-oxathiin. Thus the cycloaddition of sulfene, unlike dichloroketene, seems to be strongly dependent on the ring strain caused by the cyclopentane moiety.

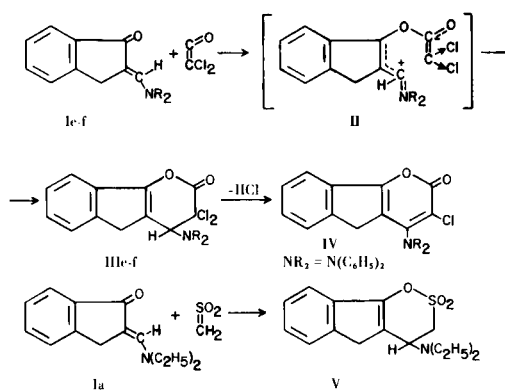
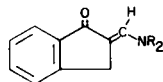


Table I

*N,N*-Disubstituted 2-Aminomethylene-1-indanones Ia-f

Compound No.	NR <sub>2</sub>	Yield %	M.p., °C	Molecular Formula	Analyses % Calcd./Found		
					C	H	N
Ia	-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	64	78 (a)	C <sub>14</sub> H <sub>17</sub> NO	78.10 78.27	7.96 7.79	6.51 6.37
Ib		89	192 (b)	C <sub>14</sub> H <sub>15</sub> NO	78.84 79.14	7.09 7.24	6.57 6.71
Ic		92	155 (b)	C <sub>15</sub> H <sub>17</sub> NO	79.26 79.05	7.54 7.75	6.16 5.89
Id		80	157 (b)	C <sub>14</sub> H <sub>15</sub> NO <sub>2</sub>	73.34 73.25	6.59 6.81	6.11 6.13
Ie	-N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	81	159 (b)	C <sub>17</sub> H <sub>15</sub> NO	81.90 81.93	6.06 6.05	5.62 5.64
If	-N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	72	139 (b)	C <sub>22</sub> H <sub>17</sub> NO	84.86 84.91	5.50 5.75	4.50 4.26

(a) From anhydrous diethyl ether. (b) From ethyl acetate.

Reaction between 2-hydroxymethylene-1-indanone and diisopropylamine did not take place, even under conditions described in (4).

Table II

## Uv, Ir and Nmr Spectral Data of Compounds Ia-f

Compound No.	Uv λ max nm (log ε)	Ir (Chloroform) cm <sup>-1</sup>		Nmr (Deuteriochloroform), δ
		C=O	C=C	
Ia	253 (4.02), 289 sh (3.43), 297 (3.47), 361 (4.42)	1660	1560	1.22 (t, J = 7, 2CH <sub>3</sub> ), 3.38 (q, J = 7, 2NCH <sub>2</sub> ), 3.71 (near s, CH <sub>2</sub> ), 7.30 (m, 3H ar + =CH), 7.68 (m, 1H ar)
Ib	256 (4.02), 290 (3.47), 298 (3.49), 367 (4.45)	1665	1565	1.89 (m, 2CH <sub>2</sub> pirr.), 3.54 (m, 2NCH <sub>2</sub> ), 3.82 (near s, CH <sub>2</sub> ), 7.40 (m, 3H ar), 7.67 (s, =CH), 7.78 (m, 1H ar)
Ic	253 (4.04), 258 sh (4.01), 2.90 (3.47), 297 (3.51), 360 (4.44)	1668	1566	1.65 (m, 3CH <sub>2</sub> pip.), 3.50 (m, 2NCH <sub>2</sub> ), 3.75 (near s, CH <sub>2</sub> ), 7.40 (m, 3H ar + =CH), 7.80 (m, 1H ar)
Id	254 (3.96), 289 sh (3.39), 297.5 (3.47), 359 (4.41)	1674	1572	3.70 (m, 2OCH <sub>2</sub> + 2NCH <sub>2</sub> + CH <sub>2</sub> ), 7.44 (m, 3H ar + =CH), 7.82 (m, 1H ar)
Ie	258 (4.10), 290 sh (3.55), 298 (3.56), 371 (4.44)	1678	1567	3.58 (m, NCH <sub>3</sub> + CH <sub>2</sub> ), 7.28 (m, C <sub>6</sub> H <sub>5</sub> ), 7.42 (m, 3H ar), 7.89 (m, 1H ar + =CH)
If	259 (4.18), 290 sh (3.84), 379 (4.44)	1678	1566	2.84 (near s, CH <sub>2</sub> ), 7.30 (m, 13H ar), 7.79 (m, 1H ar), 8.04 (m, =CH)

## 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 spectrophotometer; nmr spectra were recorded on a Perkin-Elmer Model R12 instrument. Chemical shifts are reported as  $\delta$  (ppm) relative to TMS as an internal standard; J in Hz. Melting points were determined with a Mettler FP1 apparatus and are uncorrected.

Compounds Ia-d were prepared according to (3) and Ie-f according to (4).

**3,3-Dichloro-3,4-dihydro-4-methylphenylamino-2-oxoindeno[1,2-*b*]pyran (IIIe).**

This compound was obtained in a yield of 58% by a previously described procedure (5), m.p. 156-157° from anhydrous diethyl ether; uv  $\lambda$  max nm (log  $\epsilon$ ): 250 (4.33), 267 sh (4.22); ir (carbon tetrachloride)  $\nu$  max: 1807, 1796, 1664  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.67 (s, NCH<sub>3</sub>), 3.48 (near s, CH<sub>2</sub>), 5.42 (near s, CHN), 6.7-7.7 (m, 9 H ar).

*Anal.* Calcd. for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub>NO<sub>2</sub>: C, 63.35; H, 4.20; N, 3.89. Found: C, 63.18; H, 4.31; N, 4.15.

**3,3-Dichloro-3,4-dihydro-4-diphenylamino-2-oxoindeno[1,2-*b*]pyran (III f).**

This compound was obtained in a yield of 55% by the same procedure as for IIIe, m.p. 163-164° from anhydrous diethyl ether; uv  $\lambda$  max nm (log  $\epsilon$ ): 242.5 (4.30), 275 (4.20); ir (carbon tetrachloride)  $\nu$  max: 1794, 1664  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  3.56 (near s, CH<sub>2</sub>), 5.66 (near s, CHN), 6.7-7.9 (m, 14 H ar).

*Anal.* Calcd. for C<sub>24</sub>H<sub>17</sub>Cl<sub>2</sub>NO<sub>2</sub>: C, 68.26; H, 4.06; N, 3.32. Found: C, 68.54; H, 4.36; N, 3.33.

**3-Chloro-4-diphenylamino-2-oxoindeno[1,2-*b*]pyran (IV).**

To a solution of III f (2 g., 4.7 mmoles) in anhydrous benzene (20 ml.), a solution of DBN (1.25 g., 10 mmoles) in the same solvent (10 ml.) was added slowly. The mixture was refluxed for 15 minutes under nitrogen, cooled and poured into LN hydrochloric acid (10 ml) and crushed ice. The solution was extracted

with benzene, the extracts were washed with water and dried (magnesium sulfate) to give a solid (0.8 g., 44%), m.p. 250-251° from anhydrous diethyl ether-acetone; uv  $\lambda$  max nm (log  $\epsilon$ ): 246 (4.21), 275 (4.26), 360 (4.36); ir (carbon tetrachloride)  $\nu$  max: 1725, 1620  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.91 (near s, CH<sub>2</sub>), 6.90-7.85 (m, 14 H ar).

*Anal.* Calcd. for C<sub>24</sub>H<sub>16</sub>ClNO<sub>2</sub>: C, 74.71; H, 4.18; N, 3.63. Found: C, 74.47; H, 4.30; N, 3.49.

**4-Diethylamino-3,4-dihydroindeno[2,1-*e*]-1,2-oxathiin 2,2-Dioxide (V).**

This compound was obtained in a yield of 9% starting from Ia by a previously described procedure (3), using anhydrous tetrahydrofuran as the solvent. The other compound recovered was Ia. M.p. 181° from ethyl acetate, after chromatography on Florisil® (diethyl ether); uv  $\lambda$  max nm (log  $\epsilon$ ): 216 sh (4.17), 224 sh (4.03), 259 (4.10); ir (potassium bromide)  $\nu$  max: 2810, 1638, 1353, 1187, 1171  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  1.13 (t, J = 7, 2CH<sub>3</sub>), 2.39 and 2.72 (2 q, J' = J'' = 7, 2NCH<sub>2</sub>), 3.26 and 3.59 (dq, J<sub>AB</sub> = 13.2, CH<sub>2</sub>SO<sub>2</sub>), 3.59 (near s, CH<sub>2</sub>), 4.45 (near q, J<sub>AX</sub> = 5.43, J<sub>BX</sub> = 11.96, CHN), 7.32 (m, 4H ar) [compare (2)].

*Anal.* Calcd. for C<sub>15</sub>H<sub>19</sub>NO<sub>3</sub>S: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.64; H, 6.17; N, 4.50.

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