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Studies of Benzoylsulfene. IV.[1] The Cycloaddition Reactions of Benzoylsulfene with Cinnamylideneamines

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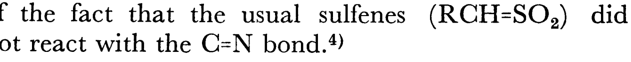
The reaction of benzoylmethanesulfonyl chloride with cinnamylideneamines in the presence of triethylamine has been investigated; the products were identified, by spectral studies as well as by chemical transformations, as the corresponding Diels-Alder adducts of benzoylsulfene as a dienophile to the α,β-unsaturated anils, 2-substituted 5*H*, 6*H*-6-benzoyl-5-phenyl-1,2-thiazine 1,1-dioxides, in which the phenyl and benzoyl groups are quasi-equatorial and quasi-axial respectively. The cycloadducts underwent inversion, on treatment with sodium methoxide in methanol or with silica gel in chloroform, to the corresponding epimers, in which both the phenyl and benzoyl groups are quasi-equatorial.

Recently, we found that benzoylsulfene PhCO-$CH{=}SO_2$), generated *in situ* from benzoylmethanesulfonyl chloride (I) and triethylamine (NEt_3), reacts with the C=N bonds of anils[2] and carbodiimides[3] to give the (2+2) and/or (4+2) cycloadducts, in spite of the fact that the usual sulfenes ($RCH{=}SO_2$) did not react with the C=N bond.[4]

This might indicate that the electron-attracting benzoyl group makes benzoylsulfene more reactive than the sulfenes ($RCH{=}SO_2$), and that benzoylsulfene behaves as a 1,2- and/or 1,4-dipole.



$$Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}SO_2 \leftrightarrow Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\ominus}{C}H\text{-}\overset{\oplus}{S}O_2 \leftrightarrow Ph\text{-}\overset{O^{\ominus}}{\overset{|}{C}}{=}CH\text{-}\overset{\oplus}{S}O_2$$

On the other hand, Sakamoto and Tomimatsu[5] found that the adduct obtained from the reaction of phenylketene with cinnamylideneaniline is not the Diels-Alder adduct, as proposed by Pfleger and Jäger,[6] but the corresponding (2+2) cycloadduct of ketene to the C=N bond.

In this connection, it seemed that it would be interesting to investigate the reaction of benzoylsulfene with α,β-unsaturated anils.

In the present paper, we wish to report on the formation of the Diels-Alder adducts by the reaction of benzoylsulfene with cinnamylideneamines.

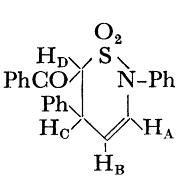
Results and Discussion

The reaction of benzoylmethanesulfonyl chloride (I) with equimolar amounts of cinnamylideneaniline (IIa) and NEt_3 in dioxane at room temperature for 1.5 hr gave a crystalline compound, IIIa, mp 159—160°C (decomp.), and triethylammonium chloride in 43% and quantitative yields respectively. The elemental analysis and the molecular weight (M^+ m/e 389) of IIIa were consistent with those of the expected 1 : 1 adduct of benzoylsulfene and IIa. The Diels-Alder adduct of benzoylsulfene as a dienophile to IIa, and the (2+2) and (4+2) cycloadducts of benzoylsulfene to the C=C or C=N bond in IIa, are possible for the structure of IIIa.

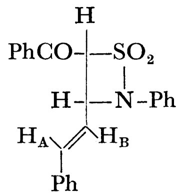
The IR spectrum of IIIa showed characteristic band at 1686 (νC=O), 1655 (νC=C or νC=N), 1340, and 1140 cm^{-1} (νSO_2), while the PMR spectrum in deuteriochloroform ($CDCl_3$) exhibited the four signals (each 1H) shown in Fig. 1, and also multiplets around τ 2.2—3.1 (15H, aromatic protons). Moreover, a solution of IIIa in benzene absorbed an equimolar amount of bromine.

These observations suggest that the 1 : 1 adduct is either the Diels-Alder adduct (IIIa) or the (2+2) cycloadduct (IIIa′) to the C=N bond.

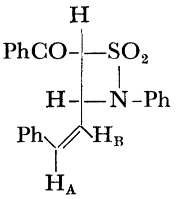
$$\underset{\text{I}}{PhCOCH_2SO_2Cl} + \underset{\text{IIa}}{PhCH{=}CH\text{-}CH{=}N\text{-}Ph} \xrightarrow{NEt_3}$$



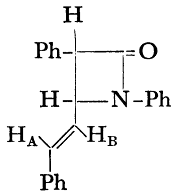
IIIa



IIIa′-1



IIIa′-2



IV

It is well known[7] that *trans* ethylenic coupling constants are always larger than *cis* ethylenic coupling constants for any pairs of 1,2-disubstituted ethylenes. The value of the ethylenic coupling constants, J_{AB} of the β-lactam IV obtained from phenylketene and IIa has been reported to be 17 Hz.[4] Also, the value of the ethylenic coupling constant of *trans*-cinnamaldehyde, the starting material of IIa, is 16.2 Hz.[8]

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[1] Part III: O. Tsuge and S. Iwanami, *Nippon Kagaku Zasshi*, **92**, 448 (1971).

[2] O. Tsuge and S. Iwanami, This Bulletin, **43**, 3543 (1970).

[3] O. Tsuge and S. Iwanami, *Nippon Kagaku Zasshi*, **92**, 448 (1971).

[4] H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, London (1967), p. 286.

[5] M. Sakamoto and Y. Tomimatsu, *Yakugaku Zasshi*, **90**, 1386 (1970).

[6] R. Pfleger and A. Jäger, *Chem. Ber.*, **90**, 2460 (1957).

[7] L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Ed., Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, Braunschweig (1969), p. 301.

The value of J_{AB} (8.6—8.8 Hz) in IIIa, as obtained its PMR spectrum (see Fig. 1 and Table 2), implies that H_A and H_B in IIIa are *cis*;[9,10] this observation excludes the possible formation of 4-benzoyl-2-phenyl-3-*trans*-styrylthiazetidine 1,1-dioxide (IIIa'-1).

It was very difficult to distinguish between the Diels-Alder adduct, 5*H*,6*H*-6-benzoyl-2,5-diphenyl-1,2-thiazine 1,1-dioxide (IIIa), and the (2+2) cycloadduct, 4-benzoyl-2-phenyl-3-*cis*-styrylthiazetidine 1,1-dioxide (IIIa'-2), on the basis of the spectral data. Since the olefinic hydrogens of IIa are *trans*, however, the predominant formation of the (2+2) cycloadduct with the *cis*-styryl group does not seem reasonable.

On the basis of the above observations and the chemical transformations, which will be discussed below, we can conclude that the most reasonable structure for the reaction product between benzoylsulfene and IIa is the Diels-Alder adduct IIIa.

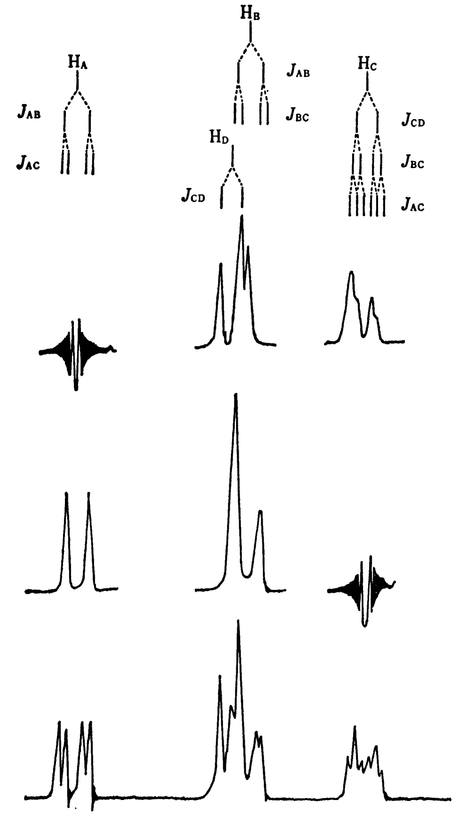

Fig. 1. PMR spectrum of IIIa in $CDCl_3$ at 60 MHz.

When a suspension of IIIa in methanol was treated with sodium methoxide at room temperature for 10 min, a compound Va, mp 175°C, was obtained as colorless needles in an exellent yield. The compound Va was also formed on treating IIIa with silica gel in chloroform.

The compound Va was proved, by the results of elemental analysis as well as by a study of its mass spectrum, to be an isomer of IIIa. The IR spectrum of Va showed characteristic bands at 1678 (νC=O), 1629 (νC=C), 1360, and 1160 cm^{-1} (νSO_2), while the PMR spectrum in $CDCl_3$ exhibited four signals (each 1H), as Fig. 2 shows, besides multiplets around τ 2.2—2.9 (15H, aromatic protons); the J_{AB} value between olefinic protons is 8.1 Hz.

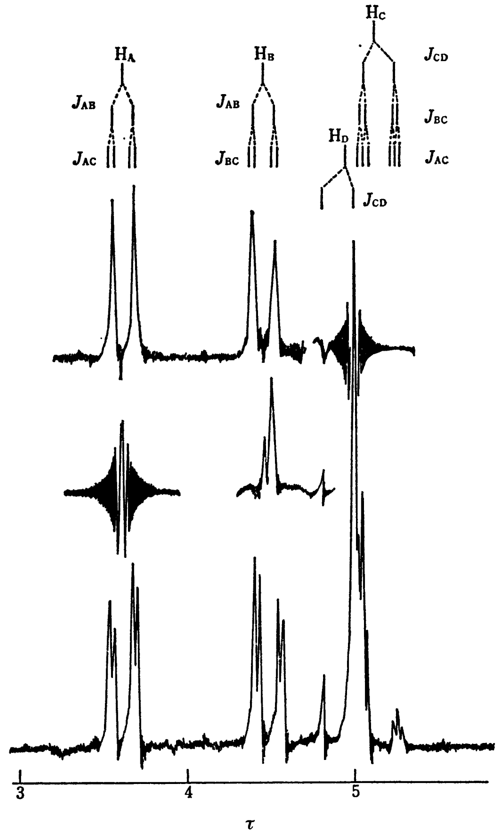

Fig. 2. PMR spectrum of Va in $CDCl_3$ at 60MHz.

From the above observations, it seems that the same ring structure as in IIIa might be involved in Va.

As is illustrated in Fig. 1, the allylic J_{AC} value between the olefinic and the allylic protons is almost equal to the vicinal J_{BC} value (2.5 Hz). This fact suggests that the hydrogen, H_C, in IIIa is quasi-axial.

An inspection of the Dreiding models indicates that the dihedral angle, θ_{CD} between H_C and H_D is about 40° if the benzoyl and phenyl groups in IIIa are *cis*. The observed J_{CD} value of 7.2 Hz is compatible with the value of 7.3 Hz calculated by a modified Karplus equation when $\theta=40°$.[11]

On the other hand, in the PMR spectrum of Va (Fig. 2) the J_{AC} value is also almost equal to the J_{BC} value (1.8 Hz); consequently, the hydrogen, H_C, in Va is quasi-axial.

Furthermore, the observed J_{CD} value of 11.7 Hz implies that the benzoyl and phenyl groups in Va are *trans*-diquasi-equatorial.

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[8] The olefinic coupling constant of IIa could not be measured, because assignments of the olefinic protons could not be made. While, the olefinic coupling constant of IId was observed to be 16 Hz.

[9] G. V. Smith and H. Krilof, *J. Amer. Chem. Soc.*, **85**, 2016 (1963).

[10] R. Bramley and M. D. Johnson, *J. Chem. Soc.*, **1965**, 1372.

[11] R. J. Abraham, *Mol. Phys.*, **1**, 513 (1962).

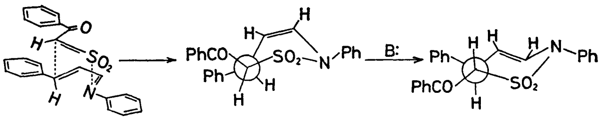
On the basis of the above observations, it is evident that IIIa is 5*H*,6*H*-6-benzoyl-2,5-diphenyl-1,2-thiazine 1,1-dioxide, in which the benzoyl and 5-phenyl groups are quasi-axial and quasi-equatorial (*cis*), while Va is its epimer, in which the benzoyl and 5-phenyl groups are both quasi-equatorial (*trans*).

It may be thought that IIIa is easily isomerized into the stable epimer, Va, under such mild conditions, because the hydrogen, H_D, in IIIa is highly activated by the neighboring electron-attracting benzoyl and sulfone groups. The treatment of IIIa with sodium methoxide in deuteriomethanol (CH_3OD) afforded the epimer-6-d (Va-d), mp 175°C, whose structure was established by a study of the PMR and mass spectra.

In general, the Diels-Alder reaction proceeds through the endo addition corresponding to the maximum accumulation of the double bond of the two reagents.

The favorable formation of IIIa can be reasonably explained in terms of the maximum accumulation of double bonds of benzoylsulfene and IIa with the *trans-s-cis-anti* configuration, as is illustrated in Scheme 1.

Furthermore, it may be considered that the active hydrogen, H_D, in IIIa is easily abstracted with a base, leading to the formation of the stable epimer, Va. However, the reaction course is not yet clear in detail.



IIa Va

Scheme 1

Both the cycloadducts, IIIa and Va, were hydrolyzed with aqueous sodium hydroxide in boiling methanol; both thus afforded the same compound, VI ($C_{16}H_{15}O_2NS$, M^+ *m/e* 285), mp 86—87°C (decomp.), as colorless plates, whose IR spectrum did not show any bands ascribable to the carbonyl and NH groups, but which did exhibit bands at 1645 ($\nu C=C$), 1350, and 1165 cm^{-1} (νSO_2).

The PMR spectrum of VI in $CDCl_3$ exhibited signals due to olefin-, methine- and methylene-protons, as is shown in Fig. 3, besides multiplets (10H, aromatic protons) around τ 2.5—2.9. The values of J_{AB}, J_{AC}, J_{BC}, J_{CD}, J_{CE}, and J_{BD} are found to be 8.3, 2.3, 2.2, 6.0, 12.5, and 1.2 Hz respectively. The long-range coupling ($J_{BD}=1.2$ Hz) may be due to the W-letter arrangement of H_B-C-C-C-H_D.[12] Furthermore, J_{DE} is 13.0 Hz.

The above observations indicate that the compound VI is 5*H*,6*H*-2,5-diphenyl-1,2-thiazine 1,1-dioxide, in which the 5-phenyl group and hydrogen H_D are both equatorial.

4-Benzoyl-2,3-diphenyl-1,2-thiazetidine 1,1-dioxide was hydrolyzed with aqueous sodium hydroxide as in the following equation,[2] while the ring skeltons of IIIa and Va were retained under similar conditions. These facts also support the proposed structures for IIIa and Va.

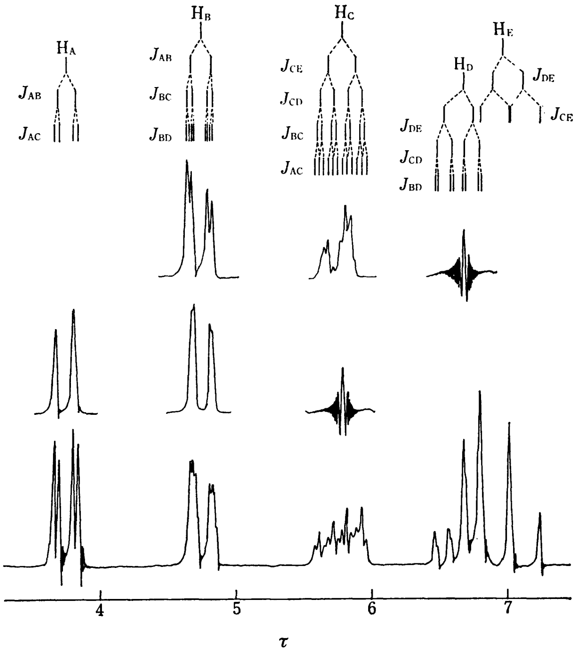
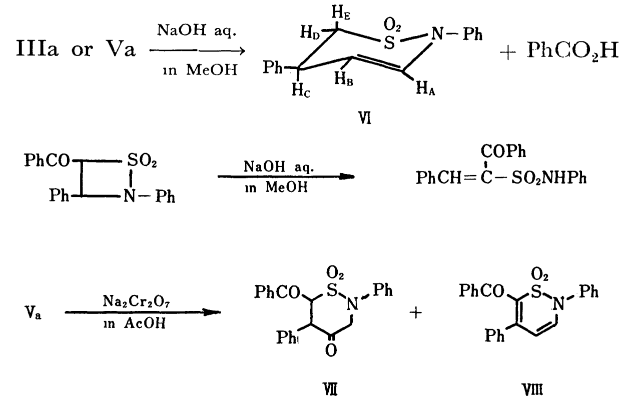


Fig. 3. PMR spectrum of VI in $CDCl_3$ at 60 MHz.



Scheme 2

The following experiment offered additional evidence for the proposed structure for Va. The oxidation of Va with sodium dichromate in acetic acid afforded perhydro-6-benzoyl-2,5-diphenyl-1,2-thiazin-4-one 1,1-dioxide (VII), mp 239—240°C, and 6-benzoyl-2,5-diphenyl-1,2-thiazine 1,1-dioxide (VIII), mp 169—170°C, in 23 and 10% yields respectively. The structures of VII and VIII were confirmed by elemental analyses and spectral studies.

Similar reactions of I with cinnamylidene-*p*-anisidine (IIb), -*p*-chloroaniline (IIc), -*n*-propylamine (IId) and α-methylcinnamylideneaniline (IIe) were investigated in the presence of triethylamine the results are summarized in Table 1.

Althogh the reaction with IIa and IId afforded the initial Diels-Alder adducts, IIIa and IIId, as crystalline compounds, oily substances were formed in the reactions with IIb, IIc, and IIe. However,

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[12] A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Lett.*, **1964**, 1233; S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

TABLE 1. 2,4-DISUBSTITUTED 6-BENZOYL-5-PHENYL-1,2-THIAZINE 1,1-DIOXIDES, III AND V

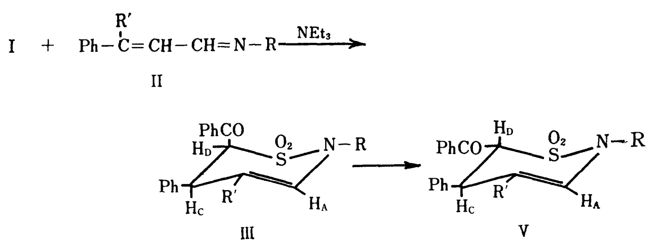
Compound	Yield (%)	Appearance	Mp (°C)	IR, cm^{-1}				Analysis (%) Found (Calcd)			Mol wt (m/e)
				νC=C	νC=C	νSO$_2$		C	H	N	
IIIa	43	colorless prisms	159 (decomp.)	1686	1655	1340	1140	71.10 (70.94)	5.07 (4.92)	3.73 (3.60)	389
IIId	37	colorless prisms	156 (decomp.)	1670	1642	1320	1130	67.32 (67.59)	6.00 (5.96)	4.00 (3.94)	355
Va	(42)$^{a)}$	colorless needles	175	1678	1628	1360	1160	71.25 (70.94)	4.68 (4.92)	3.64 (3.60)	389
Vb	43	colorless needles	189—190	1670	1642	1360	1160	68.86 (68.72)	4.88 (5.05)	3.39 (3.34)	419
Vc	26	colorless needles	189	1676	1636	1355	1150	64.98 (65.17)	4.01 (4.28)	3.22 (3.30)	423 425
Vd	(36)$^{a)}$	colorless needles	182—183	1678	1642	1335	1150	67.83 (67.59)	5.84 (5.96)	4.03 (3.60)	355
Ve	10	colorless needles	149—150 (decomp.)	1678	b)	1335	1150	71.16 (71.45)	5.12 (5.25)	3.60 (3.47)	403

a) Yield from chromatography of reaction mixture over silica gel without isolation of pure IIIa or IIId.
b) A distinct absorption band ascribed to νC=C was not observed.

TABLE 2. PMR SPECTRAL DATA ON III, V AND VIa (60 MHz)

Compound	Chemical shift (τ)					Coupling constant$^{a)}$ (Hz)					Solvent
	H_A	H_B	H_C	H_D	H_E	J_{AB}	J_{AC}	J_{BC}	J_{CD}	J_{CE}	
IIIa	3.51	4.55	5.27	4.46		8.6	2.5	2.5	7.2		$CDCl_3$
	3.76	4.82	5.24	4.44		8.8	2.6	2.4	7.2		C_6D_6
	3.41	4.43	5.25	4.23		8.7	2.6	2.4	7.2		CD_3NO_2
IIId	3.67	4.71	5.38	4.63		8.4	2.4	2.3	7.4		$CDCl_3$
Va	3.62	4.48	5.08	4.96		8.1	1.8	1.8	11.7		$CDCl_3$
	3.53	4.46	5.23	4.65		8.0	2.1	2.1	11.8		CD_3NO_2
Vb	3.66	4.53	5.10	4.98		8.2	1.8	1.8	12.0		$CDCl_3$
Vc	3.61	4.40	5.04	4.92		8.0	1.8	1.8	11.5		$CDCl_3$
Vd	3.80	4.76	5.20	5.02		8.3	2.0	2.0	11.8		$CDCl_3$
Ve	3.82	8.40$^{b)}$	5.31	4.88		—	—	—	11.8		$CDCl_3$
VIa	3.76	4.77	5.77	7.02	6.67	8.3	2.3	2.2	6.0	12.5	$CDCl_3$
	4.14	5.15	5.93$^{c)}$	7.36	7.00	8.4	2.2	2.3	6.3	12.3	C_6D_6
	3.60	4.62	5.78$^{c)}$	6.83	6.43	8.3	2.2	2.2	6.0	12.5	CD_3NO_2

a) Coupling constant, J, was measured with an error of about ±0.3 Hz.
b) Chemical shift of methyl protons.
c) This value is uncorrect, since impurity of the solvent exhibits multiplets around τ 5.6—5.8.



b: R=p-MeOC$_6$H$_4$, R′=H$_B$; c: R=p-ClC$_6$H$_4$, R′=H$_B$;
d: R=n-Pr, R′=H$_B$; e: R=Ph, R′=Me

oily substances were transformed, by chromatography on silica gel using chloroform as the eluent, to the corresponding epimers, V, as crystalline compounds. These results suggests that the oily substances contained considerable amounts of III, because IIIa and IIId were quantitatively transformed, as has been mentioned, to Va and Vd.

The structures of III and V were established by elemental analyses and by spectral studies. The yields, physical properties, elemental analyses, and spectral data are summarized in Tables 1 and 2.

Additional reactions of Va with hydrogen halides and bromine were also investigated.

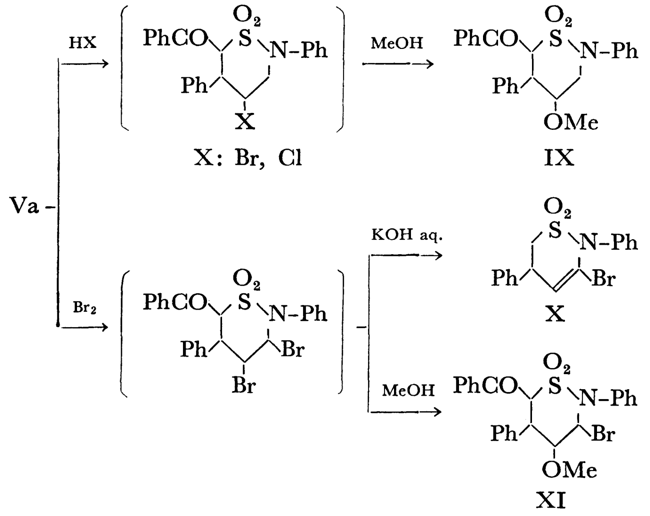
When hydrogen bromide was passed through a solution of Va in benzene, and the resulting solution was then treated with methanol, perhydro-6-benzoyl-2,5-diphenyl-4-methoxy-1,2-thiazine 1,1-dioxide (IX), mp 175°C (decomp.), was obtained quantitatively. The structure of IX was confirmed by the results of the elemental analysis and by the spectral data.

Also, the treatment of Va with concentrated hydrochloric acid in methanol at room temperature gave IX in a quantitative yield. Although an addition product of hydrogen bromide to Va could not be in a pure form, it is evident that the products from hydrogen halides are the corresponding perhydro-4-halo-1,2-thiazine 1,1-dioxide (Scheme 3).

The bromination of Va, followed by the treatment of a resulting oily dibromo compound with aqueous potassium hydroxide, afforded a crystalline compound, X ($C_{16}H_{14}O_2NSBr$), mp 147°C, in a low yield. The IR spectrum of X showed bands at 1632 (νC=C), 1355, and 1160 cm^{-1} (νSO_2), but not any carbonyl bands. The PMR spectrum in $CDCl_3$ revealed signals at τ 6.15—6.95 (2H, multiplets, $>\mathrm{C}\underline{\mathrm{H}}_2$), 5.4—5.9 (1H, multiplet, $\geqslant\mathrm{C}\underline{\mathrm{H}}$), 3.32 (1H, doublet, $-\mathrm{C}\underline{\mathrm{H}}=$, $J=1.8$ Hz), and 2.4—2.7 (10H, multiplets, aromatic protons).

The above observations indicate that the compound X is 5*H*,6*H*-3-bromo-2,4-diphenyl-1,2-thiazine 1,1-dioxide. The structure for X was also supported by the mass spectrum.

On the other hand, the treatment of the dibromo compound with methanol gave a crystalline compound XI, mp 170—171°C (decomp.), in a good yield. The compound XI ($C_{24}H_{22}O_4NSBr$) was assumed to be perhydro-6-benzoyl-3-bromo-2,5-diphenyl-4-methoxy-1,2-thiazine 1,1-dioxide on the basis of the following evidence.



Scheme 3

The IR spectrum of XI showed bands at 1685 (νC=O), 1336, and 1150 cm^{-1} (νSO_2), while the PMR spectrum in $CDCl_3$ revealed signals at τ5.47 (1H, two pairs of doublets, MeO–$\mathrm{C}\underline{\mathrm{H}}<$, each $J=2.5$ Hz), 4.98 (1H, double doublets, Ph–$\mathrm{C}\underline{\mathrm{H}}<$, $J=11.8$ and 2.5 Hz), 4.82 (1H, doublet, Br–$\mathrm{C}\underline{\mathrm{H}}<$, $J=2.5$ Hz), 3.95 (1H, doublet, PhCO–$\mathrm{C}\underline{\mathrm{H}}<$, $J=11.8$ Hz), and 1.8—2.9 (15H, multiplets, aromatic protons). The 4-bromo-3-methoxy isomer is also possible for the structure of XI. However, it may be considered that the 3-bromo-4-methoxy compound is more probable than the isomer, because the 4-bromine is more reactive than 3-bromine in the dibromo compound, as was shown in the formation of X. From the vicinal $J_{4,5}$ and $J_{5,6}$ values, it is evident that the 5-phenyl and benzoyl groups are both equatorial, and that the methoxy group is axial in XI.

Experimental

All the melting and boiling points are uncorrected. The IR spectra were measured in a KBr disk. The PMR spectra were taken on a Hitachi R-20 NMR spectrometer (60 MHz), using tetramethylsilane as the internal standard. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet and an ionization energy of 70 eV.

Materials. Benzoylmethanesulfonyl chloride (I), mp 88°C (lit,[13] mp 87.5—88.2°C) was prepared according to the method of Truce and Vriesen.[13] α,β-Unsaturated anils were prepared from the corresponding cinnamaldehydes and amines: cinnamylideneaniline (IIa), mp 109°C (lit,[14] mp 109°C), -*p*-anisidine (IIb), mp 118—119°C (lit,[15] mp 119°C), and -*p*-chloroaniline (IIc), mp 106—107°C (lit[15] mp 107°C).

Cinnamylidene-*n*-propylamine (IId), bp 140—142°C/0.2 mmHg.

Found: C, 83.40; H, 8.66; N, 7.93%. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.09%. M$^+$: *m*/*e* 173.

β-Methylcinnamylideneaniline (IIe); bp 192°C/1.2 mmHg.

Found: C, 87.18; H, 6.79; N, 6.26%. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33%. M$^+$: *m*/*e* 221.

General Procedure for the Reaction of I with II in the Presence of NEt_3. To a vigorously-stirred solution of 0.01 mol of II and 1.0 g (0.01 mol) of NEt_3 in 20 m*l* of dioxane, a solution of 2.2 g (0.01 mol) of I in 30 m*l* of dioxane was added, drop by drop, at room temperature over a period of 30 min. After the reaction mixture had been stirred at the same temperature for 1.5 hr, the triethylammonium chloride was removed by filtration. The filtrate was evaporated *in vacuo* at 40—50°C, leaving an oily substance. The oily substance obtained from the reaction with IIa or IId was triturated with methanol to give the 5*H*,6*H*-6-benzoyl-5-phenyl-1,2-thiazine 1,1-dioxide, IIIa or IIId, as crystals, but the thiazines, IIIb, IIIc, and IIIe, could not be isolated as crystals.

On the other hand, a chloroform solution of III was chromatographed over silica gel to give the epimer V.

The yields, physical properties, results of elemental analyses, and spectral data of III and V are summarized in Tables 1 and 2.

Inversion to V from III with Sodium Methoxide. A suspension of 0.5 g of IIIa in 5 m*l* of methanol was stirred with a few milligrams of metallic sodium at room temperature for 10 min. Subsequent filtration gave 0.49 g (98%) of colorless crystals, which were identical with the epimer, Va, obtained from the treatment of IIIa with silica gel described above. Similarly, IIId was transformed to the epimer Vd in a 97% yield.

A similar reaction of IIIa in deuteriomethanol (CH_3OD) gave the epimer-6-d (Va-d), mp 175°C, as colorless needles in a quantitative yield.

IR: 1673 (νC=O), 1625 (νC=C), 1354, 1158 cm^{-1} (νSO_2). PMR ($CDCl_3$): τ 3.62 (1H, double doublets, $>\mathrm{N}-\mathrm{C}\underline{\mathrm{H}}=$, $J=8.2$ and 2.1 Hz), 4.49 (1H, double doublets, $-\mathrm{C}\underline{\mathrm{H}}=\mathrm{CH}-\mathrm{N}<$, $J=8.2$ and 2.1 Hz), 5.10 (1H, multiplet, Ph–$\mathrm{C}\underline{\mathrm{H}}<$). Mass spectrum: M$^+$ *m*/*e* 390.

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[13] W. E. Truce and C. W. Vriesen, *J. Amer. Chem. Soc.*, **75**, 2525 (1953).

[14] A. T. Mason, *Ber.*, **20**, 270 (1887).

[15] A. Senier and P. H. Gallagher, *J. Chem. Soc.*, **113**, 28 (1918).

Hydrolysis of Va. A solution of 0.26 g of Va in 5 m*l* of 80% aqueous methanol, with 0.1 g of sodium hydroxide dissolved in it, was refluxed for 30 min. To the mixture was added 100 m*l* of water, and then the mixture was extracted with benzene. The benzene extract was washed with water, dried over sodium sulfate, and then evaporated *in vacuo* to give a viscous oil, which crystallized on trituration with petroleum benzine. Recrystallization from petroleum benzine (bp 45—60°C) gave 30 mg (16%) of 5*H*,6*H*-2,5-diphenyl-1,2-thiazine 1,1-dioxide (VI), mp 86—87°C, as colorless plates.

Found: C, 67.26; H, 5.16; N, 4.91%. Calcd for $C_{16}H_{15}O_2NS$: C, 67.36; H, 5.30; N, 4.91%. Mass spectrum: M^+ *m*/*e* 285.

The water layer was neutralized with concentrated hydrochloric acid to give 20 mg (24%) of benzoic acid.

Oxidation of Va. After a solution of 3.0 g of Va in 30 m*l* of acetic acid had been refluxed with 7.7 g of sodium dichromate dihydrate for 1 hr, the reaction mixture was cooled. To the mixture was added 100 m*l* of water, and then the mixture was extracted with chloroform. The chloroform extract was washed with water, dried over sodium sulfate, and then evaporated *in vacuo*. The residue was triturated with 10 m*l* of methanol to afford crystals. Subsequent filtration and recrystallization from a methanol-benzene mixture gave 0.72 g (23%) of perhydro-6-benzoyl-2,5-diphenyl-1,2-thiazin-4-one 1,1-dioxide (VII), mp 239—240°C, as colorless needles.

Found: C, 68.20; H, 4.66; N, 3.76%. Calcd for $C_{23}H_{19}O_4NS$: C, 68.14; H, 4.72; N, 3.46%. IR: 1710 (νC=O), 1672 (νC=O), 1325, 1143 cm^{-1} (νSO_2). Mass spectrum: *m*/*e* 405(M^+), 341(M^+-SO_2), 324(341^+-OH), 249(341^+-PhNH), 236(341^+-PhCO), 221(249^+-CO), 105 (PhCO$^+$).

The methanol filtrate was cooled at 0°C to give yellow crystals. Recrystallization from methanol gave 0.3 g (10%) of 6-benzoyl-2,5-diphenyl-1,2-thiazine 1,1-dioxide (VIII), mp 169—170°C, as yellow needles.

Found: C, 70.99; H, 4.27; N, 3.73%. Calcd for $C_{23}H_{17}O_3NS$: C, 71.31; H, 4.42; N, 3.62%. IR: 1640 (νC=O conjugated with C=C), 1340, 1160 cm^{-1} (νSO_2). PMR ($CDCl_3$): τ 3.12 (1H, doublet, olefinic protons). Mass spectrum: *m*/*e* 387(M^+), 323(M^+-SO_2), 322(323^+-H), 246(323^+-Ph), 230(322^+-PhNH), 217(322^+-PhCO), 105(PhCO$^+$).

Perhydro-6-benzoyl-2,5-diphenyl-4-methoxy-1,2-thiazine 1,1-Dioxide (IX). After a suspension of 0.2 g of Va in 10 m*l* of methanol has been stirred with 2 m*l* of concentrated hydrochloric acid at room temperature for 5 hr, the mixture was evaporated *in vacuo* to leave 215 mg of crystals. Recrystallization from methanol gave IX, mp 175°C (decomp.), as colorless needles.

Found: C, 68.51; H, 5.45; N, 3.25%. Calcd for $C_{24}H_{23}O_4NS$: C, 68.40; H, 5.50; N, 3.33%. IR: 1670 (νC=O), 1340, 1148 cm^{-1} (νSO_2). PMR (deuterionitromethane): τ 7.4 (2H, multiplet, $\rangle$N–C$\underline{\mathrm{H}}\langle$), 6.49 (3H, singlet, OC$\underline{\mathrm{H}}_3$), 5.5 (1H, multiplet, Ph–C$\underline{\mathrm{H}}<$), 4.92 (1H, multiplet, MeO–C$\underline{\mathrm{H}}<$), 4.23 (1H, doublet, PhCO–$\overset{|}{\mathrm{C}}\underline{\mathrm{H}}$–$SO_2$–, J=11.9 Hz), 1.9—2.9 (15H, multiplet, aromatic protons). Mass spectrum: *m*/*e* 421 (M^+), 389 (M^+-MeOH), 265 (M^+-SO_2-PhNH), 233 (265^+-MeOH), 147 (Ph–N$^+\equiv$C–$\dot{\mathrm{C}}$HOMe), 115 (147^+-MeOH), 105 (PhCO$^+$).

After hydrogen bromide gas was passed through a solution of 0.39 g of Va in 50 m*l* of benzene at room temperature for 5 hr, the benzene was evaporated *in vacuo* to leave a pale red solid. A methanol solution of the solid was refluxed for 5 min to give 0.2 g of IX.

*5*H*,6*H*-3-Bromo-2,4-diphenyl-1,2-thiazine 1,1-Dioxide (X).* To a solution of 0.8 g of Va in 50 m*l* of benzene was added, drop by drop at room temperature, a solution of bromine in benzene until there was no further disappearance of the reddish color of the bromine. The reaction mixture was then evaporated *in vacuo*, leaving an oily substance. A mixture of the oily substance in 20 m*l* of 0.5 N aqueous potassium hydroxide was heated at 70—80°C for 1 hr, after which the mixture was cooled. After 30 m*l* of concentrated hydrochloric acid had then been added to the mixture, the mixture was extracted with benzene. The benzene extract was washed with water, dried over sodium sulfate, and then evaporated *in vacuo* to leave a residue. A benzene solution of it was chromatographed over alumina and then eluted using chloroform to give colorless crystals. Recrystallization from petroleum benzine (bp 45—60°C) gave 0.1 g (13%) of X, mp 147°C, as colorless needles.

Found: C, 52.36; H, 3.83; N, 3.82%. Calcd for $C_{16}H_{14}O_2NSBr$: C, 52.76; H, 3.87; N, 3.85%. Mass spectrum: *m*/*e* 365, 363 (M^+, relative intensity 1 : 1), 301, 299, (M^+-SO_2, relative intensity 1 : 1), 220 (301^+ and 299^+-Br).

Perhydro-6-benzoyl-3-bromo-2,5-diphenyl-4-methoxy-1,2-thiazine 1,1-Dioxide (XI). The oily substance obtained from the bromination of 193 mg of Va according to the above mentioned-method was triturated with 5 m*l* of methanol, thus affording colorless crystals. Recrystallization from methanol gave 0.2 g (81%) of XI, mp 170—171°C (decomp.), as colorless needles.

Found: C, 57.36; H, 4.60; N, 2.74%. Calcd for $C_{24}H_{22}O_4NSBr$: C, 57.65; H, 4.44; N, 2.80%. Mass spectrum: *m*/*e* 501, 499 (M^+, relative intensity 1 : 1), 369, 467 (M^+-MeOH, relative intensity 1 : 1), 420 (M^+-Br), 388 (420^+-MeOH), 356 (420^+-SO_2), 227, 225 (relative intensity 1 : 1).