chloride in 20 ml. of DME was added dropwise. The mixture was moderately stirred under nitrogen at room temperature overnight, treated cautiously with about 5 ml. of methanol to ensure the complete absence of potassium, then poured into excess water and extracted with a total of 200 ml. of benzene. Concentration of the benzene solution was followed by distillation through a Vigreux column. Benzyl chloride was removed below 50°, at 0.05 mm. The pressure was lowered to 40 μ by means of an oil diffusion pump and after a forerun of 0.15 g., 6.44 g. (60%) of oil distilled at 147–155° at 36–47 μ. The oil solidified on cooling and the colorless solid melted at 70–71°. Recrystallization from hexane did not change the melting point.

The n.m.r. spectrum of the 70–71° solid in deuteriochloroform, with tetramethylsilane (TMS) as internal standard, showed phenyl (~2.8 τ), methylene (multiplet ~5.9 τ), and methyl (triplet ~8.9 τ) protons in a ratio of 5.0:3.8:3.2; calcd. 5:4:3. An absorption, presumably due to an impurity, with a relative intensity of 0.25 was observed at 8.42 τ.

Diethyl N,N'-Diallylbicarbamates.—The procedure was identical to that used for the dibenzyl derivative, except that 12.1 g. (0.10 mole) of allyl bromide in 20 ml. of DME was added to the dianion solution. Work-up as before gave 3.1 g. (40%) of oil, b.p. 92–93° (0.5 mm.); n.m.r. analysis of this oil in carbon tetrachloride solution with TMS as internal standard showed vinyl (multiplet ~4.2 τ), vinylidene (multiplet ~4.9 τ), methylene (overlapping doublet and quartet ~6.0 τ), and methyl (triplet centered at 8.8 τ) protons in a ratio of 1.00:1.93:3.83:2.95; calcd. 1:2:4:3.

Diethyl N,N'-Diethylbicarbamate.—The procedure was similar to that used for the dibenzyl derivative, except that in this case the dianion was prepared from 10.44 g. (0.06 mole) of I in 30 ml. of DME added to 4.68 g. (0.12 g.-atom) of potassium in 60 ml. of DME. The color of the solution soon after the beginning of the addition was green and turned brown only after about half the addition was complete. Treatment with 20.0 g. (0.13 mole) of ethyl iodide in 20 ml. of DME gave, after work-up and distillation, 3.77 g. (27%) of oil, b.p. 78–81° (0.1 mm.).

Diethyl Tetrahydro-1,2-pyridazinedicarboxylate.—The procedure was the same as for the diethyl derivative except that 13.0 g. (0.06 mole) of 1,4-dibromobutane was added to the dianion. Work-up and distillation afforded 2.1 g. (15%) of colorless liquid which darkened after standing several days.[7]

Electron Spin Resonance Analysis.—The e.s.r. signal was obtained at room temperature in a sealed tube by a technique previously described.[11]

Acknowledgments.—Assistance with the computations by J. H. Lehnsen is gratefully acknowledged. The authors also wish to thank W. G. Hodgson for obtaining the e.s.r. spectrum and for stimulating discussions.

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Base-Catalyzed Elimination Studies on Sulfones, Sulfoxides, Sulfides, Disulfides, and Mercaptans in Dimethyl Sulfoxide[1]

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Elimination studies on a large number of sulfur compounds and some compounds containing both nitrogen and oxygen functional groups have been carried out at 55° in the base–solvent system, potassium *tert*-butoxide–dimethyl sulfoxide (DMSO). The ease of elimination for a series of isopropyl derivatives was found to be $Br^{\ominus} = RSO_2^{\ominus} = RSO^{\ominus} > NO_3^{\ominus} > SCN^{\ominus} > RS^{\ominus} > NO_2^{\ominus} > S^{\ominus} > CN^{\ominus}$ based on the yield of propylene. A variation in the structure of the alkyl moiety of the sulfur compounds indicated that the ease of carbanion formation follows the order *p* > *sec* > *tert* which is consistent with a β-elimination. The yields of olefinic products were markedly dependent on the solvent and size of the alkali metal cation of the *tert*-butoxide base. The rate of olefin production followed the order Cs > Rb > K > Na ≫ LiO*t*Bu. Some novel double elimination reactions to produce butadiene were observed with tetramethylene sulfoxide and sulfide.

Introduction

The mechanisms for the formation of olefins by 1,2-elimination of HX from RCH_2X (β-elimination) have been the subject of a large number of investigations.[2,3] Three principal mechanisms for this reaction are recognized. The E1 mechanism involves stepwise loss of HX by a carbonium ion intermediate. The E2 mechanism involves simultaneous loss of HX from RCH_2X in the presence of base. Finally, the carbanion mechanism involves initial abstraction of a proton by base to give an intermediate β-carbanion. Subsequent loss of $X^{\ominus}$ from the α-carbon atom yields the olefinic product. The last mechanism has only recently been established with any certainty.[4] The leaving group, X, in these reactions is usually a halogen, sulfonoxy ($RSO_2O^{\ominus}$), sulfonio ($R_2S^{\ominus}$), or ammonio ($R_3N^{\oplus}$) group. Some studies involving elimination of the sulfinoxy group ($RSO_2^{\ominus}$) have also been reported.[5,6] Until recently, little work has been reported on base-catalyzed elimination reactions involving sulfenoxy ($RSO^{\ominus}$), mercapto ($RS^{\ominus}$), and sulfhydro ($SH^{\ominus}$) groups.[7,8] In addition, it should be noted that no systematic study on the base-catalyzed elimination reactions of sulfur compounds has been carried out in the past. For these reasons, the base-catalyzed elimination reactions of sulfones, sulfoxides, disulfides, sulfides, mercaptans, and some compounds containing nitrogen and oxygen functional groups have been investigated in the dipolar solvent dimethyl sulfoxide. The unusual solvating properties of this solvent for carbanion reactions have recently been reviewed.[9] In the present study, the scope of our base-catalyzed elimination studies in DMSO will be described. No attempts to distinguish between a bimolecular or stepwise carbanion elimination mechanism will be made in the present paper.

Results

The base-catalyzed elimination reactions of a large number of sulfur compounds and some compounds containing both nitrogen and oxygen functional groups have been studied in the base–solvent system potassium *tert*-butoxide–dimethyl sulfoxide at 55 ± 0.1°. The reaction mixtures were sampled at the desired time and the olefinic products were determined by gas chromatography according to the method outlined in

(1) This work was presented before the Petroleum Division of the American Chemical Society, 145th National Meeting, New York, N. Y., September, 1963.

(2) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII; (b) C. K. Ingold, *Proc. Chem. Soc.*, 265 (1962).

(3) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

(4) J. Hine, R. Wiesboeck, and O. B. Ramsay, *J. Am. Chem. Soc.*, **83**, 1222 (1961).

(5) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 705 (1930), and references therein.

(6) E. S. Gould, "Mechanism and Structure in Inorganic Chemistry," Henry Holt and Co., New York, N. Y., 1959.

(7) J. E. Hofmann, T. J. Wallace, P. A. Argabright, and A. Schriesheim, *Chem. Ind.* (London), 1243 (1963).

(8) It has previously been reported that benzyl sulfide and sulfoxide undergo carbanion rearrangement–elimination reactions to KO*t*Bu–DMF: T. J. Wallace H. Pobiner, J. E. Hofmann, and A. Schriesheim, *Proc. Chem Soc.*, 437 (1963).

(9) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

the Experimental section. The results of our elimination studies on a series of isopropyl derivatives appear in Table I. The compounds are arranged in their descending order of reactivity.[10] Isopropyl bromide, isopropyl sulfone, and isopropyl sulfoxide were the most reactive compounds in this series since the minimum yield of propylene obtained in 17–24 hr. was 90%. Isopropyl nitrate, isopropyl thiocyanide, and isopropyl sulfide displayed intermediate activity giving a 16 to 53% yield of propylene in an 18- to 45-hr. reaction period. Isopropyl nitrite, isopropyl mercaptan, and isopropyl cyanide were only slightly reactive and yielded propylene in 2–7% yield in 96 to 117 hr. of reaction. Isopropyl ketone, isopropyl ether, and isopropyl alcohol did not undergo elimination after 168 to 192 hr. of reaction.

TABLE I

ELIMINATION REACTIONS OF ISOPROPYL DERIVATIVES AT 55 ± 0.1° IN 0.62 *M* KO*t*Bu–DMSO

Reactant, isopropyl (mmoles)	Propylene, mmole, mole % yield	Time, hr.
Bromide (1.96)	1.74, 88.7	1
	1.77, 90.3	20
Sulfone (1.97)	0.95, 48.0	1
	2.51, 127	24
Sulfoxide (2.24)	2.13, 90.0	17
Nitrate (2.02)	0.44, 21.8	1
	1.07, 53.0	18
Thiocyanide (1.93)	0.09, 4.40	18.5
	.26, 13.3	96
	.76, 39.3	117
Sulfide[a] (1.97)	.08, 4.0	20
	.31, 16.0	144.5
Nitrite (1.43)	.09, 6	1
	.10, 7	96
Mercaptan (1.90)	.02, 1.2	1
	.04, 2.1	24
	.05, 2.8	100
Cyanide (1.89)	.02, 1.2	1
	.04, 2.0	18
	.04, 2.0	117
Ketone (2.00)	No reacn.	168
Ether (2.00)	No reacn.	168
Alcohol (2.00)	No reacn.	192

[a] The corresponding mercaptan was identified by g.c.

The base-catalyzed elimination reactions of a large number of different types of sulfur compounds was investigated in KO*t*Bu–DMSO and these results are summarized in Table II. The general order of reactivity based on the yields of olefin obtained was sulfone > sulfoxide > disulfide > sulfide > mercaptan. This sequence follows the expected ease of carbanion formation for these compounds. In addition, if the statistical factors for the number of β-carbon–hydrogen bonds are taken into consideration, the results are also consistent with a β-elimination for all compounds studied, *i.e.*, elimination proceeds by formation of the most stable carbanion. In the reactions where isomeric olefins were observed, the isomer distribution is that which would be expected on the basis of thermodynamic equilibrium. Tetramethylene sulfone, in contrast to tetramethylene sulfide and sulfoxide, did not yield any butadiene. However, gas chromatographic analysis indicated that the sulfone was completely converted to an unidentified product. *tert*-Butyl cyanide was twice as reactive as the isopropyl derivative giving 5% of isobutylene in 112 hr. The sodium salts of butanesulfonic acid and butyric acid and the isomeric butylamines were found to be unreactive in KO*t*Bu–DMSO at 55°.

A brief study on the effect of solvent was also carried out. As shown in Table III, isopropyl sulfide, isopropyl sulfoxide, and isopropyl sulfone showed little tendency to undergo elimination in potassium *tert*-butoxide–*tert*-butyl alcohol media at 55° over extensive reaction periods. The effect of alkoxide base on the ease of elimination was also studied in DMSO and these results are summarized in Table IV. Isopropyl sulfone and isopropyl sulfoxide, which were highly reactive in KO*t*Bu–DMSO, also yielded propylene in NaO*t*Bu–DMSO and LiO*t*Bu–DMSO but the yield of olefin decreased in the order K > Na > LiO*t*Bu. Isopropyl sulfide and isopropyl mercaptan, which were less reactive than the sulfoxide and sulfone in KO*t*Bu–DMSO, were found to be more reactive in the presence of the stronger bases rubidium and cesium *tert*-butoxide. Thus, the ease of carbanion formation in DMSO with the alkali metal *tert*-butoxides follows the over-all order of Cs > Rb > K > Na > Li for the compounds studied.

Discussion

Based on the results of our elimination studies on the various isopropyl derivatives it is evident that the yield of olefin depends on several factors. The ease of elimination follows the general order $Br^{\ominus} = RSO_2^{\ominus} = RSO^{\ominus} > NO_3^{\ominus} > SCN^{\ominus} > RS^{\ominus} > NO_2^{\ominus} > S^{\ominus} > CN^{\ominus}$. In the case of the bromide, sulfone, sulfoxide, and perhaps even the nitrate, the high yield of olefin suggests that the rate-determining step is proton abstraction followed by rapid or simultaneous loss of the leaving group in question. As one proceeds to more electronegative groups it appears that the rate-determining step changes to one in which elimination of the functional group is rate limiting. In order to resolve this problem further, rate studies in the presence of labeled DMSO would be required.[11] It should also be noted that other factors may be responsible for the results obtained. In the case of the mercaptan and alcohol, proton abstraction occurs predominantly at the acidic –SH and –OH groups and this tends to inhibit elimination. Isopropyl ketone and isopropyl cyanide form resonance-stabilized α-carbanions that are capable of undergoing enolate and Thorpe condensations, respectively. The latter is reasonable since olefin production from *tert*-butyl cyanide was greater than that for the isopropyl derivative (see Table II). Obviously, stronger bases are required to activate the ether and amine.

The brief study on the effect of solvent (Table III) is important since it emphasizes the unique ability of polar solvents for promoting carbanion elimination reactions. In the alcohol system the base and solvent exist as agglomerates which decrease the reactivity of the base. In DMSO, base–solvent agglomeration is decreased and specific cation solvation is enhanced. This theory has been advanced by several groups of workers and is now well accepted.[9,12] Hence, further discussion on the difference in rates in the two solvents is not warranted. The theory of specific cation solvation by the polar solvent is substantiated to some extent by our results obtained with the various alkali metal butoxides (Tables I and IV). The data suggest that as the size of the cation increases, specific cation solvation increases. The activity of the base would be expected to increase proportionately. This can be seen more clearly in Fig. 1 and 2 where the mole % yield of propylene from isopropyl sulfoxide and isopropyl

(10) All sulfones, sulfoxides, sulfides, and disulfides studied were symmetrical, *i.e.*, both alkyl groups were identical.

(11) Detailed kinetics studies on the mechanism of these reaction have been carried out using tritiated DMSO and will be submitted for publication in *J. Am. Chem. Soc.* in the near future.

(12) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961).

TABLE II

ELIMINATION STUDIES ON VARIOUS SULFUR COMPOUNDS AND SOME MISCELLANEOUS NITROGEN AND OXYGEN COMPOUNDS IN 0.62 *M* KO*t*Bu–DMSO AT 55 ± 0.1°

Reactant (mmoles)	Olefinic product,[a] mmoles	Mole % yield[b] of olefin	Time, hr.
n-Butyl sulfone	1-Butene, *cis*-2-butene, *trans*-2-butene		
(2.02)	0.048 0.150 0.360	28	17
Tetramethylene sulfone[d]	No olefin, no sulfone remaining	...	17, 117
(2.08)			
Butadiene sulfone[d]	Butadiene		
(2.01)	0.160	8	17
	.382	19	47
	.666	33	117
n-Butyl sulfoxide	1-Butene, *cis*-2-butene, *trans*-2-butene		
(1.97)	0.034 0.096 0.205	17	17
Tetramethylene sulfoxide	Butadiene		
(2.11)	0.85	45	17
	1.67	80	117
tert-Butyl sulfoxide	Isobutylene		
(1.95)	1.31	67	1
	1.88	96	19.5
	2.58	132	168
Isobutyl sulfide	Isobutylene trace	~0.1	168
(2.00)			
n-Butyl sulfide[c]	1-Butene, *cis*-2-butene, *trans*-2-butene		
(2.00)	0.003 0.025 0.040	3.4	117
Tetramethylene sulfide	Butadiene		
(3.13)	0.111	3.5	264
tert-Butyl sulfide[c]	Isobutylene		
(1.92)	0.22	11.4	96
n-Butyl disulfide[c]	1-Butene, *cis*-2-butene, *trans*-2-butene		
(1.88)	0.051 0.157 0.381	31.4	168
tert-Butyl disulfide	Isobutylene		
(1.63)	0.35	21.5	1
	1.39	85	96
Isobutyl mercaptan	No reaction	...	96
(2.00)			
sec-Butyl mercaptan	No reaction	...	168
(2.00)			
n-Propyl mercaptan	Propylene		
(1.98)	0.023	1.1	144
n-Butyl mercaptan	1-Butene, *cis*-2-butene, *trans*-2-butene		
(2.05)	0.006 0.018 0.043	3.4	96
tert-Butyl cyanide	Isobutylene		
(2.90)	0.075	2.6	16
	.136	5.0	112
Sodium *n*-butyl sulfonate	No reaction	...	96
(2.00)			
Sodium *n*-butyrate	No reaction	...	96
(2.00)			
n-, iso-, *sec*-, and *tert*-Butylamines	No reaction	...	168

[a] In cases where isomers are possible, the isomer distribution reported is that which would be expected on the basis of thermodynamic equilibrium. [b] The yields are based on the total yield of olefinic product. [c] The corresponding mercaptan was identified by g.c. [d] Identical results were obtained in duplicate experiments.

TABLE III

ELIMINATION REACTIONS IN 0.62 *M* KO*t*Bu–*tert*-C_4H_9OH AT 55 ± 0.1°

Reactant (mmoles)	Propylene, mmole, mole % yield	Time, hr.
Isopropyl sulfide (2.05)	0.039, 1.9	216
Isopropyl sulfoxide	.060, 3.0	164
Isopropyl sulfone	.051, 2.6	216

sulfide is plotted as a function of time. In Fig. 1, the yield of propylene from isopropyl sulfoxide indicates the order of base activity is K >> Na >> Li. The yield of propylene from the less reactive species, isopropyl sulfide, indicates the order of base activity to be Cs > Rb > K. This activity sequence indicates that as the size of the cation increases the ease of solvation also increases, *i.e.*, Cs > Rb > K >> Na > Li. If this were not true, the rate of olefin production would be the same for all the butoxides. Based on the data, one might also conclude that the degree of base dissociation follows the same order. Although this

TABLE IV

EFFECT OF ALKOXIDE BASE ON THE EASE OF ELIMINATION OF VARIOUS SULFUR COMPOUNDS IN 0.62 *M* BASE–DMSO AT 55 ± 0.1°

Reactant, isopropyl (mmoles)	Alkoxide base	Propylene, mmoles, mole % yield	Time, hr.
Sulfone (1.99)	LiO*t*Bu	0.15, 7.5	143
Sulfone (2.00)	NaO*t*Bu	1.03, 51.5	143
Sulfoxide (2.00)	LiO*t*Bu	0.06, 2.9	143
Sulfoxide (2.00)	NaO*t*Bu	0.58, 28.9	168
Sulfide (2.00)	RbO*t*Bu	1.14, 57.0	191
Sulfide (1.98)	CsO*t*Bu	1.21, 61.1	96
Mercaptan (2.00)	RbO*t*Bu	0.08, 4.0	191
Mercaptan (2.00)	CsO*t*Bu	0.11, 5.7	96

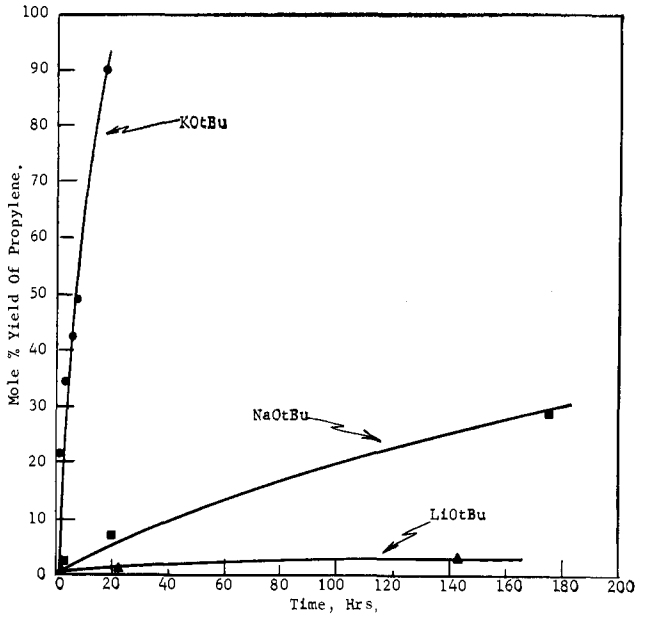
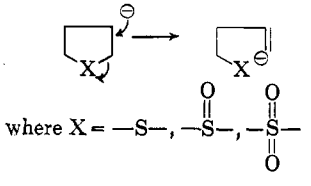


Fig. 1.—Elimination studies on isopropyl sulfoxide with Li, Na, and K *tert*-butoxides in DMSO.

could be true, such a conclusion cannot be definitely made without conductivity measurements. Finally, it should be noted that these results are consistent with those previously obtained on the oxidation of mercaptide ions in the presence of these bases.[13] Previous studies on cleavage and racemization reactions in DMSO indicated the order of *tert*-butoxide activity was K > Na > Li.[14]

The elimination studies on the various sulfones, sulfoxides, sulfides, disulfides, and mercaptans (Table III) have resulted in some unique carbanion reactions. Further, the results allow certain mechanistic conclusions to be made. In all cases studied, the yield of olefinic product follows the expected ease of carbanion formation from the reactant, *i.e.*, primary > secondary >> tertiary. Also, if one takes into account the statistical factor involved for the number of β-hydrogens in each isomer, there is a loose correlation between the yield of olefin and the number of β-hydrogens. This also suggests a β-elimination mechanism is operative.

In the acyclic compounds investigated, the elimination reaction appears to be straightforward. Since an equilibrium mixture of olefinic product was observed when isomers were possible, it appears that the initially formed terminal olefin undergoes a base catalyzed isomerization to the more thermodynamically stable isomer.[15] In the case of tetramethylene sulfide, sulfoxide, and sulfone and butadiene sulfone the reactions are more complex. The sulfide, sulfoxide, and saturated sulfone apparently first undergo β-proton abstraction. Subsequent decyclization of the resulting carbanion occurs to give an olefinic mercaptide, sulfenate, or



(1)

sulfinate anion. In the presence of excess base, the mercaptide and sulfenate ions react further to form a

(13) T. J. Wallace and A. Schriesheim, *J. Org. Chem.*, **27**, 1514 (1962).
(14) D. J. Cram, *et al.*, *J. Am. Chem. Soc.*, **81**, 5774 (1959).
(15) A. Schriesheim and C. A. Rowe, Jr., *ibid.*, **84**, 3160 (1962), and references therein.

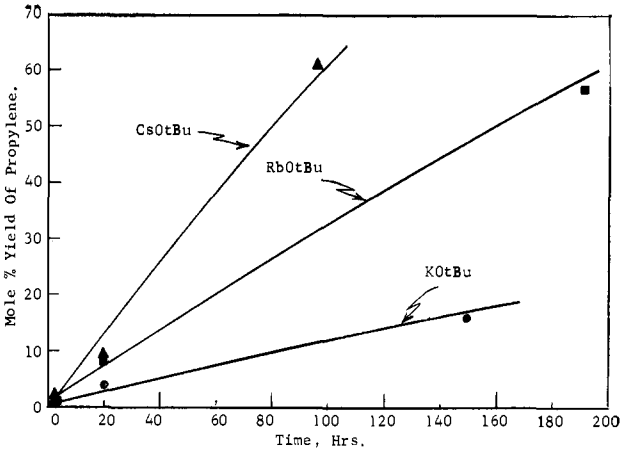
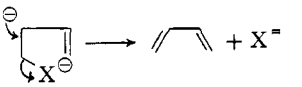


Fig. 2.—Elimination studies on isopropyl sulfide with K, Rb, and Cs *tert*-butoxides in DMSO.

β-allylic carbanion which then eliminates the sulfur moiety to give butadiene. No evidence for the last



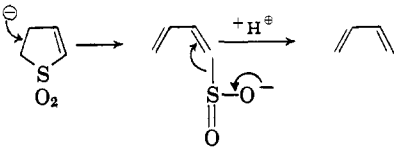
(2)

reaction was found with the sulfone. Thus, the reaction stops at the monoelimination stage or some side reaction occurs. The latter seems more reasonable. In view of the results obtained by Weygand and Daniel,[16] the formation of butadiene from the cyclic sulfide and sulfoxide is unique. These workers have reported that 3-methyltetramethylene sulfonium iodide fragments ethylene and vinyl methyl sulfide, but this requires a base such as phenyllithium and proton abstraction occurs α to the sulfonium group.

With butadiene sulfone, the complexity of the reaction appears to be even greater. Apparently, there is an initial isomerization to the conjugated isomer *via* a carbanoid path. The resulting anion can then β-eliminate to form an unstable diene intermediate

(3)

which eliminates SO_2 and in the presence of a proton source (DMSO) forms butadiene. The above reaction



(4)

sequence is somewhat analogous to that proposed by Krug and co-workers[17] to explain the formation of acyclic alkyl sulfonylidenes from the reaction of Grignard reagents with 2- and 3-methylbutadiene sulfone. However, no olefinic products were observed in these studies.

The large yield of isobutylene from *tert*-butyl disulfide is of interest since *tert*-butyl disulfide or unsymmetrical disulfides containing a *tert*-butyl group are highly resistant to nucleophilic attack[18,19] and reduction.[20] Thus, it appears that decomposition occurs predominantly by a β-elimination. The greater reactivity of the *tert*-disulfide in comparison to the normal

(16) F. Weygand and H. Daniel, *Ber.*, **94**, 3145 (1961).
(17) R. G. Krug, J. A. Rigney, and G. R. Tichelaar, *J. Org. Chem.*, **27**, 1305 (1962).
(18) J. P. Danehy and L. A. Kreuz, *J. Am. Chem. Soc.*, **83**, 1109 (1961).
(19) R. G. Hiskey and F. I. Carroll, *ibid.*, **83**, 4644 (1961).
(20) M. E. Hall, *Anal. Chem.*, **25**, 556 (1953).

isomer is further evidence for this mechanism. The low yield of olefinic product from the mercaptans listed in Table II was previously explained. The lack of olefinic products from the *n*-butyl sulfonate and *n*-butyrate ions is probably due to formation of stable α-carbanions.

Experimental

Reagents.—Lithium, sodium, potassium, rubidium, and cesium *tert*-butoxides were obtained from the Mine Safety Appliance Co. (Callery, Pa.) as the sublimed white powders in wax-sealed containers. All samples were at least 98.5% pure. Dimethyl sulfoxide and *tert*-butyl alcohol were dried and distilled over Linde 13X Molecular Sieves. Gas chromatographic analysis of both solvents indicated the presence of only one compound. Isobutylene, 1-butene, *cis*- and *trans*-2-butene, propylene, and butadiene, which were used for g.c. calibration, were all API samples.

Most reactants were obtained from either Columbia Organic Chemicals or Matheson Coleman and Bell as reagent grade materials and analyzed for purity by g.c. before use. Materials less than 98% pure were distilled under a nitrogen atmosphere through an 18-in. silvered column equipped with a tantalum-wire spiral. In the case of the sulfoxides and sulfones, distillation was carried out in the presence of Linde 13X Molecular Sieves to ensure complete removal of water. All reagents were stored in a nitrogen drybox before use.

Preparation of Reaction Mixtures.—All base–solvent systems were prepared in a nitrogen drybox equipped with a moisture conductivity cell attachment. Each solution was prepared to give the desired molarity (0.62 *M*) and stored in sealed containers in the drybox. At the desired time, 7 ml. of the standard solution was withdrawn by a pipet and transferred to a vial containing about 2 mmoles of each reactant. The vial was sealed (under nitrogen) with a self-sealing neoprene diaphragm and immediately transferred to a constant temperature bath (55 ± 0.1°). *n*-Pentane (0.3 ml.) was immediately injected into each reaction mixture by means of a hypodermic syringe thus providing an internal standard for quantitative determination of olefinic products. The total operation required about 2–3 min.

Analysis of Reaction Mixtures.—At the desired time, 0.5 ml. of the reaction mixture was withdrawn from the vial by a precooled hypodermic syringe and injected into a neoprene-sealed vial containing a mixture of water and inert hydrocarbon. The sample was then cooled in the presence of Dry Ice. This removed the base and solvent from the hydrocarbon layer. The hydrocarbon layer was then sampled with a syringe and analyzed for the olefin in question on a gas chromatographic unit. This unit was a Perkin–Elmer Model 154 equipped with a 21 ft. DC-200 column (30 wt. % silicone oil, 0.25 in. in diameter). The unit was operated under 12 p.s.i.g. of helium in the temperature range of 40 to 75°. All final yields of olefinic products were based on at least two g.c. determinations. Absolute olefin yields were determined from the g.c. area of the internal standard (*n*-pentane) and the area of the olefin in question; percentage yields were calculated on the basis of one mole of olefin/mole reactant in all cases. In those reactions which were unsuccessful or gave a low yield of olefinic product, analysis for the starting material was desirable. This was carried out on an F & M Flame Ionization Unit (Model 609) equipped with a 2-ft. silicone rubber column (30 wt. %, 0.25 in. in diameter). This unit was temperature programmed at 9°/min. from 75–250°. The latter conditions were also employed in the identification of mercaptans referred to in Tables I and II.

Miscellaneous Experimental Methods.—In two cases starting materials were synthesized. *n*-Butyl disulfide was prepared from the reaction of the sodium salt of *n*-butyl mercaptan with iodine according to the method described by Vogel.[21] When isolated, the physical properties of the disulfide were identical to those recorded in Reid.[22] *tert*-Butyl sulfoxide was prepared by the oxidation of *tert*-butyl sulfide with hydrogen peroxide in acetic acid (m.p. 64°, reported[23] m.p. 63.5–65°).

Acknowledgment.—The authors are indebted to the Esso Research and Engineering Co., especially the Process Research Division, for the privilege of publishing this work.

(21) E. I. Vogel, "Practical Organic Chemistry," Longmans Green and Co., New York, N. Y., 1959, pp. 496–498.

(22) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p. 396.

(23) L. Bateman, *et al.*, *J. Chem. Soc.*, 5339 (1961).

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The Isomerization of Aziridine Derivatives. VII

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Four new isomerizations of aziridine derivatives are described. They include the rearrangement of 1-phenylthiocarbonylaziridine into 2-phenylthioethyl isocyanate or methyl N-2-phenylthioethylcarbamate and the isomerization of 1-(*o*-chloromethylbenzoyl)-aziridine into either N-2-chloroethylphthalimidine or 1-(2-chloroethylimino)-phthalan. The reaction of equimolar quantities of phthaloyl chloride with aziridine to form N-2-chloroethylphthalimide is also reported.

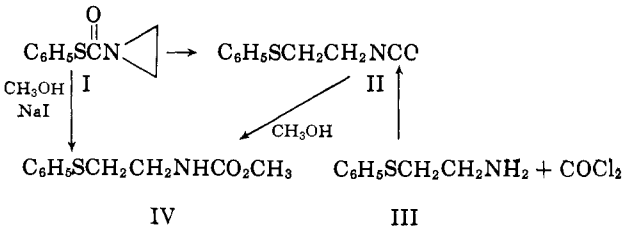
Introduction

Derivatives of aziridines have been isomerized into oxazolines, imidazolines, imidazolidinones, thiazolines, pyrazolines, triazolines, picramides, N-β,γ-unsaturated amides, and anils.[1] The present communication describes a number of new isomerizations of appropriately substituted aziridines into (1) an isocyanate, (2) an N-2-chloroethylphthalimide, (3) a phthalimidine, and (4) a phthalan.

Results

1-Phenylthiocarbonylaziridine (I, N,N-ethylene-S-phenylthiocarbamate) is rearranged in refluxing xylene into the isomeric 2-phenylthioethyl isocyanate (II). The structure of II was established by analysis and by comparison of infrared spectra with an authentic sample prepared by reaction of 2-phenylthioethylamine (III) with phosgene.

The action of sodium iodide in methanol on 1-phenylthiocarbonylaziridine at room temperature gave methyl



N-2-phenylthioethylcarbamate (IV). The structure of IV was confirmed by an independent synthesis involving the reaction of 2-phenylthioethyl isocyanate with methanol. A control run with I in methanol without sodium iodide gave a liquid residue whose infrared spectrum indicated mostly starting material, an isocyanate peak, and some of the peaks characteristic of the carbamate. After compound I was refluxed in methanol for 22 hr. the solvent was evaporated. A white solid whose infrared spectrum was identical with that of IV was obtained. However, this product had an odor characteristic of thiophenol.

(1) For a review of isomerizations of aziridines see H. W. Heine, *Angew. Chem.*, **74**, 772 (1962); *Angew. Chem. Internat. Edit. Engl.*, **1**, 528 (1962).