

Derivatives of Thiacyclobutene (Thiete). VII.¹ Reaction of Thietes with Bases^{2,3}

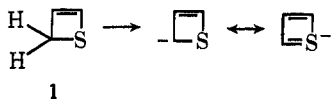
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Received August 6, 1971

Proton abstraction from thiete (1) by sodium methoxide in CH₃OD and other bases has been observed by nmr spectroscopy, but the thiete could not be recovered on acidification of the alkaline solution. The proton abstraction from thiete appeared faster than the abstraction from allyl sulfide. Wine-red or purple colors are observed when thietes 1 or 2 are treated with strong bases (e.g., lithium piperidide, *n*-butyllithium) at low temperatures. Treatment of 1 with *n*-butyllithium gave a mixture of allyl *n*-butyl sulfide and *n*-butyl propenyl sulfide. With trityllithium a mixture of *cis*- and *trans*-4,4,4-triphenyl-1-mercapto-2-butene was obtained; whereas with tritylpotassium, 4,4,4-triphenylbutanethial (identified as the 2,4-dinitrophenylhydrazone) was obtained. Potassium dimsylate and 1 yield the thioaldehydes (identified as 2,4-dinitrophenylhydrazones) corresponding to crotonaldehyde and 3-butenal. Treatment of 2 with *tert*-butyllithium gave 1-cyclohexenylmethyl *tert*-butyl sulfide.

The anion of thiete, which could be formed by proton abstraction from thiete (1), is an analog of the cyclopentadienyl anion in that it contains six π electrons. Simple HMO calculations indicate a delocalization energy of from 1.5 to 1.6 β which is nearly one β unit less than calculated for the anion of cyclopentadiene.⁴ Inclusion of the sulfur 3d orbitals does not change the calculated delocalization energy significantly. A rather low energy for the $\pi \rightarrow \pi^*$ transition is predicted (as compared with the calculated energy for the cyclopentadienyl anion) which indicates that the thiete anion may be colored. However, the simple Hückel treatment does not, among other things, properly account for electronic repulsions which would be expected to be of considerable magnitude in such a small molecule. The electronically similar dianion of cyclobutadiene has resisted efforts for its synthesis.^{5a} The stability of 3,4-bis(trifluoromethyl)-1,2-dithiete^{5b} can be attributed to the two electron-withdrawing trifluoromethyl groups, which decrease the energy of the six π electrons by an inductive effect and possibly by fluorine hyperconjugation. In addition, the two large polarizable sulfur atoms with their d orbitals may help to reduce electronic repulsions. In the absence of such stabilizing factors, the thiete anion might be quite reactive. In all of the reactions with bases to be described, either the anion appears not to be formed at all (other reactions intervene) or, if it is formed, it is unstable and the ring is destroyed. Work is in progress to prepare thietes with electron-withdrawing groups which can stabilize the anion.



1

Reactions with Alkoxides and Lithium Piperidide.—Evidence for removal of a proton from thiete is obtained by examination by means of nmr of a carefully

dried solution of thiete, sodium methoxide, and methanol-*d*. Undeuterated methanol (CH₃OH) appears in the reaction mixture and after 8–10 hr at ambient temperature, the thiete proton spectrum has disappeared and the intensity of CH₃OH is at a maximum. A similar experiment with allyl sulfide showed no formation of CH₃OH in 24 hr. This would indicate that the protons of thiete possess considerable kinetic acidity relative to those of allyl sulfide. The proton abstraction by potassium *tert*-butoxide in *tert*-butyl alcohol-*d* is faster and with potassium *tert*-butoxide in dimethyl sulfoxide-*d*₆ is almost instantaneous. In the latter case, a rapid increase in absorption for dimethyl sulfoxide-*d*₆ is observed which corresponds to ca. 1.6 protons. A similar experiment, in which phenylacetylene was treated with potassium *tert*-butoxide in dimethyl sulfoxide-*d*₆, showed a rapid increase in the absorption of dimethyl sulfoxide-*d*₆ corresponding to 0.8 proton. In these reactions with base, the thiete ring system is destroyed and an apparently polymeric material is formed.

When 1 is treated with potassium *tert*-butoxide in dimethylformamide or when 2 is treated with potassium *tert*-butoxide in tetrahydrofuran (THF) and the reaction mixture is quenched with D₂O, no deuterium incorporation into the recovered thiete could be detected. When thiete is treated with potassium 1-methylcyclohexoxide, the nmr absorption of the thiete protons disappears immediately.



2

Treatment of 2 with lithium piperidide in dimethoxyethane (DME) at -20° followed by acidification and treatment with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazones of 2-mercaptocyclohexane carboxaldehyde (3) and 2-mercaptomethylcyclohexanone (4) in low yield. This contrasts with the reaction of 2 with 2,4-dinitrophenylhydrazine alone, which yields the hydrazone of 1-cyclohexene aldehyde.¹ The products from the reaction of 2 with lithium piperidide may arise from hydrolysis of enamines produced by addition of piperidide ion to the double bond of the thiete followed by elimination of a mercaptide ion. The addition of lithium piperidide to a solution of 2 results in immediate formation of a purple color. Treatment of 2 at -10° with potassium *tert*-butoxide in *n*-pentane or tetrahydrofuran, lithium diethylamide in pentane, so-

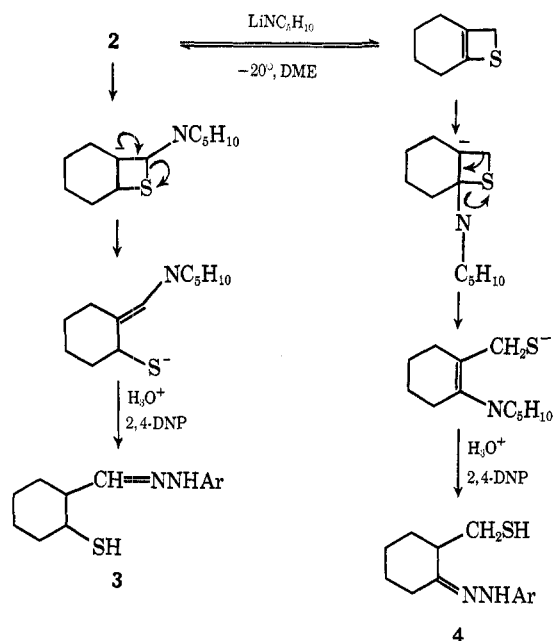
(1) Paper VI: D. C. Dittmer, P. L.-F. Chang, F. A. Davis, M. Iwanami, I. Stamos, and K. Takahashi, *J. Org. Chem.*, **37**, 1111 (1972).

(2) The authors are grateful for support of this research by the National Science Foundation.

(3) Taken in part from P. L.-F. Chang, Ph.D. Thesis, Syracuse University, 1970; F. A. Davis, Ph.D. Thesis, Syracuse University, 1966; and I. Stamos, Ph.D. Thesis, Syracuse University, 1969.

(4) R. Zahradnik and C. Parkanyi, *Collect. Czech. Chem. Commun.*, **30**, 3018 (1965); R. Zahradnik, *Advan. Heterocycl. Chem.*, **5**, 1 (1965). Recent calculations by F. A. Davis in which a different Coulomb integral for sulfur was used ($e_{3s} = \alpha_C + 1.5\beta$) indicate a much larger delocalization energy (2.6 β) for thiete anion.

(5) (a) W. Adam, *Tetrahedron Lett.*, 1387 (1963). (b) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **82**, 1515 (1960); C. G. Krespan, *ibid.*, **83**, 3434 (1961).



dium methoxide in tetrahydrofuran, lithium aluminum hydride in ether, or potassium hydroxide in tetrahydrofuran gave no purple color and no evidence of isomerization of the thiete, which was recovered in yields of 60–100%. Formation of the mercaptomethylcyclohexanone derivative (4) may involve an isomerization by way of the thiete anion,⁶ although isomerization can also occur by way of an addition, proton migration, and elimination.⁷

Reactions with Alkylolithium and Alkylpotassium Bases.—When 1 or 2 is treated with alkylolithium reagents, good yields of ring-opened products are obtained in which the alkyl group of the alkylolithium is attached to sulfur.⁸ No unchanged thiete is recovered. If wet tetrahydrofuran is added to the reaction mixture of 2 and *tert*-butyllithium in pentane at -78° a wine-red color is obtained instantly. The color is stable at -78° but fades at -50° . Work-up of the reaction mixture gives 1-cyclohexenylmethyl *tert*-butyl sulfide (80–90%). If the reaction of 1 with *n*-butyllithium is done in tetrahydrofuran a wine-red color (λ_{\max} 524 $m\mu$) also is observed (unlike the reaction in pentane in which there is no color). The red color is discharged immediately to yellow on addition of water. No thiete could be recovered, only the sulfides 5 and 6.

Further investigation of the reaction of thiete with *n*-butyllithium in tetrahydrofuran revealed that in addition to 5 and 6, small amounts of a high-boiling oil and an apparently polymeric material were obtained. These products may result from a secondary ring opening of thiete by a lithium derivative of one of the primary products.

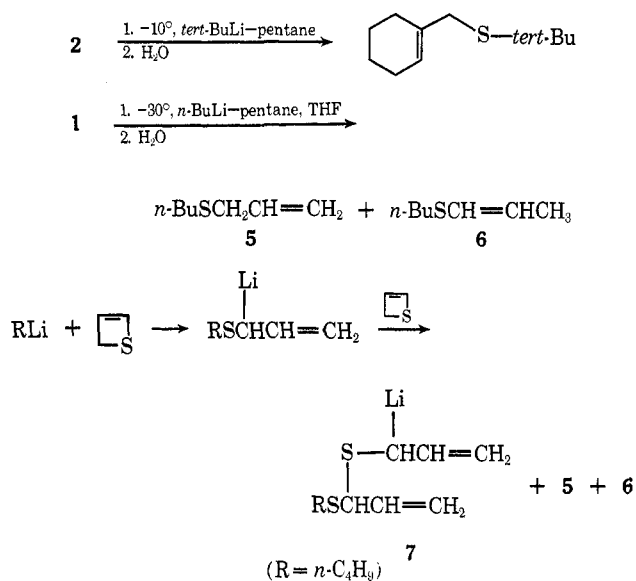
Since the complex of *n*-butyllithium with *N,N,N',N'*-tetramethylethylenediamine (TMED) is reported to be more reactive than the alkylolithium alone,⁹ thiete was

(6) The temptation to assume that the purple color is caused by the anion should be resisted in the absence of definite proof. This point is discussed subsequently.

(7) An addition-elimination mechanism for the isomerization of 2-sulfolene has been disproven: reviewed by C. D. Broaddus, *Accounts Chem. Res.*, **1**, 236 (1968).

(8) Trimethylene sulfide (thietane) yields *n*-butyl *n*-propyl sulfide when treated with *n*-butyllithium: F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *J. Amer. Chem. Soc.*, **76**, 1082 (1954).

(9) G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).

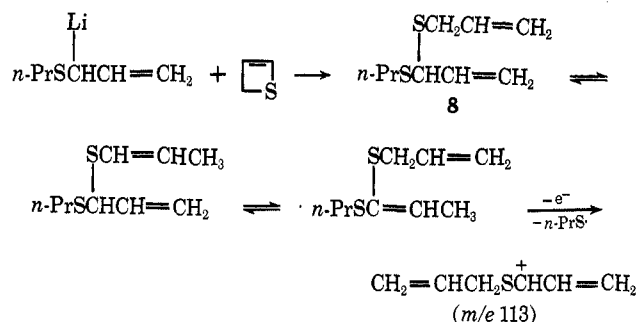


treated with this complex. The two sulfides 5 and 6 were the only products isolated in pentane, ether, or tetrahydrofuran. The pentane solution was pale yellow, the ether, pale pink, and the tetrahydrofuran, wine red. If the red color is caused by a free anion, the solvent behavior is explicable in terms of an equilibrium between a covalent lithium compound and the free anion. As the ability of the solvent to stabilize the lithium ion increases, more free anion is formed and the color deepens.

The wine-red color may be attributed to the thiete anion. However, an anion of a product also may be red, or the color may be produced by an intermediate thiocarbonyl compound. An esr spectrum of the red solution indicated the absence of any detectable anion-radical. The possibility that the red color from 1 and *n*-butyllithium was caused by anions of the products, 5 and 6, was investigated, but no red color could be produced from these compounds nor was any red color observed when 1-cyclohexenylmethyl *tert*-butyl sulfide was treated with *tert*-butyllithium.

The possibility that an anion of an intermediate (e.g., 7) may be responsible for the observed red color was investigated. A solution of *n*-propylthioallyllithium in tetrahydrofuran was prepared from allyl *n*-propyl sulfide and *n*-butyllithium in the presence of TMED. Addition of 1 resulted in formation of a wine-red color (λ_{\max} 512 $m\mu$) within 2–3 min which deepened during 10 min. Addition of aqueous acid discharged the color, and work-up of the reaction mixture gave a colorless liquid (A) and a high-boiling yellow oil (B) together with some polymeric material. Although A could not be obtained pure, a mass spectrum showed ions at m/e 188 and 113 and intense ions at m/e 115 ($n\text{-PrSC}^+\text{HCH}=\text{CH}_2$), 73 ($\text{S}^+\text{CH}_2\text{CH}=\text{CH}_2$), 43 (C_3H_7^+), and 41 ($\text{C}^+\text{H}_2\text{CH}=\text{CH}_2$). The ions m/e 188 and 113, as well as the others, can be derived from a logical structure, 8 (or a tautomer), resulting from attack of *n*-propylthioallyllithium on thiete. The infrared spectrum of A shows absorption at 1640 and 1620 cm^{-1} ($\nu_{\text{C}=\text{CH}_2}$, $\nu_{\text{C}=\text{CS}}$) indicating a mixture of tautomers. Oil B was not investigated but its infrared spectrum indicated that its structure was similar to that of A. Anions derived from 8 could react with thiete to give a higher molecular weight mate-

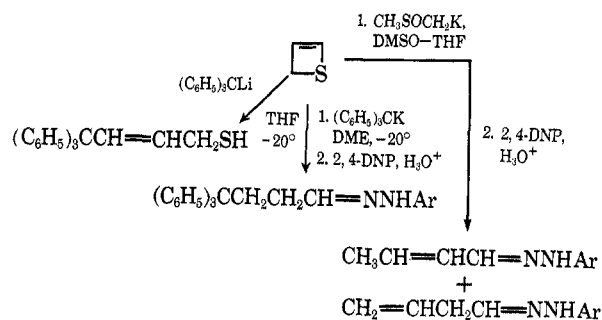
rial. Treatment of A with *n*-butyllithium in tetrahydrofuran gave a violet color (λ_{\max} 550 m μ) and similar treatment of B gave a wine-red color (λ_{\max} 495 m μ).



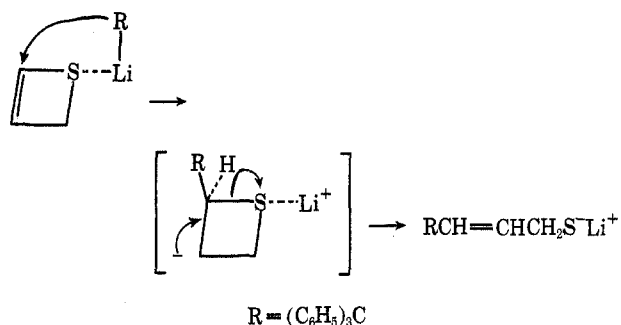
Another possible chromophore is a dianion of a sulfide, *e.g.*, $\text{S}(\bar{\text{C}}\text{HCH}=\text{CH}_2)_2$. Treatment of allyl sulfide in tetrahydrofuran with TMED and 1 equiv of *n*-butyllithium gave only a pale yellow solution, but addition of a second equivalent gave an orange solution which changed gradually to a wine red (λ_{\max} 490 m μ) during 1 hr at room temperature. However, no starting material or isomerized starting material could be recovered from the red solution after addition of water. Therefore, the red color produced when thiete is treated with *n*-butyllithium in tetrahydrofuran may not be caused by the anion of thiete but by an anion or dianion of a small amount of oligomeric product. However, the production of color by the thiete anion is not excluded.¹⁰ The very rapid production of the red color from thiete may militate against the products as the source of color unless they are formed instantly.

Ring opening of **1** also occurs on treatment with trityllithium, tritylpotassium, and potassium dimethylsulfate ($\text{CH}_3\text{SOCH}_2\text{K}$). There is, however, a difference in the mode of cleavage between the first-named reagent and the last two. Trityllithium yields *cis*- and *trans*-4,4,4-triphenyl-1-mercapto-2-butene (38%) after work-up of the reaction mixture. Tritylpotassium after work-up of the reaction mixture and treatment of it with 2,4-dinitrophenylhydrazine yields the 2,4-dinitrophenylhydrazone of 4,4,4-triphenylbutanal (74%) and potassium dimethylsulfate yields, after a similar work-up, the 2,4-dinitrophenylhydrazones of crotonaldehyde and 3-butenal. Conceivably, the reaction with tritylpotassium also could yield 4,4,4-triphenyl-1-mercapto-2-butene, which, on treatment with the acidic 2,4-dinitrophenylhydrazine reagent, may be isomerized to the enol of 4,4,4-triphenylbutanethial, which subsequently yields the observed hydrazone. This hypothesis was discarded because treatment of the mercaptobutene with 2,4-dinitrophenylhydrazine reagent gave no reaction.

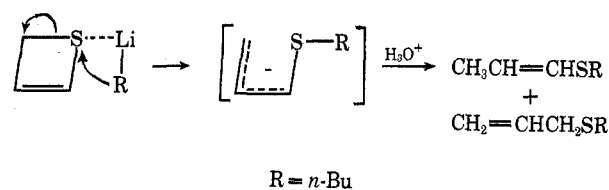
Alkylolithium reagents have considerable covalent character and are associated in solution; they are much less ionic than potassium derivatives.¹¹ Reaction of thiete with an alkylolithium reagent may be expected to proceed by association of the lithium with the unshared electrons on sulfur.⁸ Two extreme orientations of the lithium-alkyl bond with respect to the plane of the thiete ring may be considered. In one, the bond lies in



the plane; in the other it lies perpendicular to it. If a displacement reaction on sulfur proceeds by an attack on the back side of the bond being displaced, then the in-plane orientation of R-Li is more suitable. If the R-Li bond is perpendicular to the plane of the ring, the alkyl group is situated well for attack on the π -orbital system of the double bond. Which of the two modes of attack of alkylolithium compounds occurs may well depend on steric factors and perhaps on weak secondary valence interactions, such as an attraction between the double bond and a polarizable group (*e.g.*, phenyl). In the reaction of thiete with trityllithium, the bulky trityl group may cause the in-plane pathway of attack to be of higher energy than the attack on the double bond. Furthermore, there may be an attraction between the phenyl rings and the double bond which favors the perpendicular orientation of R-Li. Thus, one would predict that trityllithium would react *via* an addition-elimination mechanism, which gives the observed product. The more stable olefin would be expected to be formed.



The in-plane mode of attack of *n*-butyllithium on thiete occurs because of the less bulky nature of the butyl group as compared with the trityl group. Also, the butyl group would have less affinity for association with the double bond. The in-plane attack ordinarily may be preferred over the perpendicular one because of the development of an allylic anion in the former case. This would provide electronic stabilization for the in-plane pathway, and only when steric factors become important does the other mode of attack occur.



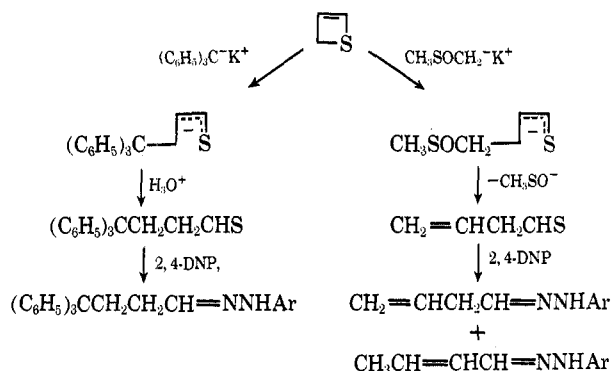
(10) The 1,3-bis(methylthio)allyl anion is purple: E. J. Corey, B. W. Erickson, and R. Noyori, *J. Amer. Chem. Soc.*, **93**, 1724 (1971).

(11) G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, "Principles of Organometallic Chemistry," Methuen, London, 1968, Chapter 3.

The reaction of *tert*-butyllithium with thiete **2** may seem contradictory to the above discussion, since apparently an in-plane attack on sulfur by the bulky

tert-butyl group occurs. Consideration of a model reveals unfavorable steric interactions with the hydrogens of the six-membered ring in the above-the-plane attack on the double bond, and the electronically more favorable pathway is followed.

Since tritylpotassium is more ionic than trityllithium, the trityl ion no longer is necessarily very near the potassium ion. The large potassium ion also has less need for stabilization by solvation by the sulfur atom. The same applies to the dimsyl ion. The relatively free trityl and dimsyl ions can attack the methylene group to displace mercaptide ion. This last mode of attack may be favored over the in-plane attack on sulfur, since making a carbon-carbon bond is favored energetically.



Experimental Section

Thiете 1 and Sodium Methoxide.—Thiете (0.038 g, 0.53 mmol) was treated with a saturated solution (0.3 ml) of sodium methoxide in methanol-*d*₁ in an atmosphere of nitrogen. The solution was transferred by means of a syringe into a nitrogen-flushed nmr sample tube. The tube was closed by a pressure cap. The sample was examined at ambient temperature by nmr. The absorption of the thiете protons at δ 6.50, 5.60, and 3.80 gradually disappears and a new band appears upfield from the δ 5.60 absorption. Maximum intensity of the new band is reached in 8–10 hr. The rate of decrease of the absorption at δ 3.80 (–CH₂–) seems slightly greater than that at δ 6.50 as determined by integration (during a 1.5-hr time period) of the peak areas by means of a planimeter. The new absorption at *ca.* δ 5.50 is observed immediately on addition of water or methanol to the saturated solution of sodium methoxide in methanol-*d*. This supports the assignment of the new peak to the hydroxyl protons of undeuterated methanol.

After 24 hr at room temperature, no change was observed in the nmr spectrum of a solution of diallyl sulfide in a saturated solution of sodium methoxide in methanol-*d*.

Thiете 1 and Potassium *tert*-Butoxide. A.—Deuterium oxide (2 mg, 0.1 mmol) and dry potassium *tert*-butoxide (56 mg, 0.5 mmol) were added to thiете (0.36 g, 0.5 mmol) in dimethylformamide (3 ml). The nmr spectrum of this thiете solution was examined during 30 min. The ratios of the areas of absorption at δ 6.56 (C₅=C₂H), 5.65 (C₂=C₃H), and 3.88 (CH₂) were determined at 10-min intervals as follows (time, min; rel ratios): 0, 1, 1, 2.0; 10, 1, 1, 1.8; 20, 1, 1, 1.5; 30, 1, 1, 1.3. At the end of this period the initially colorless solution had become red and viscous. Treatment of this solution with 2,4-dinitrophenylhydrazine reagent gave the 2,4-dinitrophenylhydrazone of β -mercaptopropionaldehyde¹ (0.075 g, 6%) which showed no absorption in the C–D stretching region (2200 cm⁻¹) in the infrared.

B.—The nmr spectrum of a solution of thiете (0.072 g, 1 mmol, dried over MgSO₄ or KH) and dry potassium *tert*-butoxide (0.056 g, 0.5 mmol) in dry (4A molecular sieves) dimethyl sulfoxide-*d*₆ (0.5 ml) was examined. As soon as the base was added, a substantial increase (*ca.* 111%) in the absorption at δ 2.50 for dimethyl sulfoxide-*d*₆ was observed. The increase in absorption corresponds to *ca.* 1.6 protons (based on the area of the absorption of the nine protons of the *tert*-butyl group). A con-

trol experiment with phenylacetylene replacing thiете showed a similar immediate increase in dimethyl sulfoxide-*d*₆ absorption which corresponded to 0.8 proton.

Thiете 2 and Lithium Piperidide.—*n*-Butyllithium (1.22 ml of a 21% solution in hexane) was added by syringe through a septum to piperidine (0.4 ml, dried over KOH and distilled from sodium) in a dry, three-necked flask equipped with a mechanical stirrer and a nitrogen inlet. The hexane was removed under vacuum and the flask was cooled in a Dry Ice-isopropyl alcohol bath. Thiете 2, prepared from 2 g of the quaternary salt, in cold dimethoxyethane (20 ml, distilled from LiAlH₄) was added by syringe through the septum. The mixture became purple at once and after 20 min was yellow-brown. Stirring was continued for 4 hr at bath temperature and 12 hr at –20°. The mixture was acidified to pH 2–3 with hydrochloric acid and treated with 2,4-dinitrophenylhydrazine (1 g, 0.005 mol). The reaction mixture was allowed slowly to come to room temperature, stirred for 2 hr, and heated for a few minutes at 40–50°. Water was added and the mixture was extracted with chloroform. The chloroform was dried (MgSO₄) and removed by evaporation on a rotary evaporator. The residue was chromatographed on alumina (CHCl₃) and on Florisil (CHCl₃) to separate two 2,4-dinitrophenylhydrazones, mp 168–170° and 235–238°. The lower melting compound was considered to be the 2,4-dinitrophenylhydrazone of 2-mercaptomethylcyclohexanone (0.2 g, 0.0006 mol, recrystallized from ethyl acetate) because it lacked absorption in the nmr at *ca.* δ 7.6 for the aldehydic proton:¹² nmr (CDCl₃) δ 11.10 (s, 1, NH), 9.00 (s, 1, ArC₆H), 8.25 (d, 1, ArC₆H), 7.90 (d, 1, ArC₆H), 1.2–3.1 (m, 12).

Anal. Calcd for C₁₃H₁₆N₄O₄S: C, 48.11; H, 4.94; N, 17.22; S, 9.88. Found: C, 48.10; H, 4.76; N, 16.95; S, 9.80.

The other compound was assigned the structure of the 2,4-dinitrophenylhydrazone of 2-mercaptocyclohexyl-1-carboxaldehyde. Its nmr spectrum could not be obtained because of its insolubility. An isomeric structure, the 2,4-dinitrophenylhydrazone of 2-methylthiocyclohexanone, was eliminated on the basis of the melting point of the derivative, 141°.¹³

Anal. Calcd for C₁₃H₁₆N₄O₄S: C, 48.11; H, 4.94; N, 17.22; S, 9.88. Found: C, 47.94; H, 4.75; N, 16.90; S, 9.47.

Thiете 2 and *tert*-Butyllithium (1-Cyclohexenylmethyl *tert*-Butyl Sulfide).—*tert*-Butyllithium in pentane (0.0045 mol, 2.5 ml)¹⁴ was added by syringe to thiете 2 (0.5 g, 0.004 mol) in pentane (100 ml) in a cooled (–10°) 300-ml, three-necked flask equipped with a mechanical stirrer, serum cap, and nitrogen inlet tube. The reaction mixture was stirred for 4 hr, water (10 ml) was added, and stirring was continued for 1 hr. The pentane solution was separated from the water and dried (Na₂SO₄, –10°) and the solvent was removed to give a clear oil (0.8 g, 80%) which was distilled through a 20-cm spinning band column to give 1-cyclohexenylmethyl *tert*-butyl sulfide: bp 36–38° (0.25 mm); ir (neat) 1663 (w, C=C), 940 (w), 910, (w), 790 cm⁻¹ (w); uv max (CH₃CN) 255 m μ (ϵ 790); nmr (CDCl₃) δ 5.6 (m, 1, C=CH), 3.08 (s, 2, C=CCH₂S), 2.0 (m, 4, C=CCH₂CH₂), 1.5 (m, 4, C=CCH₂CH₂), 1.3 (s, 9, CH₃); mass spectrum (70 eV) *m/e* (rel intensity) 95 (88), 57 (100).

Anal. Calcd for C₁₁H₂₀S: C, 71.64; H, 10.94; S, 17.39. Found: C, 71.51; H, 10.69; S, 17.72.

The same reaction was done at –78° in pentane. After 2 hr the pentane solution was pink. Addition of water (0.09 ml)-tetrahydrofuran (10 ml) cooled to –78° caused the reaction mixture to become wine red. Addition of more water or warming the mixture destroyed the color. Only 1-cyclohexenylmethyl *tert*-butyl sulfide was isolated. When a 1:1 pentane-ether solvent was used instead of pentane alone, a red color was obtained on addition of *tert*-butyllithium.

Thiете 1 and *n*-Butyllithium (*n*-Butyl Propenyl Sulfide and *n*-Butyl Allyl Sulfide). A. In Pentane.—*n*-Butyllithium in hexane (2 ml, 20%) was added to a stirred solution of thiете 1 (0.30 g, 0.0042 mol) in pentane (30 ml) at –30° under nitrogen. Water was added after 10 min and the mixture was extracted with pentane. Neither the water nor pentane layer gave a reaction with 2,4-dinitrophenylhydrazine. The pentane was washed (H₂O), dried (MgSO₄), and removed by evaporation. The res-

(12) G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and J. S. Ratka, *J. Amer. Chem. Soc.*, **85**, 2784 (1963).

(13) v. F. Asinger, M. Thiel, and H. Kaltwasser, *Justus Liebig's Ann. Chem.*, **606**, 67 (1957).

(14) The solution of *tert*-butyllithium was standardized by the method of H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).

idue was distilled (1 atm) to give a colorless liquid (0.25 g, 0.0019 mol) which was identified as a mixture of *cis*- and *trans*-*n*-butyl propenyl sulfide (6) and *n*-butyl allyl sulfide (5) by vpc (comparison with authentic samples): ir (film) 3080 (w), 2950 (s), 2880 (s), 1830 (w), 1640 (m, C=CCH₂S), 1620 (m, C=CS), 1460 (s), 1425 (s), 1400 (m), 1377 (s), 1330 (m), 1290 (m), 1275 (m), 1225 (s), 988 (s), 935 (m), 915 (s), 787 (w), 750 (m); ir (film, *n*-C₄H₉SCH₂CH=CH₂) 3080 (m), 2930 (s), 2875 (s), 1830 (w), 1640 (s), 1455 (s), 1420 (s), 1395 (m), 1377 (m), 1290 (w), 1270 (m), 1220 (s), 988 (s), 915 (s), 787 (w), 750 (m); ir (film, *n*-C₄H₉SCH=CHCH₃) 3020 (m), 2950 (s), 2880 (s), 1620 (m), 1460 (s), 1425 (m), 1377 (m), 1330 (s), 1290 (w), 1275 (m), 1225 (m), 935 (s), 750 (m). The nmr spectrum of the mixture was consistent with the combined spectra of allyl *n*-butyl sulfide and *n*-butyl propenyl sulfide.¹⁵

An authentic sample of *n*-butyl allyl sulfide was prepared from *n*-butanethiol and allyl chloride.^{15,16} Isomerization of *n*-butyl allyl sulfide with potassium *tert*-butoxide gave *n*-butyl propenyl sulfide.^{15,17}

The reaction of 1 with the complex of *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMED) in pentane gave a yellow solution and the products 5 and 6.

B. In Ether with TMED.—*n*-Butyllithium (2 ml, 20% in hexane) was added to a solution of TMED (2 ml) in dry (KH) ether at 0°. This mixture was added to a solution of 1 (0.200 g) in dry (KH) ether (20 ml) at -30°. A faint pink color appeared immediately. After 20 min, the reaction mixture was treated with aqueous tetrahydrofuran and worked up as before to give allyl *n*-butyl sulfide and *n*-butyl propenyl sulfide.

C. In Tetrahydrofuran with TMED.—A solution of 1 (0.350 g) and TMED (2 ml) in anhydrous tetrahydrofuran was dried (KH) at 0°. The supernatant liquid was removed and cooled to -60° under nitrogen. Addition of *n*-butyllithium (3 ml, 20% in hexane) produced a deep wine-red color, λ_{\max} 524 m μ . The color was stable up to 1 hr at room temperature. Addition of D₂O (2 ml) after 30 min caused the solution to become yellow immediately. The only products were allyl *n*-butyl sulfide (6) and *n*-butyl propenyl sulfide (5), which contained deuterium as indicated by infrared and nmr spectra.

Thiete 1 and *n*-Propylthioallyllithium.—*n*-Butyllithium (3.3 ml, 20% in hexane) was added to a dry (KH) solution of allyl *n*-propyl sulfide (1.61 g) and TMED (1.6 g) in anhydrous tetrahydrofuran (40 ml) and the resulting mixture was stirred for 2 hr. Thiete (0.500 g) in dry (KH) tetrahydrofuran (10 ml) was added to the pale orange solution of *n*-propylthioallyllithium at -20°. Within 2 or 3 min a wine-red color developed which deepened during 10 min, λ_{\max} 512 m μ . Addition of water caused a color change to green, then yellow. The reaction mixture was poured into ice-water, neutralized with hydrochloric acid, and extracted with pentane, which was washed with water and sodium bicarbonate solution and dried (MgSO₄). The pentane was removed by evaporation under reduced pressure and the residue was distilled to yield a colorless liquid, bp 28° (5 mm), identified as *n*-propyl propenyl sulfide by its infrared spectrum (1620 cm⁻¹, C=CS; 940 cm⁻¹, trans CH=CH).¹⁸ The residue was separated by chromatography on Florisil into two fractions, A (0.2 g), a colorless oil eluted with pentane, and B (0.5 g), a yellow oil eluted with ether. The mass spectrum and infrared spectrum of A indicated that it might be a mixture of isomers of 3-(propylthio)-4-thia-1,6-heptadiene (8) (calcd mol wt 188): ir (film) 3090, 1640 (C=C), 1620 (C=CS-), 990 (CH=CH₂), 920 cm⁻¹ (CH=CH₂); mass spectrum (70 eV) *m/e* (rel intensity) 188 (10), 115 (100), 113 (25), 79 (60), 73 (75), 43 (78), 41 (47). Oil B appeared to be similar to A: ir (film) 3090, 1640, 1620, 990, 920 cm⁻¹; nmr (CDCl₃) δ 4.8-6.2 (m), 2.5 (m), 1.6 (m), 0.9 (t).

Treatment of A with *n*-butyllithium in tetrahydrofuran gave a violet color (λ_{\max} 550 m μ); likewise, B gave a wine-red color (λ_{\max} 495 m μ).

Treatment of allyl sulfide (2 g) in dry tetrahydrofuran (50 ml) with TMED (4 g) and *n*-butyllithium (5.6 ml, 20% in hexane) at -30° resulted in no color change. Addition of more *n*-butyllithium (5.6 ml) caused development of a yellow color which gradually changed to orange. Finally, at room temperature

after 1 hr a wine-red color appeared (λ_{\max} 490 m μ). Neither allyl sulfide nor its isomers could be identified in the reaction mixture after addition of water.

Thiete 1 and Trityllithium (4,4,4-Triphenyl-1-mercapto-2-butene).—Trityllithium was prepared by treatment of a dry (KH) solution of triphenylmethane (2.7 g, 0.011 mol) and TMED (1.3 g) in THF (40 ml) with *n*-butyllithium (2 ml, 20% in hexane) at room temperature. The solution of trityllithium was stirred for 1 hr and cooled to -20°. Thiete 1 (0.40 g, 0.0056 mol) in dry (KH) tetrahydrofuran (10 ml) was added, discharging the red color of the trityllithium. After 30 min the light orange reaction mixture was poured into ice-water and the solution was neutralized with hydrochloric acid. The product was removed by filtration. The filtrate gave no reaction with 2,4-dinitrophenylhydrazine. The product was washed with ether and recrystallized from CCl₄ to give white crystals of *cis*- and *trans*-4,4,4-triphenyl-1-mercapto-2-butene (0.66 g, 0.0021 mol, 38%): mp 172°; ir (KBr) 3050, 2580 (-SH); nmr (CDCl₃) δ 7.2 (s, 15, C₆H₅), 5.3-6.2 (m, 2, CH=CH), 3.45 (d, 0.5, C=CCH₂), 3.35 (d, 0.5, C=CH₂), 2.7 (s, 0.5, SH), 2.55 (s, 0.5, SH).

Anal. Calcd for C₂₂H₂₀S: C, 83.50; H, 6.37; S, 10.13. Found: C, 83.58; H, 6.41; S, 10.34.

Thiete 1 and Tritylpotassium (4,4,4-Triphenylbutanal 2,4-Dinitrophenylhydrazone).—Thiete 1 (0.43 g, 0.059 mol) in dimethoxyethane (5 ml) was added to tritylpotassium (0.5 M, prepared from 2.23 g of triphenylmethane)¹⁹ in dimethoxyethane (25 ml) at -20° under nitrogen. The original red solution at first became colorless, then again red. After 1 hr, water and 2,4-dinitrophenylhydrazine reagent were added. The yellow, crystalline precipitate was recrystallized from ethanol to give the 2,4-dinitrophenylhydrazone of 4,4,4-triphenylbutanal (2.8 g, 0.0058 mol, 96%): mp 86-87°; nmr (DMSO-*d*₆) δ 11.40 (m, 1, NH), 8.90 (d, 1), 8.00, 8.27 (m, 1), 7.90 (d, 1), 6.20 (m, 1, CH=N), 2.70 (m, 2, CH₂CPh₃), 2.20 (m, 2, CH₂CH₂CPh₃).

Anal. Calcd for C₂₅H₂₄N₄O₄: C, 69.99; H, 5.03. Found: C, 69.71; H, 4.80.

Thiete 1 and Potassium Dimsylate (Crotonaldehyde and 3-Butenal 2,4-Dinitrophenylhydrazones).—Thiete was generated *in situ* by treatment of trimethyl-3-thietanylammonium iodide¹ (1.0 g, 0.0038 mol) in DMSO (7 ml) with potassium *tert*-butoxide (0.8 g, 0.007 mol) in DMSO (3 ml) at 15°. After 10 min the reaction mixture was poured into acidic (2 N HCl) 2,4-dinitrophenylhydrazine. The orange crystals (0.45 g, 0.0018 mol) of hydrazone were removed by filtration, washed (H₂O), and dried. Tlc (silica gel-benzene) indicated that two products were present. One recrystallization of the mixture (CHCl₃-C₂H₅OH) gave red crystals (0.05 g, 0.002 mol), which after several further recrystallizations gave the 2,4-dinitrophenylhydrazone of crotonaldehyde, mp 192° (lit.²⁰ mp 190°), whose mixture melting point with an authentic sample showed no depression and whose ir spectrum was identical with that of an authentic sample.

The solution remaining from the recrystallization of the crotonaldehyde derivative was concentrated and washed with cold methanol to give yellow crystals (0.3 g, 0.001 mol) of the 2,4-dinitrophenylhydrazone of 3-butenal, which was purified further by chromatography (Florisil, CCl₄) and recrystallization (CH₃-OH), mp 125-129° (lit.²¹ mp 128-129°). The infrared spectrum of an authentic sample²¹ was identical with that of the above sample.

In a similar reaction with thiete itself, the same result was obtained. Isomerization occurs under the conditions employed for the formation of the 2,4-dinitrophenylhydrazones: treatment of 3-butenal diethyl acetal with acidic (2 N HCl) 2,4-dinitrophenylhydrazine gave a mixture of the 2,4-dinitrophenylhydrazones of 3-butenal and crotonaldehyde.

Registry No.—1, 503-31-1; 5, 5399-19-9; *cis*-6, 33531-82-7; *trans*-6, 33531-83-8; 8, 33527-71-8; sodium methoxide, 124-41-4; potassium *tert*-butoxide, 865-47-4; lithium piperidide, 4442-11-9; 2-mercapto-methylcyclohexanone (2,4-DNPH derivative), 33527-74-1; *tert*-butyllithium, 594-19-4; 1-cyclohexenylmethyl *tert*-butyl sulfide, 33608-38-7; *n*-butyllithium, 109-72-8;

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n-propylthioallyllithium, 33527-76-3; trityllithium, 733-90-4; *cis*-4,4,4-triphenyl-1-mercapto-2-butene, 33608-39-8; *trans*-4,4,4-triphenyl-1-mercapto-2-butene, 33531-

84-9; tritylpotassium, 1528-27-4; 4,4,4-triphenylbutanal (2,4-DNPH derivative), 33527-79-6; potassium dimsylate, 17609-15-3.

Iminosulfuranes (Sulfilimines). IV.^{1a} The Preparation and Properties of *N*-Acetylminodialkylsulfuranes^{1b}

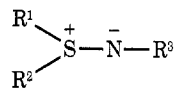
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Received July 19, 1971

N-Acetylminodialkylsulfonium bromides, (R¹R²S⁺NHCOCH₃)Br⁻ [R¹ = R² = CH₃; R¹ = CH₃, R² = C₂H₅; R¹ = R₂ = C₂H₅; R¹ = R² = *n*-C₃H₇; R¹ = R² = *i*-C₃H₇; R¹, R² = -(CH₂)₄-], were prepared in 38–81% yields by the reaction of *N*-bromoacetamide with alkyl sulfides in a mixture of CCl₄ and acetone. The sulfonium bromides were converted in excellent yields (88–98%) to the *N*-acetylminodialkylsulfuranes, R¹R²S⁺N⁻COCH₃, by treatment with triethylamine in methylene chloride. Some *N*-acetylminodialkylsulfonium chlorides were also prepared. Spectroscopic data show that the iminosulfuranes have extensive charge delocalization over the SNCO system, and the S–N bond is considered to be semipolar. The first detailed mass spectral fragmentation of iminosulfuranes and their salts is reported.

The nature of the N substituent in iminosulfuranes (1) has a significant effect on the polarity of the sulfur-



1

nitrogen bond and hence on their reactivity. Iminosulfuranes with alkyl,² aryl,³ halogen,⁴ nitrile,⁵ carboethoxy,⁶ sulfonyl,⁷ benzoyl,⁸ and halogenated acetyl⁹ groups on the nitrogen atom are known.

N-(Haloacetyl)iminosulfuranes have also been prepared by the condensation of di- and trichloroacetylisocyanates with dimethyl sulfoxide,¹⁰ and by the reaction of α -dichloro- and α -dibromoacetamide with sulfides in the presence of sodium hypochlorite.¹¹

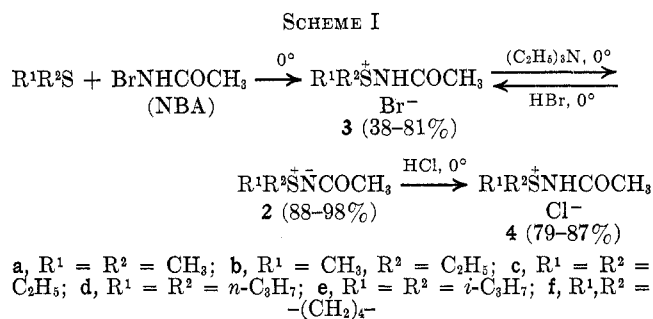
In 1947, Likhosherstov¹² reported that *N*-chloroacetamide reacts with dimethyl sulfide in CCl₄-acetone solution to give *N*-acetylminodimethylsulfonium chloride, a compound which could not be obtained pure and was highly sensitive to moisture. Treatment of the sulfonium chloride with ammonia was reported to give an oil, suspected to be *N*-acetylminodimethylsulfurane. The iminosulfurane was not purified nor was its structure established.

We report here (a) the first preparations of pure *N*-acetylminodialkylsulfuranes by a modification and

improvement of Likhosherstov's method and (b) establishment of their structure by ir, nmr, uv, and mass spectrometry. This is the first in a series of papers in which the effects of the substituent on nitrogen on reactivity, nucleophilicity, basicity, and spectral properties of iminosulfuranes are being systematically explored.

Results and Discussion

Preparation of *N*-Acetylminodialkylsulfuranes and Their Salts.—The synthetic route used is shown in Scheme I (yields in parentheses).



The yields and melting points of the iminosulfuranes (2), sulfonium bromides (3), and sulfonium chlorides (4) are given in Table I.

N-Bromoacetamide (NBA) is a source of positive bromine and is an oxidizing agent in aqueous media. Consequently, a thoroughly dry and inert solvent system is required for the preparation of the sulfonium bromides (3). In carbon tetrachloride, the reaction of NBA with sulfides is slow and in ether the major product is acetamide hydrobromide, (CH₃-CONH₂)₂HBr. Chloroform and ethyl alcohol are also unsatisfactory solvents because of the predominance of substitution and oxidation reactions. The best solvent system found for the reaction is a mixture of carbon tetrachloride and acetone (4–8:1 by volume); under these conditions the reaction mixture is heterogeneous. The sulfonium bromides (3) precipitate at the reaction temperature (0°).

The sulfonium bromides (3) are white, crystalline

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