Derivatives of Thiacyclobutenes (Thietes). III.[1] Synthesis of Highly Unsaturated Thiete Sulfones[2,3]

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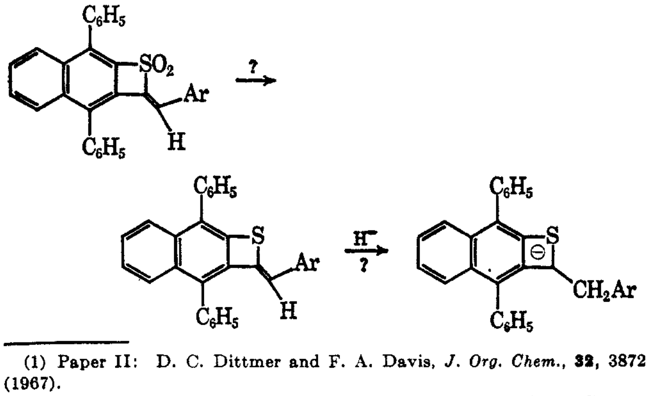
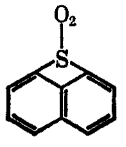
Condensations of 3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide with benzaldehyde, *p*-chlorobenzaldehyde, and *p*-methoxybenzaldehyde yield thiete sulfones which are unsaturated at every position. *p*-Nitrobenzaldehyde reacts anomalously. Reduction of the 2-benzylidene derivative by lithium aluminum hydride at −70° occurs with reduction of the double bond but not the sulfone group to give 2-benzyl-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide admixed with starting sulfone from which it could not be separated. The large difference in chemical shift between the diastereomeric methylene protons of this compound is attributed to restricted rotation.

The α hydrogens of sulfones are acidic,[4] and condensation reactions occur between α-sulfonyl anions and carbonyl groups.[5]

This investigation into the condensation reactions of aromatic aldehydes and cyclic, four-membered ring sulfones was undertaken to prepare derivatives of thietane sulfone with unsaturation exocyclic to the ring. We hoped that such sulfones might be reduced to the corresponding unsaturated sulfides, the reduction of the double bond or ring opening which occurs with thiete sulfones (where the olefinic bond is in the four-membered ring) being avoided.[6] Only 2,2-dimethyl-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide and 2,2-dimethyl-3,10-diphenyl-2H-anthra[3,2-*b*]thiete 1,1-dioxide are reduced cleanly to the sulfides and these thiete sulfones have no active methylene group.[6c]

Thietes are of theoretical interest because their anions are formally isoelectronic with the anion of cyclopentadiene. Reduction of the sulfone group in the 2-benzylidene derivative of 3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide might yield a thiete anion. Naphtho[8,1-*bc*]-thiete 1,1-dioxide (**1**)[7a] and some methylene thiete sulfones[7b] are the only known four-membered cyclic sulfones unsaturated at every position.





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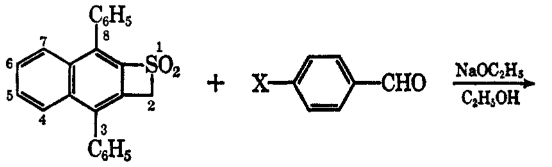
The naphthothiete sulfone **2**, when treated with benzaldehyde and sodium ethoxide in refluxing ethanol for 20 min, gave the unsaturated derivative **3a** in 96% yield. Similarly, *p*-chlorobenzaldehyde and *p*-methoxybenzaldehyde gave **3b** and **3c** (X = Cl, 77%; -OCH_3, 58%). No condensation reactions of this type with thiete sulfones are known; and the reaction is difficult with thietane sulfone, low yields of hydroxy compounds being obtained.[5b]



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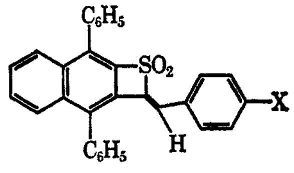

3a, X = H
b, X = Cl
c, X = OCH_3

All compounds had absorption in the infrared at 1300 and 1130–1145 cm^{-1} characteristic of the sulfone group.[1,6,6c] Absorptions caused by the olefinic group or by carbon–hydrogen bending vibrations of the olefinic group could not be assigned with assurance because of absorption by the aromatic rings. The proton nmr spectrum showed absorption at δ 6.20–6.33 (singlet) for a lone proton in addition to a multiplet for the aromatic protons.

The aryl group is probably *cis* to the sulfone group since models[8] indicate considerable steric interaction

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[1] Paper II: D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **32**, 3872 (1967).

[2] This work was aided by National Science Foundation Grant GP 726 and by National Institutes of Health Grant CA 08250.

[3] Taken from the Ph.D. Thesis of J. M. Balquist, Syracuse University, Syracuse, N. Y., 1966.

[4] For recent determinations of pK_a values, see F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, **89**, 3905 (1967).

[5] (a) W. E. Truce and R. H. Knospe, *ibid.*, **77**, 5063 (1965); H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963); G. A. Russell, H.-D. Becker, and J. Schoeb, *ibid.*, 3584; M. L. Oftedahl, J. W. Baker, and M. W. Dietrich, *ibid.*, **30**, 296 (1965). For condensations of Grignard reagents of sulfones, see L. Field and E. T. Boyd, *J. Org. Chem.*, **29**, 3273 (1964), and references cited therein. (b) For condensations with thietane sulfone, see S. M. Kotin, Ph.D. Thesis, University of Pennsylvania, Philadelphia, Pa., 1962.

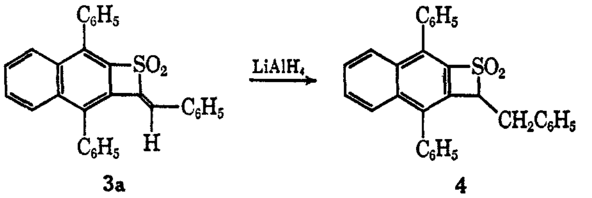
[6] (a) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962); D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **29**, 3131 (1964); C. L. Schilling, M.S. Thesis, Syracuse University, Syracuse, N. Y., 1964. (b) D. C. Dittmer and N. Takashina, *Tetrahedron Lett.*, 3809 (1964). (c) L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965).

[7] (a) R. W. Hofmann and W. Sieber, *Angew. Chem. Intern. Ed. Engl.*, **4**, 786 (1965); *Ann. Chem.*, **703**, 96 (1967). (b) L. A. Paquette and M. H. Rosen, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p 14S.

[8] Framework Molecular Orbital Models, Prentice Hall, Inc.

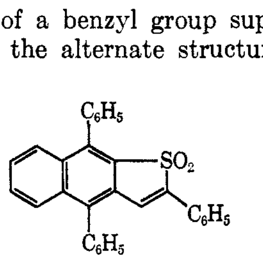
between the benzylidene phenyl group and the 3-phenyl group in a *trans* configuration.

Attempts were made to reduce the sulfone group of the benzylidene derivative **3a** by a tenfold excess of lithium aluminum hydride in tetrahydrofuran at −70° during 1–14 hr. The product recovery was 49–60% and consisted of a mixture of 13–32% of starting sulfone and 68–87% of 2-benzyl-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide (**4**). The mixture was not able to be separated into its components. Elemental and mass spectrometric analyses of the product were consistent with its being a mixture of $C_{30}H_{20}O_2S$ (mol wt, 444) and $C_{30}H_{22}O_2S$ (mol wt, 446). The infrared spectrum of the product mixture is nearly identical with that of the starting unsaturated sulfone (**3a**) and of the sulfone **2**. The ultraviolet spectra of mixtures richer in **4** have greater absorption at 243, 313, and 343 mμ [ultraviolet spectrum of **2**: 241 (log ϵ 4.72), 315 (4.08), and 338 (3.96) mμ] which indicates saturation of the double bond; mixtures richer in **3a** have relatively greater absorption at 361 and 375 mμ.



3a **4**

The mass spectrum of the mixture showed the most intense ion above *m/e* 100 at *m/e* 355 which corresponds to the loss of a benzyl group from **4**. The formation of $C_7H_7^+$ is inferred from an ion at *m/e* 91. The easy loss of a benzyl group supports structures **3a** and **4** over the alternate structures **5** and **6**. Further evidence against structure **5** is the observation that the sulfone group of alkyl-substituted benzthiophene sulfones is invariably reduced whereas the double bond may or may not be reduced.[9] The lack of reduction of the sulfone group of **4** may be caused by steric hindrance to attack on the sulfone or the sulfone anion (**7**); or its aluminohydride complex may be resistant to further attack by the reducing agent.



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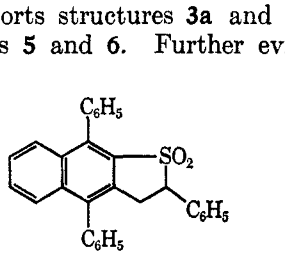

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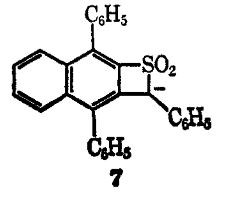

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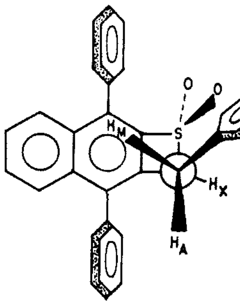

Figure 1.—Suggested preferred conformation of 2-benzyl-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide.

From the proton nmr spectra the compositions of the mixtures from reduction can be determined. When the spectrum of the starting unsaturated sulfone **3a** is subtracted from the spectrum of the mixture, the relative intensities of the remaining absorptions for **4** are 19:1:1:1. The absorptions consist of a multiplet at δ 8.32–6.87 (19 aromatic protons), a quartet at 5.82–5.47 (one proton), a quartet at 3.67–3.10 (one proton), and a quartet at 2.94–2.52 (one proton). The quartet at δ 5.82–5.47 can be assigned to the proton H_X in Figure 1 since the absorption of the methylene protons in the naphthothiete sulfone **2** occurs at δ 5.10.[6b,c] The other two quartets ($\Delta\delta_{AM} \sim 0.7$ ppm) can be explained by the nonequivalence of protons H_A and H_M with $J_{AM} = 15$ cps, $J_{AX} = 3$ cps, and $J_{MX} = 11$ cps. These protons H_A and H_M do not alter their chemical shifts even at 200°. Proton H_A is assigned to the absorption at higher field because it is over the plane of the 3-phenyl group.[10] Models[8] indicate restricted rotation about the bond connecting the benzyl group to the four-membered ring because of steric hindrance by the 3-phenyl group and the sulfone group. The spin–spin coupling constant between two vicinal protons is related to the dihedral angle ϕ between the protons.[11] If ϕ_{AX} is about 70–45° and ϕ_{MX} about 140–160°, which are reasonable values according to a model, J_{AX} is calculated, according to the equation of Williamson and Johnson,[11a] to be about 3–5 cps and J_{MX} about 10–14 cps in agreement with the observed values. These calculated values are uncorrected for effects caused by changes in hybridization, in electronegativity, in H–C–C bond angles and in bond distances.

The relatively large difference in chemical shift of the two diastereomeric methylene protons H_A and H_M has analogies in the relatively large differences between the absorptions of methylene protons in [2.2]-metacyclophane,[12] in a pleiadene derivative,[13] in certain asymmetric benzyl ethers,[14] and in N,N-dimethylbenzylamines in which there was no plane of molecular symmetry.[15] The coupling constant of 15

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(9) D. S. Rao, Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, p 26O. See also F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, **73**, 2251 (1951); G. Van Zyl, D. C. De Jongh, V. I. Heasley, and J. W. Van Dyke, *J. Org. Chem.*, **26**, 4946 (1961); G. Van Zyl and R. A. Koster, *ibid.*, **29**, 3558 (1963).

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, Chapter 7.

(11) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.*, **83**, 4623 (1961); (b) A. A. Bothner-By, *Adv. Magnetic Resonance*, **1**, 195 (1965).

(12) D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *J. Amer. Chem. Soc.*, **82**, 6302 (1960).

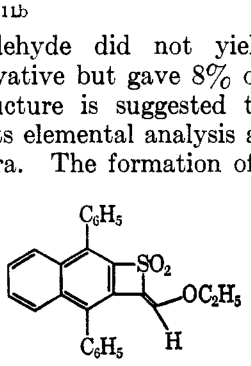
(13) P. T. Lansbury, *ibid.*, **81**, 4325 (1959).

(14) G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964); G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *ibid.*, **87**, 1058 (1965).

(15) J. C. Randall, J. J. McLeskey, III, P. Smith, and M. E. Hobbs, *ibid.*, **86**, 3229 (1964).

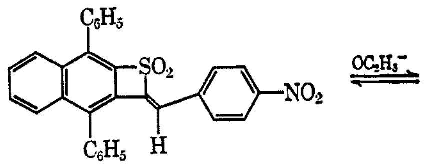
cps between H_A and H_M is in the range reported for geminal protons.[11b]

p-Nitrobenzaldehyde did not yield the *p*-nitrobenzylidene derivative but gave 8% of a light orange solid whose structure is suggested tentatively as **8** on the basis of its elemental analysis and infrared and ultraviolet spectra. The formation of **8** may proceed



8

by loss of the *p*-nitrophenyl group from the anion formed by addition of ethoxide ion to an intermediate benzylidene derivative, **9**. This reaction is somewhat analogous to the elimination of 1,3-dinitro-4,6-dimethoxybenzene from 2,6-dinitro-3,5-dimethoxybenzaldehyde when the latter is treated with 5% potassium hydroxide.[16]



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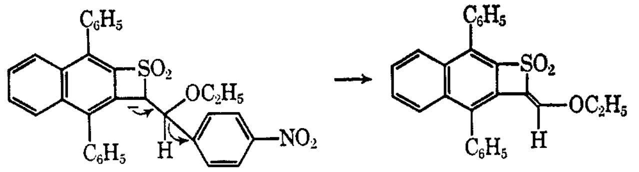

Experimental Section[17]

2-(Benzylidene)-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-Dioxide (3a).—To a refluxing solution of sodium ethoxide in ethanol, prepared by addition of 0.5 g (0.022 g-atom) of sodium to 100 ml of absolute ethanol, was added 1.78 g (0.005 mol) of 3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide (**2**)[6b,c] and 4 ml of benzaldehyde. The solution was refluxed for 15 min and cooled to room temperature. The precipitate was filtered, washed with cold absolute ethanol, and dried in a vacuum oven to give a light yellow powder (2.13 g, 96%, green-yellow fluorescence), mp 233–236°. Three recrystallizations from chloroform–ethanol produced an analytical sample, mp 240–241°.

Anal. Calcd for $C_{30}H_{20}O_2S$: C, 81.07; H, 4.54; S, 7.20; mol wt, 444. Found: C, 81.01; H, 4.60; S, 7.20; mol wt, 450 (osmometric).

The benzylidene sulfone had the following spectral properties: infrared (KBr) 3010 (w), 1600 (w), 1490 (w), 1440 (m), 1360 (m), 1300 (s), 1175 (s), 1130 (s), 790 (m), 770 (s), 695 (s) cm^{-1}; ultraviolet (CH_3CN), 219 mμ (log ϵ 4.03), 239 sh (3.85), 245 sh (3.83), 303 sh (4.18), 312 (4.22), 361 sh (3.85), 375 (3.86); nmr ($CDCl_3$), δ 8.38–7.18 (multiplet, 19 H), 6.34 (singlet, 1 H).

2-(*p*-Chlorobenzylidene)-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-Dioxide (3b).—To a refluxing solution of sodium ethoxide in ethanol (prepared by dissolving 0.5 g (0.022 g-atom) of sodium in 50 ml of absolute ethanol) was added 1.44 g (0.004 mol) of 3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide followed by 4 ml of *p*-chlorobenzaldehyde. The solution was refluxed for 5 min, cooled to room temperature, and diluted with a 2:1 ethanol–water solution. The precipitate was collected by filtration, washed with cold ethanol, and dried in a vacuum oven to give a yellow solid (1.48 g, 77%) green-yellow fluorescence), mp 222–228°. Two recrystallizations from chloroform–ethanol produced an analytical sample, mp 236–238°.

Anal. Calcd for $C_{30}H_{19}ClO_2S$: C, 74.97; H, 3.99; Cl, 7.44; S, 6.67; mol wt, 478. Found: C, 75.25; H, 3.98; Cl, 7.30; S, 6.68; mol wt, 490 (osmometric), 478 (mass spectroscopy).

The *p*-chlorobenzylidene derivative had the following spectral properties: infrared (KBr) 3010 (w), 1590 (m), 1495 (m), 1300 (s), 1145 (s), 1095 (m), 840 (m), 770 (s), 700 (s) cm^{-1}; ultraviolet (CH_3CN), 223 mμ (log ϵ 4.17), 250 sh (4.00), 308 sh (4.29), 317 (4.33), 360 sh (4.00), 380 (4.07); nmr ($CDCl_3$), δ 8.28–7.03 (multiplet, 18 H) and 6.20 (singlet, 1 H); mass spectrum, *m/e* 478 (22%), 379 (24%), 378 (25%), 377 (20%), 376 (22%), 388 (29%), 337 (38%), 321 (24%), 310 (32%), 309 (38%), 302 (28%), 289 (22%), 262 (20%), 188 (23%), 187 (22%), 141 (39%), 139 (20%), 79 (25%), 78 (100%), 77 (92%), 76 (24%).

2-(*p*-Methoxybenzylidene)-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-Dioxide (3c).—To a refluxing solution of sodium ethoxide in ethanol, prepared by dissolving 0.5 g (0.022 g-atom) of sodium in 70 ml of absolute ethanol, was added 1.0 g (0.0028 mol) of 3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide and 3 ml of redistilled *p*-anisaldehyde. The solution was refluxed for 1 hr, cooled to room temperature, diluted with 100 ml of saturated sodium chloride solution, and extracted with three 50-ml portions of chloroform. The organic layer was dried over anhydrous magnesium sulfate, concentrated to about 10 ml, and chromatographed on a Florisil column. The column was eluted with 1:1 benzene–chloroform. The eluent containing the first yellow band was collected and concentrated on a rotary evaporator by means of a water aspirator. Ethanol was added to precipitate a yellow powder (0.78 g, 58%, green-yellow fluorescence), mp 238–240°. Two recrystallizations from chloroform–ethanol produced an analytical sample, mp 245–247°.

Anal. Calcd for $C_{31}H_{22}O_3S$: C, 78.47; H, 4.67; S, 6.74; mol wt, 474. Found: C, 78.56; H, 4.93; S, 6.63; mol wt, 477 (osmometric), 474 (mass spectroscopy).

The *p*-methoxybenzylidene derivative had the following spectral properties: infrared (KBr), 3010 (w), 1600 (m), 1510 (m), 1300 (s), 1245 (s), 1175 (m), 1140 (s), 1020 (s), 860 (m), 770 (s), 760 (s), 695 (s) cm^{-1}; ultraviolet (CH_3CN), 223 mμ (log ϵ 4.53), 256 (4.44), 291 (4.39), 335 (4.66), 392 (4.44); nmr ($CDCl_3$), δ 8.28–7.30 (multiplet, 16 H), 7.02–6.72 (doublet, J = 9 cps., 2 H), 6.25 (singlet, 1 H), 3.77 (singlet, 3 H).

Partial Reduction of 2-(Benzylidene)-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-Dioxide.—A solution of lithium aluminum hydride (1.90 g, 0.50 mol) in 200 ml of anhydrous tetrahydrofuran was cooled in a Dry Ice–acetone bath and the 2-benzylidene derivative (**3a**) (2.22 g, 0.005 mol) was added in powdered form. The solution was stirred 5 hr; then 20 ml of water in 100 ml of tetrahydrofuran was added slowly; and the solution was allowed to warm to room temperature. The solution was acidified with 5% hydrochloric acid solution, diluted with 300 ml of saturated sodium chloride solution, and extracted with three 200-ml portions of ether. The ether extract was dried over anhydrous magnesium sulfate, concentrated, and chromatographed on a Florisil column. The column was eluted with chloroform and the eluent containing the first yellow band was collected. The eluent was concentrated to *ca.* 3 ml and 40 ml of ethanol was added. The light yellow precipitate which formed was collected by filtration and dried in a vacuum oven to give 1.04 g (47% based on the weight of the recovered material) of a yellow solid, mp 186–194°, which was shown by proton nmr measurements to be a mixture of 13% starting material and 87% 2-benzyl-3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide (**4**). Three recrystallizations of a sample from a similar reaction (shown to contain 32% compound **3a** and 68% compound **4**) from chloroform–ethanol produced a sample, mp 188–189°, which was analyzed. The nmr spectrum indicated the sample was still contaminated with unreduced starting material.

Anal. Calcd for $C_{30}H_{20}O_2S$: C, 81.07; H, 4.54; S, 7.20; mol wt, 444. Calcd for $C_{30}H_{22}O_2S$: C, 80.70; H, 4.97; S, 7.17; mol wt, 446. Found: C, 80.90; H, 4.73; S, 7.08; mol wt, 450 (osmometric).

This mixture had the following spectral properties: infrared (KBr), 3010 (w), 2900 (w), 1590 (w), 1485 (m), 1435 (m),

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[16] G. Lock and G. Nottes, *Monatsh.*, **68**, 51 (1936).

[17] Nmr spectra were recorded on a Varian A-60 spectrometer (60 Mc) and chemical shifts are reported with respect to tetramethylsilane. Infrared spectra were taken on a Perkin-Elmer Model 137 or 521 spectrophotometer. Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrometer. Melting points are uncorrected and were obtained on a Fisher-Johns melting point block. Mass spectra were obtained on an Hitachi RMU-6D single-focusing mass spectrometer.

1360 (m), 1300 (vs), 1145 (vs), 775 (s), 755 (m), 700 (s) cm^{-1}; ultraviolet (CH_3CN), 219, 243 303 (sh), 313, 343, 358 (sh), and 375 mμ; nmr ($CDCl_3$), δ 8.32–6.88 (multiplet, relative area 19), 6.29 (singlet, relative area 0.13), 5.82–5.47 (quartet, relative area 0.87), 3.67–3.10 (quartet, relative area 0.87), and 2.94–2.52 (quartet, relative area 0.87); mass spectrum, *m/e* 446 (30%), 444 (42%), 412 (90%), 355 (100%), 262 (57%), 141 (37%), 105 (60%), 91 (18%) (base peak is at *m/e* 78 but *m/e* 355 was used as base for above).

Attempts at further reduction of **3a** by using a greater hydride to sulfone ratio or by using longer reaction times appear to lead to a complex mixture of undetermined nature.

Attempted Condensation of 3,8-Diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-Dioxide with *p*-Nitrobenzaldehyde.—To a refluxing solution of sodium ethoxide in ethanol, prepared by dissolving 0.5 g (0.022 g-atom) of sodium in 40 ml of absolute ethanol, was added 3,8-diphenyl-2H-naphtho[3,2-*b*]thiete 1,1-dioxide (1.78 g, 0.005 mol) followed by *p*-nitrobenzaldehyde (1.25 g, 0.008 mol). The solution was refluxed for 1 hr, cooled, diluted with 100 ml of saturated sodium chloride solution, and extracted with three 50-ml portions of chloroform. The organic layer was dried over magnesium sulfate, concentrated to about 10 ml, and chromatographed on a Florisil column. The column was eluted with 1:1 benzene–chloroform. The eluent containing the first orange band was collected and was concentrated on a rotary evaporator using a water aspirator. Ethanol was added to precipitate a light orange solid (0.18 g, 8%), mp 215–220°. Two recrystallizations from chloroform–ethanol produced an analytical sample, mp 227–228°, of a compound tentatively identified as 2-(ethoxymethylene)-3,8-diphenyl-2H-naphtho-[3,2-*b*]thiete 1,1-dioxide (**8**) which had the following spectral properties: infrared (KBr), 3000 (w), 1590 (m), 1500 (m), 1430 (m), 1325 (s), 1285 (vs), 1170 (s), 1120 (s), 950 (m), 850 (m), 825 (m), 770 (s), 695 (s), cm^{-1}; ultraviolet (CH_3CN), 218, 241, 316 (sh), 339, and 401 mμ. There was insufficient sample left for a proton nmr spectral analysis.

Anal. Calcd for $C_{26}H_{20}O_3S$: C, 75.79; H, 4.89; S, 7.78; mol wt, 412. Found: C, 75.82; H, 4.70; S, 7.62; mol wt, 416 (osmometric).

Further elution of the remaining column with chloroform produced 0.44 g of a red-orange solid which could not be recrystallized from chloroform–ethanol or from ethanol, but which precipitated from a concentrated chloroform solution on addition of an excess of petroleum ether (bp 65–75°). The red-orange solid from the second fraction had infrared and ultraviolet spectra similar to those of the previously obtained $C_{26}H_{20}O_3S$ compound. There was no characteristic aromatic nitro group absorption in the 1570–1500- and 1370–1330-cm^{-1} regions.

Registry No.—**3a**, 15856-32-3; **3b**, 15892-86-1; **3c**, 15856-33-4; **4**, 15814-50-3; **8**, 15814-51-4.

2-Oxazolidinones from an N-Dealkylation Reaction of Phosgene with Dialkylaminoalkanols. The Isolation and Reactivities of an N-Acyl Quaternary Ammonium Intermediate

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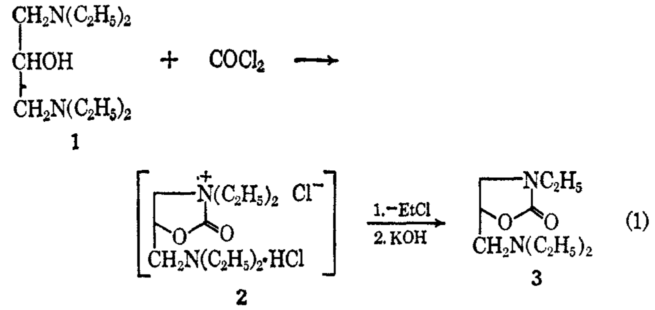
Phosgene condensed with 1-dimethylamino-2-propanol in the presence of pyridine to form a labile, cyclic N-acylium salt, **4**. This salt behaved as a powerful acylating agent toward *p*-toluenethiol, aniline, and methanol to form adducts **6**, **7**, and **8**. Toward chloride ion it was a mild methylating agent, concurrently forming 3,5-dimethyl-2-oxazolidinone **5**. Analogous formation of other oxazolidinones required a C substituent geminal to either the amino or hydroxyl group of the amino alcohol. A conformational explanation of this requirement for branching is proposed.

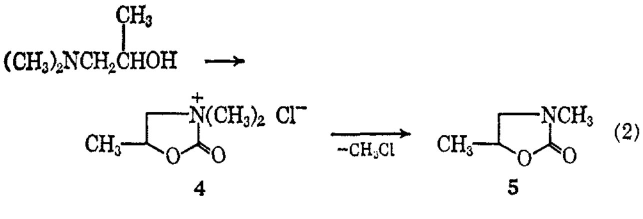
In another investigation phosgene was allowed to react with nonvicinal dialkylamino alcohols. Subsequent reaction of the unisolated condensation products with alcohols or nontertiary amines gave the expected carbonate esters or urethans,[1] but with bisdiethylamino alcohol **1** and phosgene the reaction took another course. With or without later addition of a secondary amine a cyclization-N-dealkylation reaction gave oxazolidinone **3**. By analogy with results described below it is probable that the cyclization proceeded *via* an N-acyl ammonium salt such as **2** (eq 1). Apparently one amino group served to bind hydrogen chloride, allowing acylation of the remaining free amino group.



1 2 3 (1)

This report describes the isolation of a very reactive N-acyl ammonium analog of **2** and a study of its reactions with some representative nucleophiles. The scope of a novel synthesis of 2-oxazolidinones from phosgene and 2-dialkylaminoalkanols has also been explored.

When equimolar amounts of 1-dimethylamino-2-propanol and pyridine were added to excess phosgene in methylene chloride solution at ⩽ −40°, then allowed to come to room temperature, a crystalline solid separated. This solid gave analyses and an infrared absorption peak at 5.42 μ which were in accord (see below) with a cyclic N-acyl ammonium structure (**4**), but, when the crystalline acylium salt was allowed to remain at 25° in the stirred reaction mixture, it disappeared within 5 hr, forming 3,5-dimethyl-2-oxazolidinone (**5**) (see eq 2).



4 5 (2)

The same product was obtained instantly, along with gaseous methyl chloride, when the acylium salt was heated above its melting point (97°).

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[1] R. B. Angier, K. C. Murdock, and W. V. Curran, *J. Med. Chem.*, in press.