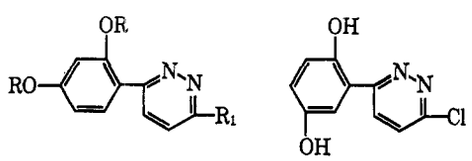
and the only recorded examples of such alkylations are with 2-chloroquinoline and 4,7-dichloroquinoline[2] or with 2-substituted 4,6-dichloro-1,3,5-triazines and 2,4,6-trichloro-1,3,5-triazine.[3]

We wish to report alkylation of resorcinol and hydroquinone with 3,6-dichloropyridazine under the conditions of a Friedel–Crafts reaction. Formation of I (R = H, R_1 = Cl) and II was effected by treating the corresponding phenol with 3,6-dichloropyridazine in the presence of anhydrous $AlCl_3$ in nitrobenzene. The structure of I (R = H, R_1 = Cl) was proved on the basis of elemental analysis and infrared and nmr spectra. The *ortho* ring protons of resorcinol appear at τ 2.09 and 3.44 (relative to TMS) in the nmr spectrum as an AB quartet, the B portion of which is further split by coupling with *meta* H_3. No *para* coupling was observed. The two *ortho* heteroannular protons are located as a quartet at τ 1.58 and 2.09. Both hydroxyl groups could be acetylated to give I (R = CH_3CO, R_1 = Cl) and the chlorine atom could be substituted with hydrogen in a hydrogenolysis reaction with hydrazine in the presence of palladium on carbon.

Attempts to replace the chlorine with a methoxy group failed and also attempts to use 6-chloroimidazo-[1,2-*b*]pyridazine[4] as an alkylating agent proved to be unsuccessful. At lower temperatures a very stable complex with $AlCl_3$ was formed, but at higher temperatures a complete decomposition occured.



I

II

Experimental Section

Melting points were determined on a Kofler apparatus and are corrected. The infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. The nmr measurements were determined in dimethyl sulfoxide solution on a Varian A-60 instrument, using tetramethylsilane (TMS) as an internal standard. The aluminium chloride used was anhydrous reagent grade. The nitrobenzene used was reagent grade material and was washed with water, dried over anhydrous $MgSO_4$, and distilled. The phenols used were reagent grade material.

3-Chloro-6-(2′,4′-dihydroxyphenyl)pyridazine (I, R = H; R_1 = Cl).—To a solution of 22.4 g (0.15 mole) of 3,6-dichloropyridazine in 200 ml of anhydrous nitrobenzene, 25.0 g (0.225 mole) of resorcinol was added. Into the externally cooled and stirred mixture 20.0 g (0.15 mole) of anhydrous $AlCl_3$ was added portionwise at such a rate that the temperature remained below 20°. After the addition of $AlCl_3$ was complete, stirring was continued and the mixture was heated on an oil bath at 100° for 1.5 hr. After this period the evolution of hydrogen chloride was practically completed. The cooled reaction mixture was poured into a mixture of 500 ml of water, 500 g of ice, and 50 ml of concentrated HCl. The supernatant liquid was separated from the suspension in nitrobenzene by decantation and washed successively with several portions of water (1000-ml total) until free of acid. The suspension in nitrobenzene was transferred to a distilling flask and nitrobenzene distilled off with steam. The residue was treated with 100 ml of cold methanol, filtered, and air dried. Recrystallization from methanol–water (2:1) afforded colorless needles (21.5 g, 65% yield) with a melting point of 225–226°. The infrared spectrum (Nujol) indicated the presence of OH functions (absorption band at 3289 cm^{-1}). The nmr spectrum of the compound showed the following peaks: AB quartet centered at τ 1.58 and 2.09 for $H_{4,5}$, $J_{4,5}$ = 9 cps; AB quartet centered at 2.09 and 3.44 for $H_{5',6'}$, $J_{5',6'}$ = 10 cps. Part B is split, $J_{3',5'}$ = 2.5 cps, by *meta* $H_{3'}$ (*para* coupling, $J_{3',6'}$, was not observed) and doublet for $H_{3'}$, centered at 3.42, J = 2.5 cps.

Anal. Calcd for $C_{10}H_7ClN_2O_2$: C, 53.94; H, 3.17; N, 12.58. Found: C, 53.71; H, 3.43; N, 12.81.

3-Chloro-6-(2′,4′-diacetoxyphenyl)pyridazine (I, R = CH_3CO; R_1 = Cl).—One gram of the above compound was dissolved in 6.0 ml of anhydrous pyridine, 9.0 ml of acetic anhydride was added, and the reaction mixture was set aside at room temperature for 24 hr. The separated crystals were filtered and the filtrate was evaporated *in vacuo* leaving more of the product. Recrystallization from methanol gave colorless needles (95% yield) melting at 175–176°. The infrared spectrum (Nujol) indicated the loss of the OH groups.

Anal. Calcd for $C_{14}H_{11}ClN_2O_4$: C, 54.80; H, 3.61; N, 9.13. Found: C, 55.01; H, 3.81; N, 9.22.

3-(2′,4′-Dihydroxyphenyl)pyridazine (I, R = H; R_1 = H).—To a suspension of 2.2 g of I (R = H, R_1 = Cl; 0.01 mole) in 50 ml of methanol, 7.5 ml of 80% hydrazine hydrate was added, the mixture was heated to boiling, and 0.3 g of palladium on carbon (10% Pd) was added. The mixture was heated under reflux for 30 min and filtered hot and the filtrate was evaporated *in vacuo*. After the addition of 40 ml of water the solution was neutralized with acetic acid to pH 7 and the formed precipitate was filtered, washed with water, and air dried. The product was crystallized from methanol–DMF (3:1) to give 1.75 g (94%) of colorless crystals, mp 274–275°.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.28; N, 14.89. Found: C, 63.55; H, 4.24; N, 14.86.

3-Chloro-6-(2′,5′-dihydroxyphenyl)pyridazine (II).—This compound was prepared in essentially the same way as I (R = H, R_1 = Cl) starting with 7.5 g (0.05 mole) of 3,6-dichloropyridazine, 8.25 g (0.075 mole) of hydroquinone, 100 ml of nitrobenzene, and 6.7 g (0.05 mole) of anhydrous $AlCl_3$. The crude product, obtained in 64% yield, was purified from methanol–water (2:1) to give colorless needles which had mp 195–196°.

Anal. Calcd for $C_{10}H_7ClN_2O$: C, 53.94; H, 3.17; N, 12.58. Found: C, 53.92; H, 3.52; N, 12.65.

Acknowledgment.—We take pleasure in thanking Professor K. Balenović for providing facilities in connection with the recording of nmr spectra. This work was partially supported by the Yugoslav Federal Research Fund.

(2) G. Olah, "Friedel-Crafts and Related Reactions," Vol. 2, Part I, Interscience Publishers, Inc., New York, N. Y., 1964, p 433.

(3) (a) French Patent 1,381,452 (1964); (b) Netherlands Application 6,400,983 (1964); *cf. Chem. Abstr.*, **62**, 7782 (1965).

(4) B. Stanovnik and M. Tišler, *Tetrahedron*, in press.

Alcoholysis of 1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine in Basic and Acidic Media

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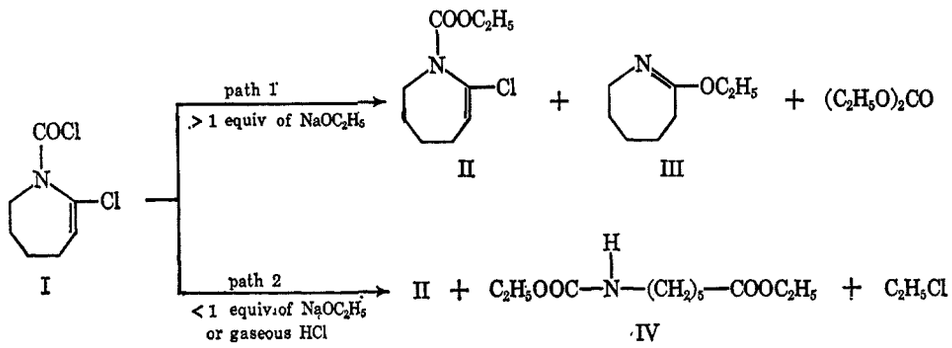
1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine (I), which is readily prepared in high yield from caprolactam and excess phosgene,[1] has been shown to undergo reaction with hypohalous acids[2] and nitric acid[3] to give α-substituted caprolactams. Hydrolysis in 10% hydrochloric acid yielded ϵ-aminocaproic acid

(1) British Patent 901,169 (to Stamicarbon N.V.) (July 18, 1962).

(2) J. H. Ottenheym and J. W. Garritsen, U. S. Patent 3,000,881 (Sept 19, 1961).

(3) B. J. Hoek, J. P. H. von den Hoff, and J. W. M. Steeman, U. S. Patent 3,093,635 (June 11, 1963).



hydrochloride.[4] In view of our interest in caprolactam derivatives, we have examined the chemical behavior of this very reactive heterocyclic compound in anhydrous ethanol under both alkaline and acidic conditions. The data are summarized in Table I.

TABLE I
REACTIONS OF 1-CHLOROCARBONYL-2-CHLORO-4,5,6,7-TETRAHYDRO-1H-AZEPINE (I) WITH SODIUM ETHOXIDE IN ANHYDROUS ETHANOL[a]

Mole of $NaOC_2H_5$	Mole of products I	II	III	IV	$(C_2H_5O)_2CO$
0.000	0.039	0.006	...	0.003	...
0.0125	0.026	0.009	...	0.007	...
0.025	0.017	0.012	...	0.027	...
0.050	Trace	0.048	...	...	...
0.100	0.001	0.025	0.021	...	0.034

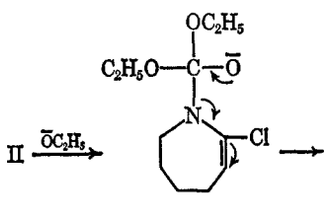
[a] All solutions originally contained 0.05 mole of I in 100 ml of ethanol and were refluxed for 24 hr. Analyses were by vpc and subject to a 5% error.

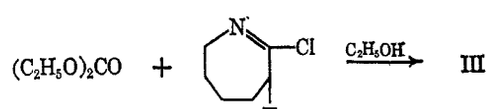
When I was refluxed in ethanol containing varying amounts of sodium ethoxide or hydrogen chloride, the transformations depicted below were found to occur.

The structure of 1-carbethoxy-2-chloro-4,5,6,7-tetrahydro-1H-azepine (II) was confirmed by elemental analysis and by the characteristic ester carbonyl and carbon–carbon double bond bands in the infrared at 5.80 and 6.06 μ, respectively. 3,4,5,6-Tetrahydro-7-ethoxy-2H-azepine[5] (III) and ethyl N-carbethoxy-ϵ-aminocaproate[6] (IV) had been described previously. Repetition of the published procedures and infrared comparison of the products, as well as elemental analyses served to confirm the identities of our derivatives.

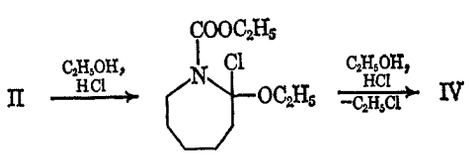
In order to provide a mechanism consistent with these observations, we considered the possibility that II is a precursor common to both reaction paths. To test this hypothesis, II was synthesized and refluxed in ethanol containing first various concentrations of sodium ethoxide and then hydrogen chloride. In the first case, the products of path 1 were obtained, while in the latter case, the products of path 2 formed.

These experiments made it appear probable that II had been initially formed and then reacted *via* the two paths in accordance with the basicity or acidity of the reaction medium. Thus, when excess alkali was present, ethoxide ion displaced the N-carbethoxyl group forming diethyl carbonate and the cyclic imino chloride. Reaction of the latter with ethanol gave III (path 1). Alternatively, where less than 1 full





equiv of base was available, the excess hydrogen chloride generated in forming II catalyzed the double-bond addition of ethanol. Alcoholysis and ethyl chloride elimination then produced IV (path 2).



Experimental Section[7]

1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine (I) was synthesized from caprolactam and phosgene as described in ref 1.

General Procedure for the Basic Solvolysis of 1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine (I).—The requisite amount of sodium was dissolved in 100 ml of anhydrous ethanol, and 19.4 g (0.1 mole) of I was added slowly. When the exotherm had subsided, the mixture, now containing a white precipitate was stirred and refluxed for 24 hr, cooled, and filtered. Where chromatographic separations were done, a sample of the filtrate was injected directly into the instrument; otherwise, the alcohol was distilled and the residual oil was fractionated through a 10-cm Vigreux column.

A. Greater Than 0.1 Mole of Sodium Ethoxide.—Vapor phase chromatography of the alcoholic filtrate showed diethyl carbonate to be present. Evaporation of the alcohol (filtering periodically) and distillation of the residue produced the following fractions.

3,4,5,6-Tetrahydro-7-ethoxy-2H-azepine (III) had bp 30–31° (0.7 mm), $n^{22}D$ 1.4570 [lit.[5] bp 81–82° (26 mm), $n^{25}D$ 1.4564]. The infrared spectrum was identical with that of an authentic sample.

Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.32; H, 10.38; N, 10.28.

1-Carbethoxy-2-chloro-4,5,6,7-tetrahydro-1H-azepine (II) had bp 69° (0.1 mm), $n^{22}D$ 1.4880. Infrared (film) showed bands at

(4) T. Fukumoto and M. Murakami, *Nippon Kagaku Zasshi*, **84** (9), 736 (1963).
(5) R. E. Benson and T. L. Cairns, *J. Am. Chem. Soc.*, **70**, 2117 (1948).
(6) B. Taub and J. B. Hino, *J. Chem. Eng. Data*, **9**, 106 (1964).
(7) Boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 21 recording spectrograph. Chromatographic separations were done on an F and M Model 500 programmed-temperature gas chromatograph using a nitrile silicone gum column (GE XE-60).

5.80 and 6.06 μ, indicative of the ester carbonyl and carbon–carbon double bond, respectively.

Anal. Calcd for $C_9H_{14}ClNO_2$: C, 53.07; H, 6.93; Cl, 17.41; N, 6.88. Found: C, 53.34; H, 6.98; Cl, 16.96; N, 7.10.

B. Less Than 0.1 Mole of Sodium Ethoxide.—Evaporation of the ethanol (filtering periodically) and distillation of the residual oil produced, following a small forerun of II, ethyl N-carbethoxy-ϵ-aminocaproate (IV), bp 132.5–134° (0.2 mm), $n^{24}D$ 1.4446.

Anal. Calcd for $C_{11}H_{21}NO_4$: C, 57.12; H, 9.15; N, 6.06. Found: C, 57.17; H, 9.13; N, 6.08.

During the reflux period, placement of a cold trap after the water condenser allowed for the recovery of ethyl chloride, identified by boiling point and infrared spectrum. Furthermore, when IV was synthesized by an alternate method,[6] its boiling point and infrared spectrum were identical with that of our material.

Acid Solvolysis of 1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine (I).—Compound I (9.7 g) was dissolved in 50 ml of ethanolic hydrogen chloride and the solution was stirred and refluxed for 24 hr. Chromatography indicated 1.4% I, 13.25% II, and 85.35% IV.

Basic Solvolysis of 1-Carbethoxy-2-chloro-4,5,6,7-tetrahydro-1H-azepine (II).—Compound II (12.5 g 0.0615 mole) was added to a solution of 1.4 g (0.0615 g-atom) of sodium dissolved in 75 ml of anhydrous ethanol and the mixture was stirred and refluxed for 24 hr. After filtration and evaporation of the ethanol, 4.3 g of II and 3.3 g of III were recovered by fractional distillation. Mixtures of II and III were similarly produced when the molar ratio of sodium ethoxide to II was decreased to 0.5 and 0.2.

Acid Solvolysis of 1-Carbethoxy-2-chloro-4,5,6,7-tetrahydro-1H-azepine (II).—Three milliliters of II was added to 25 ml of anhydrous ethanol containing dissolved hydrogen chloride and the solution was stirred and refluxed for 24 hr. Chromatography indicated 58.8% II and 41.2% IV.

Acknowledgment.—The author is grateful to Mr. J. Frank for the chromatographic separations and to Drs. M. Litt and H. K. Reimschuessel for their encouragement and suggestions.

Charge Distribution, Electric Moments, and Molecular Structure of Thiols and Thio Ethers

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It is known that divalent sulfur, because of its lone pair, is capable of releasing electrons in conjugative interactions with electron-deficient groups or with electron-withdrawing unsaturated groups through their mesomeric ability.[1] It has also been shown that the sulfur atom in sulfides can expand its valence shell to a decet.[2] In this paper, using the method of Smith, *et al.*,[3] the dipole moments of thiols and thio ethers have been calculated and compared with the experimental ones. The difference in moments have been explained on the basis of the above ideas.

Calculation

In this method each bond is uniquely characterized by two parameters, but the effective moment of each depends on the whole molecule. One of the parameters (β) is derived from bond polarizabilities (Table I). The other parameter (γ) must be obtained from dipole moment data. Bond angles and bond distances are taken from Sutton's table of interatomic distances.[4] The results of the calculations are summarized in Tables II–IV.

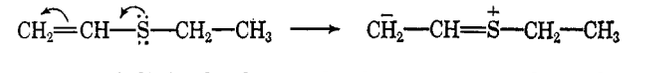
TABLE I
PARAMETERS USED IN CALCULATING THE CHARGE DISTRIBUTION

Bond (a—b)	β_{ab}	γ_{ab}	Basic molecule	Moment used[a] to derive γ_{ab}, D.
H—C	0.13	0.00	...	...
H—S	0.083	0.736	Hydrogen sulfide	1.17
Cl—C	0.71	−1.490	Methyl chloride	1.85
S—C	$\beta_S^C = 0.459$	$\alpha_{C-S} = 1.560$	Dimethyl sulfide	1.45
	$\beta_C^S = 0.832$			
C—C	$\beta_C^C = 0.718$	$\alpha_{CC} = 0$	...	...
C=C	$\beta_C^C = 1.70$	$\alpha_{CC} = 0$	...	...
C≡C	$\beta_C^C = 2.84$	$\alpha_{CC} = 0$	...	...

[a] A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman and Co., London, 1963.

Discussion

The close agreement between calculated and observed values (Table IV) for saturated thiols and thio ethers show that effects other than induction are absent. However, the observed low moments of divinyl sulfide and vinyl ethyl sulfide are due to conjugation between the unsaturated group and the lone pair (nonbonding) p electrons on the sulfur atom, leading to polar resonance structures. The negative differences in the



moment of divinyl ether and ethoxypropyne show that such structures are more predominant in oxygen than in sulfur compounds. This concept of electron-pair release, involving a contribution from 2p–3p π bond, is supported by the data on the effect of the sulfide group on chemical reactivity,[5] bond distances,[1] and spectra.[6]

It has been proved[7,8] that the nucleophilic group attaches itself to the β-carbon atom in acetylenic thio ethers because of the polarization which is possible for

an atom belonging to the second period of the periodic system. The positive difference between the observed and the calculated moments for acetylenic thio ethers, is due to contributions from such structures as given above. The sp carbon atom because of its higher

(1) C. C. Price and S. Oal, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.
(2) G. Cilento, *Chem. Rev.*, **60**, 147 (1960).
(3) R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, *J. Am. Chem. Soc.*, **73**, 2263 (1951).
(4) L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 11, The Chemical Society, London, 1958.
(5) F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Am. Chem. Soc.*, **79**, 376 (1957).
(6) C. E. Scott and C. C. Price, *ibid.*, **81**, 2672 (1959).
(7) H. C. Volger and J. F. Arens, *Rec. Trav. Chim.*, **77**, 1170 (1958).
(8) H. J. Boonstra, L. Brandsma, A. M. Wiegman, and J. F. Arens, *ibid.*, **78**, 252 (1959).