Ir spectrum (KBr disk): ν max 3292 (s) (NH stretching vibration due to $RNHCO_2R'$), 2975 (m) (CH stretching vibration), 1698 (s) (C=O stretch in $RNHCO_2R'$), 1549, 1524 (s) (NH bend, amide II band), 1478 (m) (CH asymmetrical deformation), 1370 (m) (CH symmetrical deformation), 1332 (m), 1295 (s) (unassigned), 1241, 1030 (s) (CO stretching vibration), 881 (w), 783 (w) (unassigned), 674 cm^{-1} (m) (NH o.o.p. deformation). The spectrum was identical with that reported[16] for "acetylenedicarbamic acid, diethyl ester."

Nmr spectrum (DMSO-d_6 at 90°): δ 6.64 (d*, 2.8, J = 7 Hz, NH), 5.20 (t*, 1.9, J = 7.5 Hz, $CH(NHCO_2Et)_2$), 3.99 (q, 7.8, J = 7.5 Hz, $NHCO_2CH_2CH_2$), 1.15 (t, 12.0, J = 7.5 Hz, $NHCO_2CH_2CH_3$). (Asterisk indicates broad signals with further splitting present.)

Electron impact mass spectrum (direct insertion at 200°): molecular ion absent; m/e 290 (4), M − $NHCO_2Et$, $C_{11}H_{20}N_3O_6$ (4.6 ppm); 244 (5), m/e 290 − EtOH, $C_9H_{14}N_3O_5$ (3.4 ppm); 202 (0.4), m/e 290 − $NHCO_2Et$, $C_8H_{14}N_2O_4$ (1.9 ppm); 201 (0.9), m/e 244 − NHCO, $C_8H_{13}N_2O_4$ (1.9 ppm); 198 (0.3), m/e 244 − EtOH, $C_7H_8N_3O_4$ (0.4 ppm); 189 (100), M − $CH(NHCO_2Et)_2$, $C_7H_{13}N_2O_4$ (3.6 ppm); 172 (1), m/e 244 − (CO_2 + C_2H_4), $C_6H_{10}N_3O_3$ (2.0 ppm); 161 (1.5), m/e 189 − C_2H_4, $C_5H_9N_2O_4$ (10.9 ppm); 143 (3), m/e 189 − EtOH, $C_5H_7N_2O_3$ (5.3 ppm); 117 (14), m/e 189 − (CO_2 + C_2H_4), $C_4H_9N_2O_2$ (11.6 ppm); 102 (4), m/e 117 − NH, $C_4H_8NO_2$ (5.0 ppm); 90 (1), m/e 117 − HCN, $C_3H_8NO_2$ (11.3 ppm); 89 (9), m/e 117 − C_2H_4, $C_2H_5N_2O_2$ (7.0 ppm); 62 (3), m/e 90 − C_2H_4, CH_4NO_2 (101 ppm). Metastable peaks: 378 → 189 (94.5); 290 → 244 (205.3); 290 → 172 (102.1); 244 → 198 (160.8); 244 → 172 (121.2); 189 → 161 (137.1); 189 → 143 (108.1); 189 → 117 (72.5); 117 → 89 (67.75).

Anal. Calcd for $C_{14}H_{26}N_4O_8$: C, 44.44; H, 6.93; N, 14.80. Found: C, 44.68; H, 6.88; N, 14.94.

1,1-Di(carbethoxyamino)ethane.[9]—The relevant portion of the electron impact mass spectrum is given below (direct insertion at 100°): molecular ion absent; m/e 203 (0.5), M − H, $C_8H_{15}N_2O_4$ (4.9 ppm); 189 (100), M − CH_3, $C_7H_{13}N_2O_4$ (3.8 ppm); 143 (3), m/e 189 − EtOH, $C_5H_7N_2O_3$ (6.5 ppm); 117 (15), m/e 189 − (CO_2 + C_2H_4), $C_4H_9N_2O_2$ (26.5 ppm); 90 (4), m/e 117 − HCN, $C_3H_8NO_2$ (3.0 ppm); 89 (10), m/e 117 − C_2H_4, $C_2H_5N_2O_2$ (1.3 ppm); 62 (13), m/e 90 − C_2H_4, CH_4NO_2 (35.8 ppm).

Registry No.—VI, 17350-57-1; glyoxal, 107-22-2; ethyl carbamate, 51-79-6; 1,1-di(carbethoxyamino)-ethane, 539-71-9.

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(16) "Sadtler Standard Spectra," No. 13888, Sadtler Research Laboratories Inc., Philadelphia, Pa., 1962.

The Chemistry of Sulfonyl Isocyanates. VIII. Kinetics of the Reaction with Hindered Phenols

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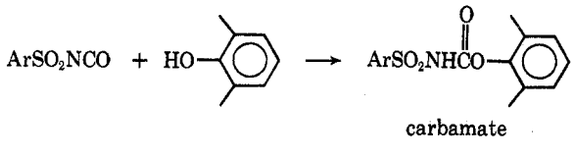
4-Chlorobenzenesulfonyl isocyanate (I) and 4-toluenesulfonyl isocyanate (II) reacted with 2,6-disubstituted and 2,4,6-trisubstituted phenols. The products were highly crystalline carbamates. Kinetic studies showed the reactions to be second order, first order in isocyanate and first order in phenol. The relative rates of reaction of the phenols were 2,6-diisopropyl- > 2,6-dimethyl- > 2,6-dibromo- > 2,4,6-tri-*tert*-butyl- > 2,6-di-*tert*-butyl- > 2,4,6-tribromo-. Isocyanate I was found to be somewhat more reactive than II.

Billeter first showed that benzenesulfonyl isocyanate reacts with phenol and reported the product to be carbamate.[2] It was shown in this laboratory that benzenesulfonyl isocyanate also reacts with 2,6-disubstituted, as well as other substituted, phenols to give crystalline solid derivatives.[3] The products were shown to be carbamates rather than para-substituted amides of phenols.



carbamate

More recently the kinetics of the reactions of hindered triarylcarbinols with sulfonyl isocyanates have been explored.[4-7] These reactions were found to be first order in alcohol and first order in isocyanate. Although the reaction products were in most cases not carbamates such intermediates could not be ruled out.[7]

This paper shows the kinetic results obtained from the reactions of 4-chlorobenzenesulfonyl isocyanate (I) and 4-toluenesulfonyl isocyanate (II) with 2,6-disubstituted phenols.

Experimental Section

Reagents.—4-Chlorobenzenesulfonyl isocyanate (I) and 4-toluenesulfonyl isocyanate (II) were obtained from the Upjohn Co., Carwin Organic Chemicals, and used without further purification. The phenols were commercial products which were redistilled or recrystallized before use. Toluene solvent was reagent grade and dried over sodium metal or molecular sieves. The di-*n*-butylamine was Eastman White Label grade reagent.

Kinetics.—The method used for measuring the concentration of isocyanate in the reaction mixture at various times was that already reported.[7] Second-order kinetics were followed with each of the phenols used from 4:1 to 1:4 isocyanate–phenol ratios. When 1:1 ratios of isocyanate–phenol were employed, plots of $1/(C - C_\infty)$ *vs.* time gave straight lines over at least 2 half-lives. For reactions in which initial isocyanate–phenol ratios were not unity, plots of log $[b(a - x)/a(b - x)]$ *vs.* time were linear.

Isolation of Products.—The products were removed from the reaction mixture (toluene solvent) by cooling to about 25° and adding 1 vol of petroleum ether (bp 60–70°). In most cases this procedure effected quantitative precipitation of the carbamate. When quantitative separation was not realized, the toluene–

(1) Taken in part from the M.A. thesis of S. P. G., DePauw University, 1969.
(2) O. C. Billeter, *Ber.*, **37**, 690 (1904).
(3) J. W. McFarland and J. B. Howard, *J. Org. Chem.*, **30**, 957 (1965).
(4) J. W. McFarland, D. E. Lenz, and D. J. Grosse, *ibid.*, **31**, 3798 (1966).
(5) J. W. McFarland, D. E. Lenz, and D. J. Grosse, *ibid.*, **33**, 3514 (1968).
(6) J. W. McFarland, D. Green, and W. Hubble, *ibid.*, **35** 702 (1970).
(7) J. W. McFarland and D. J. Thoennes, *ibid.*, **35**, 704 (1970).

petroleum ether solvent mixture was removed under vacuum and the residue recrystallized from petroleum ether.

As a typical example, I and 2,6-dimethylphenol gave 2,6-dimethylphenyl *N*-(4-chlorobenzenesulfonyl)carbamate (III), yield 95%, mp 156–157°.

Anal. Calcd for $C_{15}H_{14}NO_4SCl$: C, 53.20; H, 4.15; N, 4.12; S, 9.44; Cl, 10.43. Found: C, 53.01; H, 4.11; N, 4.34; S, 9.29; Cl, 10.54.

Results

4-Chlorobenzenesulfonyl isocyanate (I) reacted with all of the substituted phenols studied, including alkylated and brominated phenols at 85 and 100° (Table I).

TABLE I

REACTION OF 4-CHLOROBENZENESULFONYL ISOCYANATE (I) WITH PHENOLS

Phenol	Registry no.	Temp, °C	k, l. mol^{-1} min^{-1}
2,6-Diisopropyl	2078-54-8	85	2.25 ± 0.10
		100	3.70 ± 0.10
2,6-Dimethyl	576-26-1	85	1.03 ± 0.03
		100	2.32 ± 0.09
2,6-Dibromo	608-33-3	85	0.27 ± 0.03
		100	0.41 ± 0.03
2,4,6-Tri-*tert*-butyl	732-26-3	85	0.17 ± 0.02
		100	0.35 ± 0.02
2,6-Di-*tert*-butyl	128-39-2	85	0.08 ± 0.01
		100	0.19 ± 0.02
2,4,6-Tribromo	118-79-6	85	0.08 ± 0.01
		100	0.09 ± 0.01

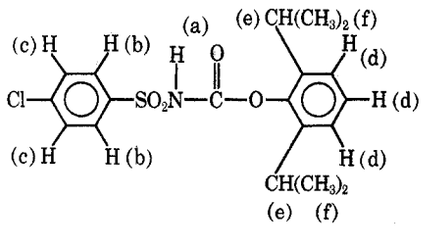
Likewise, 4-toluenesulfonyl isocyanate (II) reacted with the alkylated phenols at 100° (Table II). In all

TABLE II

REACTION OF 4-TOLUENESULFONYL ISOCYANATE (II) WITH PHENOLS AT 100°

Phenol	k, l. mol^{-1} min^{-1}
2,6-Diisopropyl	1.44 ± 0.05
2,6-Dimethyl	1.29 ± 0.04
2,4,6-Tri-*tert*-butyl	0.019 ± 0.001
2,6-Di-*tert*-butyl	0.017 ± 0.001

cases the products were the carbamates and not the phenolic amides. Evidence for the carbamate structure came largely from nmr. The product from I and 2,6-diisopropylphenol was assigned structure IV on the basis of the nmr absorption peaks. Alternative struc-

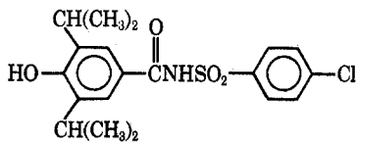


2,6-diisopropylphenyl *N*-(4-chlorobenzenesulfonyl)-carbamate (IV)

(a) singlet at τ 1.40, 1 H
(b) doublet at τ 1.86, 2 H
(c) doublet at τ 2.38, 2 H
(d) singlet (unresolved) at τ 2.80, 3 H
(e) septet at τ 7.26, 2 H
(f) doublet at τ 8.85, 12 H

ture V would give a very different spectrum. Studies with many 2,6-disubstituted phenols indicate that the phenolic hydrogen absorbs in the τ 4–6 range.

All of the reactions of sulfonyl isocyanates with the hindered phenols followed second-order kinetics, first



V

order in isocyanate and first order in phenol. The rate constants, k, were sensitive to the nature of the phenolic substituents. The alkylated phenols showed the following order of reactivity toward each of the sulfonyl isocyanates: 2,6-diisopropyl > 2,6-dimethyl > 2,4,6-tri-*tert*-butyl $\gtrsim$ 2,6-di-*tert*-butyl. The 2,6-dibromophenol was slightly more reactive than 2,6-di-*tert*-butylphenol. On the other hand, 2,4,6-tribromophenol was less reactive than 2,4,6-tri-*tert*-butylphenol (see Discussion).

The yields of carbamates were almost quantitative. The products were highly crystalline and were usually purified by recrystallizing from petroleum ether (Table III).

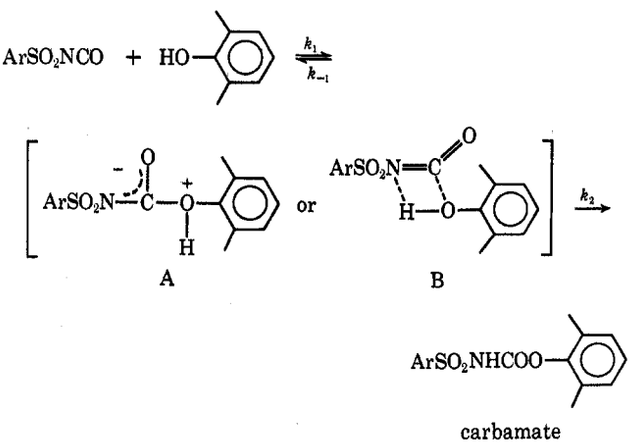
TABLE III

PRODUCTS FROM SULFONYL ISOCYANATES AND PHENOLS

Sulfonyl isocyanate	Phenol	Mp of product, °C	Registry no.
4-Chlorobenzene	2,6-Dimethyl	156–157	
	2,6-Diisopropyl	129–131	
	2,6-Di-*tert*-butyl	149–150.5	31662-23-4
	2,6-Dibromo	127–128	31662-24-5
	2,4,6-Tri-*tert*-butyl	151–152	31593-67-6
	2,4,6-Tribromo	131–132	31662-25-6
4-Toluene	2,6-Dimethyl	160–162	31662-26-7
	2,6-Diisopropyl	162–163	31593-68-7
	2,6-Di-*tert*-butyl	95–107 (crude)	31593-69-8
	2,4,6-Tri-*tert*-butyl	110–115 (crude)	31953-70-1

Discussion

The first step in the reaction of sulfonyl isocyanate with phenol is most likely the formation of some sort of a complex[8] (which may be the transition state). A similar type of complex was postulated in the reaction of sulfonyl isocyanate with triarylcarbinols.[7] Different



from the triarylcarbinols, the phenols give carbamate products. This is understandable in view of the fact

(8) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, **151**, 19 (1949).

that no stable arbonium ion can be obtained from the phenol such as can be from triarylcarbinols.

The relative rates of the reactions of the different phenols are consistent with the above postulated mechanism. Two factors must be considered in connection with the different substituents—the electronic and the steric factors. Any substituent in the ortho position would predictably hinder the approach of isocyanate to form the transition state. Phenol itself reacted very rapidly with the sulfonyl isocyanates, too fast in fact to obtain good kinetic data under the conditions of the reactions.

From the steric effects alone, it would be expected that the 2,6-dimethylphenol would be fastest reacting, followed by 2,6-diisopropyl-, and finally 2,6-di-*tert*-butylphenol.[9] Indeed, the di-*tert*-butylphenol is extremely slow. 2,6-Diisopropylphenol, however, consistently reacted at a faster rate than did 2,6-dimethylphenol under comparable conditions. The polar contributions of the ortho alkyl groups to the basicities of the phenols are, however, in the reverse order: *tert*-butyl > isopropyl > methyl.[10]

The most logical explanation for the results obtained, then, is that the polar effect of the isopropyl group is considerably stronger than that of the methyl group and more than compensates for any steric differences. In the case of the *o-tert*-butyl groups, however, the steric effect predominates.

That electronic effects are important is shown by the fact that 2,4,6-tri-*tert*-butylphenol is slightly more reactive toward each of the isocyanates than is 2,6-di-*tert*-butylphenol. The effect of the *p-tert*-butyl group is also shown by the fact that 2,4,6-tri-*tert*-butylphenol (pK_a = 12.19) is a weaker acid than 2,6-di-*tert*-butylphenol (pK_a = 11.70).[11] Placing a *tert*-butyl group in the para position should not produce additional steric effect. The electron-donating ability of the *tert*-butyl group does, however, help to stabilize the partial positive charge on phenol oxygen in the transition state.

Noteworthy is the slow reaction of either 2,6-dibromophenol or 2,4,6-tribromophenol. Since bromine has approximately the steric effect of a methyl group,[9] the electronic effect is very significant. Bromine is inductively electron withdrawing and should thereby destabilize the transition state. The presence of a bromine atom in the 4 position, where steric effects are negligible, lowers the reactivity even further. Our results are consistent with the finding that 4-bromo-2,6-dimethylphenol is a stronger acid than 2,6-dimethylphenol.[12]

An effort was made to separate the electronic and steric effects of the ortho substituents by using a Brønsted-type plot of literature[11-13] pK_a values of the phenols against the log of their rate constants (Figure 1). 2,6-Dimethylphenol and the 2,6-dibromophenols were plotted together since the steric effects are similar. The straight line through the points representing the 2,6-di-*tert*-butylphenols was parallel to that representing 2,6-dimethyl- and the bromophenols (Brønsted β = 0.546). Making the assumption that all groups with similar steric effects would fall on one straight line, the relative electronic and steric effects of the *o-tert*-butyl groups with respect to the *o*-methyl groups could be determined. The *tert*-butyl groups increased the electronic portion of the rate by 3.9 times but decreased the steric portion by 47.5 times.

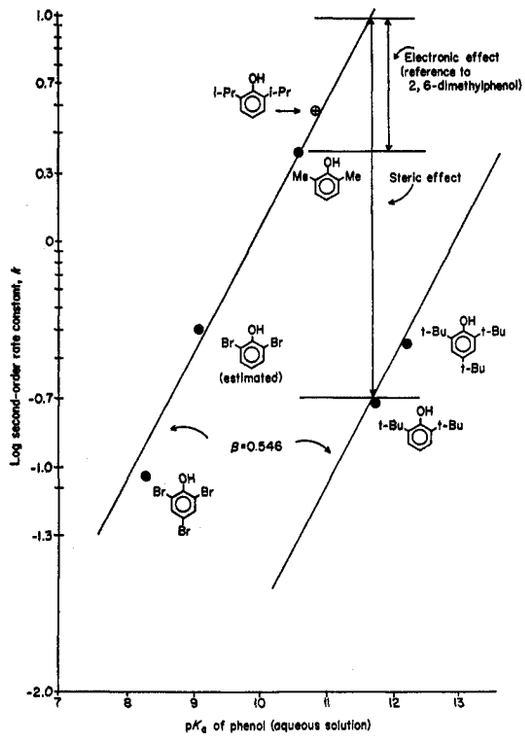


Figure 1.—Reaction of 4-chlorobenzenesulfonyl isocyanate with phenols at 100° in toluene.

Unfortunately, pK_a values for a series of 2,6-diisopropylphenols have not been reported in the literature. A value of approximately 11.0 for the pK_a of 2,6-diisopropylphenol itself was reported, although the value was determined in 20% aqueous ethanol,[14] whereas other pK_a values used herein were from aqueous solutions. The extent to which the value is reliable indicates that 2,6-diisopropylphenol falls roughly on the same line as 2,6-dimethylphenol and that the differences in their rates are mostly due to electronic effects. Models indicate that it is possible for the two methyl groups in the isopropyl group to rotate out of the way of an approaching isocyanate molecule. Further data are obviously desirable before conculsions may be drawn relative to the steric effect of the isopropyl group.

A comparison of the reactions of 4-chlorobenzenesulfonyl isocyanate (I) and 4-toluenesulfonyl isocyanate (II) with phenols shows that I is more reactive than II (Tables I and II). It was found before that II is slightly less reactive than is benzenesulfonyl isocyanate toward triarylcarbinols.[7] Apparently for both reactions there is a partial negative charge on nitrogen or carbon of the isocyanate in the transition state. A methyl group on the ring of the isocyanate destabilizes the negative charge while electron-withdrawing chlorine stabilizes it. These facts plus the substituent effects in the phenols

(9) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 601.

(10) Reference 9, p 591.

(11) L. A. Cohen and W. M. Jones, *J. Amer. Chem. Soc.*, **85**, 3397 (1963).

(12) A. Fischer, G. J. Leary, R. D. Topson, and J. Vaughan, *J. Chem. Soc. B*, 782 (1966).

(13) J. Pless, *Peptides, Proc. Eur. Symp., 5th, Oxford*, 69 (1962); *Chem. Abstr.*, **62**, 627*g* (1962).

(14) P. Demerseman, J. P. Lechartier, R. Reynard, A. Cheutin, R. Royer, and P. Rumpf, *Bull. Soc. Chim. Fr.*, 2559 (1963).

give evidence that transition state A is more probable than B.

Registry No.—I, 5769-15-3; II, 4083-64-1; III, 31593-65-4; IV, 31593-66-5.

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Asymmetric Synthesis of Diastereomeric Hydroxy Sulfides, Sulfoxides, and Sulfones by Condensation and Oxidation Reactions

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Received August 24, 1970

The oxidation of diastereomeric 2-thiophenoxy-1,2-diphenyl-1-ethanols to the corresponding sulfoxide–alcohols is shown to be dependent upon the configuration of the carbon bearing the hydroxyl group. Condensations of the lithium salts of phenyl benzyl sulfide, sulfoxide, and sulfone with benzaldehyde give predominately threo products. Crossover products and other evidence for epimerization were found in the sulfoxide condensation. Reduction of 2-phenylsulfinyl-1,2-diphenylethanone gives just one erythro sulfoxide. Evidence for configuration of sulfur and the pseudocontact shifts of the isomeric sulfoxides are briefly discussed.

Sulfoxide chemistry is characterized by a considerable number of relatively highly stereospecific reactions.[1-5] The present work is an inquiry into the stereospecificity of reactions which form the isomeric 2-phenylsulfinyl-1,2-diphenyl-1-ethanols (**4**–**7**), compared to reactions which form the corresponding sulfides **2** and **3** and the sulfones **8** and **9**. The compounds in question are shown in Scheme I in their preferred conformation at carbon.[6]

Condensation of phenyl benzyl sulfide (**10**) with benzaldehyde (**13**) gave a *ca.* 55% overall yield of the 2-thiophenoxy-1,2-diphenyl-1-ethanols of which 40% was the erythro isomer **3** and 60% was the threo isomer **2**.[7-9] This ratio of isomers was insensitive to reaction time. Isomer **2** could also be prepared by reaction of thiophenoxide with cis-stilbene oxide, which proved its threo configuration. Similarly, **3** was formed by reaction of thiophenoxide with *trans*-stilbene oxide.

Condensation of phenyl benzyl sulfoxide (**11**) with **13** gave a mixture of the four sulfoxide–alcohols in *ca.* 40% overall yield. When the reaction was worked up immediately, the following relative yields were observed: 41% **4**, 19% **5**, 8% **6**, and 32% **7**. Reactions using several other aldehydes were similar, showing low yields of the isomers analogous to **5** and **6**. When the reaction was allowed to stir for *ca.* 10 hr before work-up, the isolated products were observed to be significantly richer in the threo isomer **5**: 34% **4**, 29% **5**, 6% **6**, and 31% **7**. A crossover experiment was attempted in which *p*-chlorobenzaldehyde was added to the final reaction mixture of **11** and **13**. Two crossover products (the *p*-chlorophenyl analogs of **4** and **7**) were isolated, which suggests that the mechanism of the epimerization may be a decondensation–recondensation sequence, similar to that found for the Darzens condensation.[10]

The initial product ratio was somewhat richer in the two sulfoxide–alcohols, **4** and **7**, which exhibit substantial intramolecular hydrogen bonding through a six-membered ring. The transition state for the formation of **4** and **7** also very likely involves a six-membered ring, in which a lithium cation is chelated by two oxygen groups (Figure 1). Similar transition states involving highly coordinating cations have been postulated for the Ivanov reaction[7b] and certain carboxylation reactions.[11,12]

Reaction of phenyl benzyl sulfone (**12**) and **13** was the least successful of the condensations, as frequent failure of the reaction occurred. In most successful runs, a *ca.* 59% overall yield was observed, of which 77% was the threo product, **8**, and 23% was the erythro product, **9**.[13] Thus, each condensation gave more of the threo isomer(s), which probably reflects the stability of this isomer,[7c] and the semiequilibrating nature of the reaction.

Oxidation of the cyclic sulfide, penicillin to its sulfoxide has been reported to give predominately one

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(2) T. Durst, *J. Amer. Chem. Soc.*, **91**, 1034 (1969).

(3) (a) D. J. Abbott, S. Colonna, C. Stirling, *Chem. Commun.*, 471, 472 (1971); (b) J. Coxon, M. Hartshorn, G. Little, and S. Maister, *ibid.*, 271 (1971).

(4) E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 86 (1928).

(5) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).

(6) A previous paper has covered the conformational studies: C. Kingsbury and R. Auerbach, *J. Org. Chem.*, **36**, 1737 (1971).

(7) The stereochemistry of various condensation reactions has been investigated in older work: (a) H. E. Zimmerman and L. Ahramjian, *J. Amer. Chem. Soc.*, **81**, 2086 (1959); (b) H. E. Zimmerman and M. D. Traxler, *ibid.*, **79**, 1920 (1957); (c) H. E. Zimmerman, L. Singer, and B. Thyagaryan, *ibid.*, **81**, 108 (1959); (d) M. Stiles, R. Winkler, Y. Chang, and L. Traynor, *ibid.*, **86**, 3337 (1964); (e) A. T. Nielsen, *J. Org. Chem.*, **30**, 3650 (1965); (f) A. Wettstein, K. Hensler, H. Ueberwasser, and P. Wieland, *Helv. Chim. Acta*, **40**, 323 (1957); (g) P. Rabe, *Justus Liebigs Ann. Chem.*, **313**, 129 (1900), and related papers; (h) O. Widman, *Chem. Ber.*, **51**, 533 (1918); (i) E. P. Kohler and C. Allen, *J. Amer. Chem. Soc.*, **46**, 1522 (1924), and many related papers; (j) R. A. Abramovitch and J. Muchowski, *Can. J. Chem.*, **38**, 554 (1960); (k) I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **13**, 663 (1965); (l) W. S. Fones, *J. Org. Chem.*, **17**, 1534 (1952).

(8) The earliest example of this type of reaction is (a) E. Fromm and E. Erfurt, *Chem. Ber.*, **42**, 3823 (1909); **41**, 3397 (1909).

(9) For other work on condensations involving sulfinyl anions, see (a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1639 (1964); (b) *ibid.*, **87**, 1345 (1965); (c) G. A. Russell and G. J. Mikol, *ibid.*, **88**, 5498 (1966); (d) G. A. Russell, E. T. Sabourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966); G. A. Russell and H.-D. Becker, *J. Amer. Chem. Soc.*, **85**, 3406 (1963); (e) T. J. Wallace, H. Pobiner, J. Hoffman, and A. Schriesheim, *Proc. Chem. Soc.*, 137 (1963); L. Field, *J. Amer. Chem. Soc.*, **74**, 3919 (1952); (f) W. E. Truce and K. R. Buser, *ibid.*, **76**, 3577 (1954).

(10) H. E. Zimmerman and L. Ahramjian, *ibid.*, **82**, 5459 (1960). See also A. J. Speziale and D. Bissing, *ibid.*, **85**, 1888, 3878 (1963); M. Schlosser and K. Christmann, *Angew. Chem., Int. Ed. Engl.*, **4**, 689 (1965); E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226 (1970).

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(12) See also (a) R. Steinberger and F. H. Westheimer, *ibid.*, **73**, 429 (1951); (b) M. Bender, *Advan. Chem. Ser.*, No. 37, 19 (1963); (c) T. C. Bruice and S. Benkovic, "Bio-organic Mechanisms," Vol. I, W. A. Benjamin, New York, N. Y., 1966, pp 110–118.

(13) A crossover experiment was again successful for the condensation of **12** and **13**.