

Reaction of Sulfene and Dichloroketene with Open-Chain
N,N-Disubstituted α -Aminomethyleneketones. Synthesis
of *N,N*-Disubstituted 4-Amino-3,4-dihydro-(5-methyl-6-
phenyl)(5,6-diphenyl)-1,2-oxathiin 2,2-Dioxides and of
4-Amino-3-chloro-5-methyl-6-phenyl-2*H*-pyran-2-ones

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Cycloaddition of sulfene to *N,N*-disubstituted 3-amino-2-methyl-1-phenyl-2-propen-1-ones (I) and 3-amino-1,2-diphenyl-2-propen-1-ones (II) occurred in good to moderate yield only in the case of aliphatic *N*-substitution to give 4-dialkylamino-3,4-dihydro-(5-methyl-6-phenyl)(5,6-diphenyl)-1,2-oxathiin 2,2-dioxides. Polar 1,4-cycloaddition of dichloroketene to I and II occurred only in the former case, giving in good to moderate yield *N,N*-disubstituted 4-amino-3,3-dichloro-3,4-dihydro-5-methyl-6-phenyl-2*H*-pyran-2-ones which were dehydrochlorinated with DBN to *N,N*-disubstituted 4-amino-3-chloro-5-methyl-6-phenyl-2*H*-pyran-2-ones.

In the reaction of 2-methyl-1-phenyl-3-diphenylamino-2-propen-1-one with dichloroketene, a product was isolated which was proven by uv, ir, nmr and chemical evidence to be the dipolar ion VI, the supposed intermediate of the polar 1,4-cycloaddition of dichloroketene to *N,N*-disubstituted enaminones.

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In previous work (1) we had shown that the cycloaddition of sulfene to open-chain α -aminomethyleneketones can occur only with an alkyl substitution on C-2 of the appropriate rotamer *EZ*. In order to substantiate these findings, we have now extended this cycloaddition to other open-chain enaminones such as I and II, both bearing an aliphatic or aromatic substituent on C-2 of the *EZ* rotamer.

Enaminones I and II (Table I) were prepared by reaction of 3-hydroxy-2-methyl-1-phenyl-2-propen-1-one and 3-hydroxy-1,2-diphenyl-2-propen-1-one, respectively, with secondary amines following previously described procedures (2,3). Unlike other enaminones [cf. (1)], ir and nmr spectra (Table II) were of little value in determining the preferred conformation of I and II. Both enaminones I

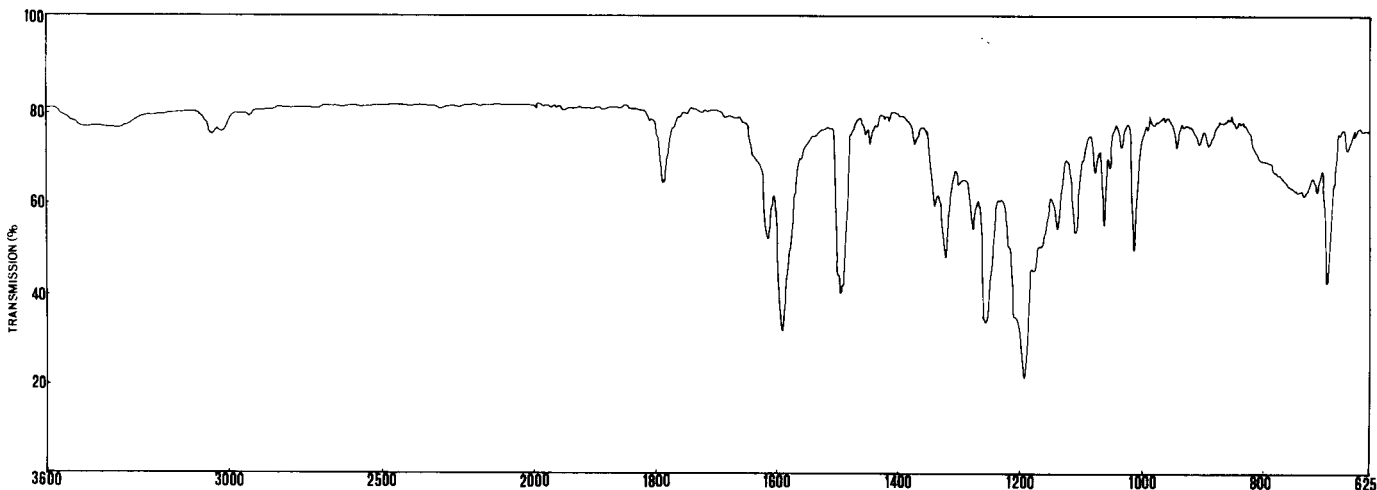
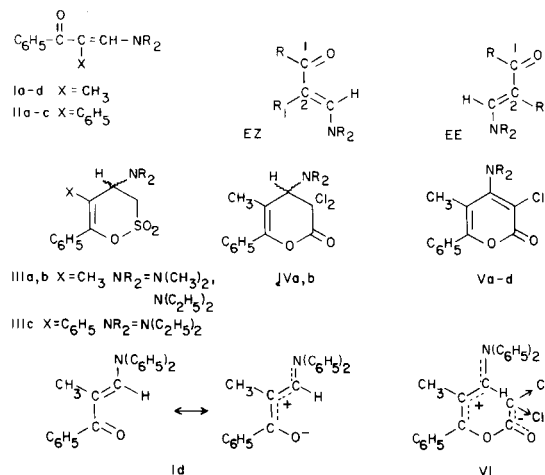


Figure 1. Ir spectrum of VI + IVb (tetrachloromethane).

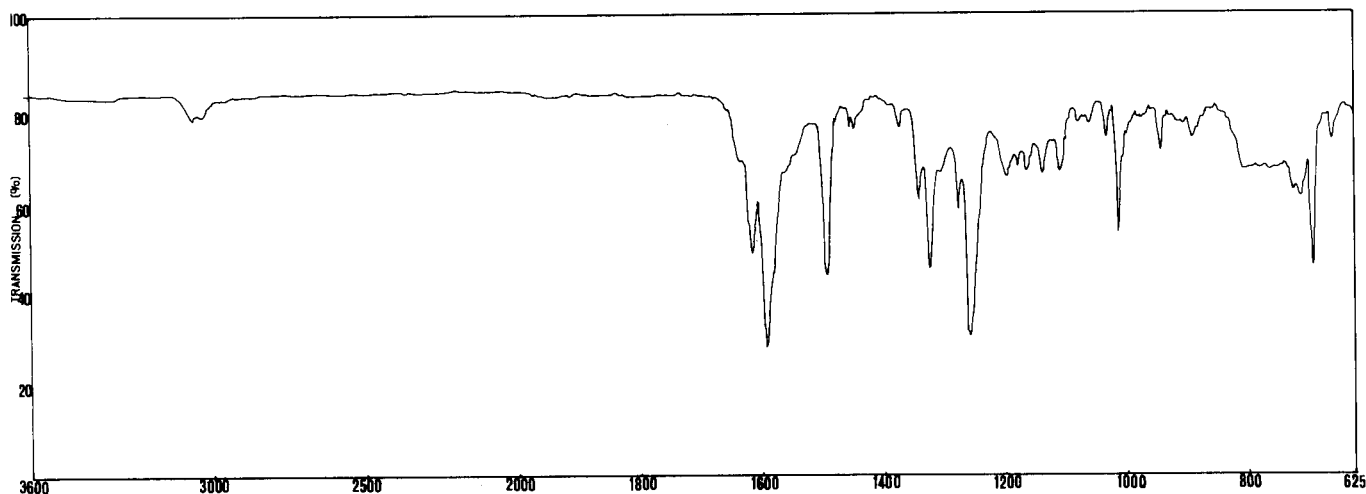


Figure 2. Ir spectrum of Id (tetrachloromethane).

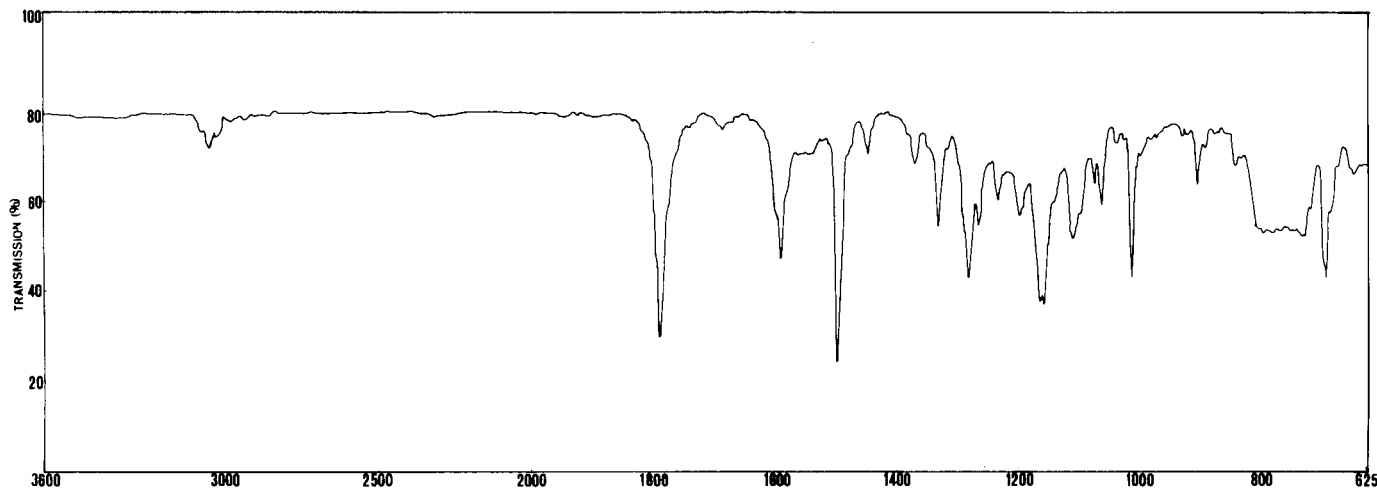


Figure 3. Ir spectrum of IVb (tetrachloromethane).

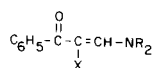
and II reacted with sulfene (prepared *in situ* from methanesulfonyl chloride and triethylamine) to give in good to moderate yield *N,N*-disubstituted 4-amino-3,4-dihydro-(5-methyl-6-phenyl)(5,6-diphenyl)-1,2-oxathiin 2,2-dioxides IIIa-c (Table III), provided that an aliphatic *N*-substituent was present. As a matter of fact, enaminones Ic,d and IIb,c were recovered unchanged from the reaction mixture; this lack of reactivity has been already explained (1). It can be noted that the reaction occurred also with the enaminone IIa, where an unfavourable conformation of the *cis* phenyl groups on C-1 and C-2 in the *EZ* rotamer was operative.

The reaction with dichloroketene (prepared *in situ* from dichloroacetyl chloride and triethylamine) occurred apparently only in the case of enaminones I, affording in moderate yield *N*-phenyl 4-amino-3,3-dichloro-3,4-dihydro-5-methyl-6-phenyl-2*H*-pyran-2-ones IVa-b (Table IV). The

cycloaddition was actually successful not only in the case of the above aromatic *N*-substitution [*cf.* (4)], but also with enaminones Ia,b bearing a full aliphatic *N*-substitution. In this case the crude adducts (showing strong ir absorptions at about 1790 cm^{-1}) were unstable and could not be purified, but gave the dehydrochlorinated products, namely *N,N*-disubstituted 4-amino-3-chloro-5-methyl-6-phenyl-2*H*-pyran-2-ones Va,b in high yield by treatment with DBN. In the same way the purified adducts IVa,b afforded the corresponding products Vc,d (Table V).

An interesting intermediate was found in the reaction of 2-methyl-1-phenyl-3-diphenylamino-2-propen-1-one Id and dichloroketene. A solid product, m.p. 135-137°, was extracted with hexane from the solid reaction mixture and found to be different both from the final cycloadduct IVb and the starting enaminone Id. Although this product could not be obtained pure, still containing 30% of IVb

Table I

N,N-Disubstituted 3-Amino-2-methyl-1-phenyl-2-propen-1-ones (Ia-d) and 3-Amino-1,2-diphenyl-2-propen-1-ones (IIa-c) (a)

Compound No.	X	NR ₂	Yield %	B.p./mm Hg or M.p., °C	Molecular Formula	Analyses %		
						Calcd./Found	C	H
Ia	CH ₃	N(CH ₃) ₂	71	145/0.1 43 (b)	C ₁₂ H ₁₃ NO	76.15	7.99	7.40
						76.20	7.81	7.20
Ib	CH ₃	N(C ₂ H ₅) ₂	87	155/0.1	C ₁₄ H ₁₉ NO	77.38	8.81	6.45
						77.40	8.78	6.30
Ic	CH ₃	N(CH ₃)C ₆ H ₅	82	81 (b)	C ₁₇ H ₁₇ NO	81.24	6.82	5.57
						81.41	6.99	5.56
Id	CH ₃	N(C ₆ H ₅) ₂	56	132 (b)	C ₂₂ H ₁₉ NO	84.31	6.11	4.47
						84.51	6.20	4.53
IIa	C ₆ H ₅	N(C ₂ H ₅) ₂	74	72 (b)	C ₁₉ H ₂₁ NO	81.67	7.57	5.01
						81.81	7.76	4.97
IIb	C ₆ H ₅	N(CH ₃)C ₆ H ₅	77	86 (b)	C ₂₂ H ₁₉ NO	84.31	6.11	4.47
						84.33	6.30	4.38
IIc	C ₆ H ₅	N(C ₆ H ₅) ₂	57	139 (b)	C ₂₇ H ₂₁ NO	86.37	5.64	3.73
						86.52	5.64	3.64

(a) Compound Ia was prepared according to (2) and compounds Ib-d, IIa-c according to (3). (b) From anhydrous diethyl ether.

Table II

Uv, Ir and Nmr Spectral Data of Compounds Ia-d, IIa-c

Compound No.	Uv λ max Nm (log ε)	Ir, Cm ⁻¹	Nmr, δ
Ia	234 (3.92)	1635, 1590, 1540	2.02 (s, CH ₃ -C=), 2.96 (s, 2NCH ₃), 6.73 (near s, CH=), 7.30 (near s, C ₆ H ₅)
	314 (4.38)		
Ib	233 (3.78)	1630, 1585, 1540	1.07 (t, J = 7.3, 2CH ₃ -CH ₂), 2.02 (s, CH ₃ -C=), 3.23 (q, J = 7.3, 2CH ₂ -CH ₃), 6.84 (near s, CH=), 7.31 (near s, C ₆ H ₅)
	313 (4.16)		
Ic	232 (3.74)	1620, 1590, 1560	1.81 (s, CH ₃ -C=), 3.31 (s, NCH ₃), 6.8-7.6 (m, CH= + 2C ₆ H ₅)
	334 (3.99)		
Id	241 (4.14)	1630, 1592, 1560	1.41 (s, CH ₃ -C=), 6.9-7.8 (m, CH= + 3C ₆ H ₅)
	280 (4.02)		
IIa	343 (4.41)	1635, 1585, 1535	0.97 (t, J = 7.3, 2CH ₃ -CH ₂), 2.99 (q, J = 7.3, 2CH ₂ -CH ₃), 7.0-7.3 (m, CH= + 2C ₆ H ₅)
	240 (3.99)		
IIb	312 (4.22)	1640, 1580, 1540	2.93 (s, NCH ₃), 7.0-7.6 (m, CH= + 3 C ₆ H ₅)
	236 (4.16)		
IIc	335 (4.27)	1640, 1590, 1540	6.74 (near s, 2NC ₆ H ₅), 6.9-7.7 (m, CH= + 2C ₆ H ₅)
	230 (3.94)		
	274 (3.91)		
	353 (4.00)		

(by nmr) derived from the ring closure, we propose for the major component the structure of dipolar ion VI on the following evidence.

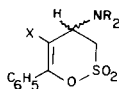
The ir spectrum (Figure 1) showed in the 1800-1100 cm⁻¹ region not only typical absorptions of Id (Figure 2) and weak bands of IVb (Figure 3), but also a strong band at 1190 cm⁻¹, absent in the ir spectra of both Id and IVb and ascribable to a C-O-C stretching. The nmr and uv spectra were a superimposition of Id and IVb spectra (Tables II and IV), but the uv spectrum, repeated after refluxing the previously used solution, changed exactly

into the IVb spectrum.

By comparing the mesomeric structures of Id and VI, it could be seen that the delocalization of the positive charge is practically the same, being absent or of little importance that of the negative charge, and this fact could justify the similarity of the uv and nmr spectra of VI and Id. On the other hand, only in the ir spectrum of VI a clear C-O-C stretching could be found. As chemical evidence we have found that impure VI, as a true intermediate, gave IVb in high yield also by refluxing its solution in hexane. As far as the stability of VI is concerned, the presence of three

Table III

4-Dialkylamino-3,4-dihydro-(5-methyl-6-phenyl)(5,6-diphenyl)-1,2-oxathiin 2,2-Dioxides (IIIa-c) (a)



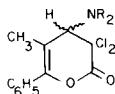
Compound No.	X	NR ₂	Yield %	M.p., °C	Molecular Formula	Analyses %		
						C	H	N
IIIa	CH ₃	N(CH ₃) ₂	43	119 (b)	C ₁₃ H ₁₇ NO ₃ S	58.41	6.41	5.24
						58.70	6.52	5.24
IIIb	CH ₃	N(C ₂ H ₅) ₂	41	89 (b)	C ₁₅ H ₂₁ NO ₃ S	60.99	7.17	4.74
						61.28	7.27	4.78
IIIc	C ₆ H ₅	N(C ₂ H ₅) ₂	80	131 (b)	C ₂₀ H ₂₃ NO ₃ S	67.20	6.48	3.92
						67.50	6.58	3.68

Ir and Nmr Spectral Data

Compound No.	C=C	Ir, Cm ⁻¹		Nmr, δ
		O=S=O		
IIIa	1660	1375	1170	1.80 (s, CH ₃ -5), 2.33 (s, 2NCH ₃), 3.37 (m, CH ₂ -3), 3.81 (m, CH-4), 7.37 (near s, C ₆ H ₅)
IIIb	1660	1380	1170	1.09 (t, J = 7.3, 2CH ₃ -CH ₂), 1.78 (s, CH ₃ -5), 2.45 and 2.58 (2q, J = 7.3, 2CH ₂ -CH ₃), 3.37 (m, CH ₂ -3), 3.95 (m, CH-4), 7.36 (near s, C ₆ H ₅)
IIIc	1640	1382	1170	0.85 (t, J = 7.3, 2CH ₃ -CH ₂), 2.45 and 2.57 (2q, J = 7.3, 2CH ₂ -CH ₃), 3.57 (m, CH ₂ -3), 4.53 (m, CH-4), 7.15 (near s, 2C ₆ H ₅)

(a) All compounds were prepared according to (2), using anhydrous benzene as the solvent. (b) From anhydrous diethyl ether.

Table IV

N,N-Disubstituted 4-Amino-3,3-dichloro-3,4-dihydro-5-methyl-6-phenyl-2*H*-pyran-2-ones (IVa-b) (a)

Compound No.	NR ₂	Yield %	M.p., °C	Molecular Formula	Analyses %		
					C	H	N
IVa	N(CH ₃)C ₆ H ₅	47	107 (b)	C ₁₉ H ₁₇ Cl ₂ NO ₂	62.99	4.73	3.87
					62.98	4.75	3.84
IVb	N(C ₂ H ₅) ₂	39	181 (c)	C ₂₄ H ₁₉ Cl ₂ NO ₂	67.93	4.51	3.30
					67.79	4.52	3.44

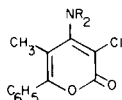
Ir and Nmr Spectral Data

Compound No.	Ir, Cm ⁻¹		Nmr, δ
	C=O	C=C	
IVa	1785	1685	1.92 (s, CH ₃ -5), 2.77 (s, NCH ₃), 4.87 (near s, CH-4), 6.8-7.6 (m, 2C ₆ H ₅)
IVb	1787	1682	2.05 (s, CH ₃ -5), 5.24 (near s, CH-4), 6.9-7.6 (m, 3C ₆ H ₅)

(d)

(a) All compounds were prepared according to (8). (b) From anhydrous diethyl ether. (c) From anhydrous diethyl ether-acetone. (d) Uv spectrum: λ_{max} 242 nm (log ε 4.25).

Table V

N,N-Disubstituted 4-Amino-3-chloro-5-methyl-6-phenyl-2*H*-pyran-2-ones (Va-d) (a)

Compound No.	NR ₂	Yield %	M.p., °C	Molecular Formula	Analyses %		
					Calcd.	Found	
					C	H	N
Va	N(CH ₃) ₂	80	84 (b)	C ₁₄ H ₁₄ ClNO ₂	63.76	5.35	5.31
					64.01	5.47	5.28
Vb	N(C ₂ H ₅) ₂	75	98 (b)	C ₁₆ H ₁₈ ClNO ₂	65.86	6.22	4.80
					65.89	6.36	4.63
Vc	N(CH ₃)C ₆ H ₅	77	109 (b)	C ₁₉ H ₁₆ ClNO ₂	70.05	4.95	4.30
					70.06	5.06	4.27
Vd	N(C ₆ H ₅) ₂	70	176 (b)	C ₂₄ H ₁₈ ClNO ₂	74.32	4.68	3.61
					74.06	4.73	3.58

Uv, Ir and Nmr Spectral Data

Compound	Uv λ max Nm (log ε)	Ir, Cm ⁻¹		Nmr, δ	
		C=O	C=C		
Va	261 (3.55)	1720	1622	1528	2.05 (s, CH ₃ -5), 3.02 (s, 2NCH ₃), 7.3-7.6 (m, C ₆ H ₅)
	312 (3.45)				
Vb	261 (4.05)	1720	1618	1510	1.11 (t, J = 7.3, 2CH ₃ -CH ₂), 2.07 (s, CH ₃ -5), 3.33 (q, J = 7.3, 2CH ₂ -CH ₃), 7.3-7.7 (m, C ₆ H ₅)
	318 (4.09)				
Vc	241 (3.73)	1730	1620	1520	1.82 (s, CH ₃ -5), 3.33 (s, NCH ₃), 6.6-7.6 (m, 2C ₆ H ₅)
	273 (3.33)				
Vd	335 (3.57)	1730	1622	1518	1.75 (s, CH ₃ -5), 6.8-7.6 (m, 3C ₆ H ₅)
	241 (4.18)				
	275 (4.29)				
	336 (4.14)				

(a) Compounds Vc,d were prepared from IVa,b, respectively, by dehydrochlorination with DBN according to (9). Compounds Va,b were prepared from Ia,b, respectively, by reaction with dichloroacetyl chloride and triethylamine according to (8). The crude, unstable products obtained were dehydrochlorinated with DBN according to (9). (b) From anhydrous diethyl ether.

phenyl groups could substantially operate by delocalizing further the positive charge.

It seems therefore proved that the 1,4-cycloaddition of dichloroketene to *N,N*-disubstituted enaminones goes through a dipolar intermediate, as we had previously supposed (5).

EXPERIMENTAL

Uv spectra were measured in 95% ethanol with a Hitachi-Perkin-Elmer Model EPS-3T spectrophotometer. Ir spectra were taken in tetrachloromethane on a Perkin-Elmer Model 257 spectrometer, and nmr spectra were recorded in tetrachloromethane on a Perkin-Elmer Model R12 instrument (60 MHz; TMS as internal standard; J in Hz).

3-Hydroxy-2-methyl-1-phenyl-2-propen-1-one.

This compound was prepared from 1-phenyl-1-propanone, ethyl formate and sodium according to the literature (6) in 72% yield, m.p. 119° from 50% ethanol [lit. (6) m.p. 118-119°]; ir (chloroform): ν max 1675, 1608, 1560 cm⁻¹; nmr (deuteriochloroform): δ 1.99 (s, CH₃-C=), 7.4-7.7 (m, C₆H₅), 8.4-8.8 (m, =CH-O-), 15.3-15.6 (m, OH; disappears with

deuterium oxide).

3-Hydroxy-1,2-diphenyl-2-propen-1-one.

This compound was prepared from 1,2-diphenylethanone, ethyl formate and sodium according to the literature (7) in 68% yield, m.p. 113° from 95% ethanol [lit. (7) m.p. 112-113°]; ir (chloroform): ν max 1670, 1605, 1555 cm⁻¹; nmr (deuteriochloroform): δ 7.0-7.5 (m, 2C₆H₅), 8.6-8.8 (m, =CH-O-), 15.8-16.2 (m, OH; disappears with deuterium oxide).

Reaction of Id with Dichloroacetyl Chloride and Triethylamine.

A solution of dichloroacetyl chloride (1.48 g., 10 mmoles) in anhydrous benzene was reacted with Id (3.8 g., 10 mmoles) and triethylamine (1.5 g., 15 mmoles) in the same solvent at 0-5°, according to the literature (5). The residue was chromatographed on Florisil® (diethyl ether-acetone 10:1) to give a pink solid (1.65 g., 39%) with a broad m.p., and whose nmr spectrum showed the presence of IVb and VI in a ratio of 45/55. The solid was extracted several times with hexane at 35-40°, leaving as residue the adduct IVb (m.p. 181°); the yellow hexane extracts were concentrated under reduced pressure at room temperature to give a precipitate (0.68 g., 16%), m.p. 135-137°, by addition of petroleum ether (b.p. 40-60°). The nmr spectrum revealed the presence of 30% IVb, but we were unable to reach a further purification by hexane extractions. Moreover, this compound was sensitive to heating and gave by refluxing

in hexane for 1 hour, the cycloadduct IVb in 85% yield. Impure VI had uv: λ max 241, 273, 344 nm [$\log \epsilon$ 4.25] after refluxing for 2 hours; ir (tetrachloromethane): ν max 1787, 1615, 1592, 1495, 1323, 1255, 1193 cm^{-1} (Figure 1); nmr (deuteriochloroform): δ 1.41 (s), 1.99 (s), 5.17 (near s), 6.8-7.7 (m).

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