

these data and the degree of ether cleavage it is possible to calculate the amount of sodium methoxide remaining prior to acidification. Concentrations agreed to within a few per cent of expected values, assuming the stoichiometry of eq 2.

The methods employed to investigate ether cleavage reactions in  $CD_3OD-CD_3ONa$  were similar to those employed when the solvent was proteo methanol. In the case of 4-methoxypyridine, methoxy group exchange was observed. The extent of this exchange was determined by comparison of the nmr area of the  $CH_3O$  group in the pyridyl ether with the H-2,6 area of this ether. The H-2,6 area provides a measure of  $CH_3O$  and  $CD_3O$  substrate while the  $CH_3O$  signal provides a measure of substrate not having undergone methoxyl group exchange. Even though hydrogen-deuterium exchange does take place at H-3,5 of 4-methoxypyridine, none was detected at H-2,6. The combined areas of H-2,6 of 4-methoxypyridine and of H-2,6 of the anion of 4-hydroxypyridine relative to added *tert*-butyl alcohol internal standard were constant throughout ether cleavage and hydrogen exchange.

**II. 3-Chloro- or 3-Bromopyridine and Sodium Methoxide-Methanol. Consecutive, Competing Reactions.**—Methods were similar to those given above with the following modifications. Equimolar quantities (Table II) of halopyridine and methanolic sodium methoxide were heated at 218° in sealed nmr tubes. The disappearance of the halo compound was followed by observing its H-2,6 signals centered at  $\tau$  1.5, the 3-methoxypyridine H-2,6 signals at  $\tau$  1.8 and the H-4,5 signals of the anion of 3-hydroxypyridine centered at  $\tau$  3.1. *tert*-Butyl alcohol  $\tau$  8.8 served as a reference standard.

The sum of the nmr areas at  $\tau$  1.5, 1.8, and 3.1 provides a measure of the total amount of the three pyridines and the ratio of one of the three areas to the total represents the fractional amount of that pyridine present. In Figure 1 these fractions, as percentages, are given as a function of time for the chloropyridine reaction. Similar curves were obtained for the bromopyridine reaction. Some difficulty was encountered with nmr determinations of the chloro reaction mixture, owing to the precipitation of

NaCl. Vigorous shaking of the sample tube prior to determinations proved to be beneficial. Sodium bromide was soluble at ambient temperatures.

3-Halopyridine, 3-methoxypyridine, and the anion of 3-hydroxypyridine approach limiting concentrations as the concentration of sodium methoxide tends to zero. For the 3-chloropyridine the limiting percentages are estimated to be 38, 24, and 38, respectively. For 3-bromopyridine these percentages are 35, 30, and 35, respectively.

The ratio of the second-order rate constants for methoxy dehalogenation and methyl ether cleavage was estimated in two ways, the method of Wells<sup>21</sup> employing concentration ratios at the end of the reaction and the method of McMillan<sup>22</sup> employing concentration ratios for arbitrary degrees of reaction. Both methods gave results in agreement. For 3-chloropyridine the ratio of the rate constants for methoxy dehalogenation and ether cleavage is 0.53, for 3-bromopyridine 0.75. Thus, methoxy debromination is about 40% faster than methoxy dechlorination. It is to be noted that the sodium halide is incompletely soluble at the reaction temperature.

In a control experiment 3-methoxypyridine was heated with NaCl in methanol at 218°. After 10 hr some 28% of the methoxypyridine had reacted but no attempt was made at characterization. Note that in the above kinetic experiments the reaction time did not exceed 90 min.

**Registry No.**—2-Methoxypyridine, 1628-89-3; 3-methoxypyridine, 7295-76-3; 4-methoxypyridine, 620-08-6; sodium methoxide, 124-41-4; anisole, 100-66-3; 3-chloropyridine, 626-60-8; 3-bromopyridine, 626-55-1.

**Acknowledgment.**—We gratefully acknowledge partial support of this research by the National Science Foundation (GP-9488).

## Basicities and H-D Exchange of Pyrazine N-Oxides

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Received January 28, 1970

The hydrogen-deuterium exchange rates of  $H_2$  and  $H_6$  in some 3-substituted pyrazine 1-oxides have been correlated with  $\sigma$  constants, and the log of the  $H_2$  exchange rates have been shown to be linearly related to the  $pK_a$ 's of these compounds. The implication of these results upon the intermediacy of an ylide-like intermediate are discussed.

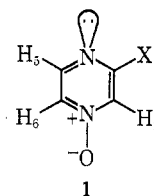
Base-catalyzed H-D exchange in pyridine N-oxide, its 3-chloro- and 3,5-dichloro derivatives have recently been described by Zoltewicz and Kauffman.<sup>1,2</sup> These studies showed that the 2,6 positions exchange more rapidly than the 3,5 positions, which in turn are more susceptible to H-D exchange than the 4 position. Similar, but qualitative, studies on pyridazine N-oxides showed that the protons undergo stepwise deuteration at the 6, 5, 4, and finally at the 3 position.<sup>3</sup>

We now wish to report the base-catalyzed H-D exchanges of the parent and of some substituted pyrazine N-oxides initiated with the aim of elucidating the effects that an additional heteroatom and different ring substituents have upon these exchange processes.

The considerable exchange-rate enhancement caused by replacement of the  $=C_4-H$  function in a pyridine N-oxide by a  $=N_4$  (formation of a pyrazine N-oxide) is evident from the following observations: The pro-

ton  $\alpha$  to the N-oxide and chloro groups ( $H_2$ ) in 3-chloropyrazine 1-oxide exchanges with a half-life of approximately 4 min, at 31° and in 0.0025 N NaOD. This compares with a half-life of 40 min for the exchange of  $H_2$  in 3-chloropyridine N-oxide under more severe conditions (0.045 N NaOD and at 74°).

Because of the facility with which the pyrazine N-oxides undergo H-D exchange, they lend themselves admirably to this type of study. Furthermore, the presence of the additional heteroatom in these compounds ( $N_4$ ) offers an "internal" reference standard with respect to the effect that a substituent (X in structure 1) has upon the  $\sigma$   $C_2-H$  bond in comparison with the similarly placed lone pair of electrons on  $N_4$ .

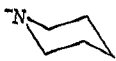


(1) J. A. Zoltewicz and G. M. Kauffman, *Tetrahedron Lett.*, 337 (1967).

(2) J. A. Zoltewicz and G. M. Kauffman, *J. Org. Chem.*, **34**, 1405 (1969).

(3) Y. Kawazoe, M. Ohnishi, and Y. Yoshioka, *Chem. Pharm. Bull.*, **12**, 1384 (1964).

TABLE I  
SECOND-ORDER RATE CONSTANTS FOR H-D EXCHANGE IN NaOD-D<sub>2</sub>O<sup>a</sup>  
AND pK<sub>A</sub>'s OF SOME 3-X-PYRAZINE 1-OXIDES

| -X  | Compd no. <sup>b</sup> | k <sub>H<sub>2</sub></sub> (l. mol <sup>-1</sup> min <sup>-1</sup> ) | k <sub>H<sub>6</sub></sub> (l. mol <sup>-1</sup> min <sup>-1</sup> ) | pK <sub>A</sub> <sup>c</sup> |
|---|------------------------|--|--|------------------------------|
| -CN   | 1                      | 2.8 ± 0.2 × 10 <sup>2</sup>  | ... <sup>d</sup>   | -1.12                        |
| -Cl   | 2                      | 7.5 ± 0.3 × 10   | 9.9 × 10 <sup>-1</sup>   | -1.05                        |
| -OCH <sub>3</sub>   | 3                      | 4.3 ± 0.1  | 2.1 × 10 <sup>-2</sup>   | -0.45                        |
| -NH <sub>2</sub>  | 4                      | 2.3 ± 0.2 × 10 <sup>-1</sup>   | 1.1 × 10 <sup>-2</sup>   | 1.50, -1.92 <sup>e</sup>     |
| -H  | 5                      | 1.6 ± 0.1 × 10 <sup>-1</sup>   | 1.6 × 10 <sup>-1</sup>   | 0.05                         |
|  | 6                      | 6.4 ± 0.5 × 10 <sup>-1</sup>   | 7.1 × 10 <sup>-4</sup>   | 1.34, -1.80 <sup>e</sup>     |
| -CH <sub>3</sub>  | 7                      | 4.6 ± 0.4 × 10 <sup>-2</sup>   | 5.8 × 10 <sup>-2</sup>   | 0.46                         |
| -N(CH <sub>3</sub> ) <sub>2</sub>   | 8                      | 3.3 ± 0.2 × 10 <sup>-2</sup>   | 4.5 × 10 <sup>-4</sup>   | 1.34, -1.77 <sup>e</sup>     |

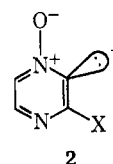
<sup>a</sup> The various concentrations of NaOD used were 1.0–0.0025 *M*, and each compound was studied at more than two base concentrations. The pyrazine N-oxide concentrations employed varied from 0.5–0.05 *M*. <sup>b</sup> See Figure 1. <sup>c</sup> It is estimated that these values, obtained at room temperature, are accurate to ±20% and are based on the *H*<sub>0</sub> values used in ref. 6. <sup>d</sup> Compound hydrolyzes before H<sub>6</sub> exchange occurs. <sup>e</sup> The second pK<sub>A</sub> corresponds to that involving protonation of the pyrazine ring nitrogen atom. Since these values are obtained from the species where the external ring nitrogen is protonated, they cannot be used for the correlation with the rate constants.

TABLE II  
UV SPECTRAL DATA OF SOME 3-X-PYRAZINE 1-OXIDES

| Compd         | Substituent X                                 | Solvent  |   |   |   |   |             |            |       |
|---------------|---|--|---|---|---|---|-------------|------------|-------|
|               |   | H <sub>2</sub> O                                     |   | H <sub>2</sub> SO <sub>4</sub>          |   | H <sub>2</sub> SO <sub>4</sub> , <i>N</i> |             |            |       |
|               |   | λ <sub>max</sub> (ε × 10 <sup>3</sup> ) <sup>a</sup> | λ <sub>min</sub> (ε × 10 <sup>3</sup> ) | λ <sub>max</sub> (ε × 10 <sup>3</sup> ) | λ <sub>min</sub> (ε × 10 <sup>3</sup> ) |   |             |            |       |
| 5             | H   | 213 (7.44)   | 230 (1.14)                              | 228 (10.23)                             | 245 (1.03)                              | 7.28                                      |             |            |       |
|               |   | 263 (12.53)  |   | 285 (12.55)                             |   |   |             |            |       |
| 7             | CH <sub>3</sub>                               | 215 (12.05)  | 234 (2.02)                              | 232 (10.25)                             | 247 (1.71)                              | 4.79                                      |             |            |       |
|               |   | 262 (12.77)  |   | 285 (14.10)                             |   |   |             |            |       |
|               |   | 288 sh <sup>a</sup> (4.11)                           |   |   |   |   |             |            |       |
|               |   | 297 sh (2.99)  |   |   |   |   |             |            |       |
|               |   |  |   |   |   |   |             |            |       |
| 3             | OCH <sub>3</sub>                              | 212 (18.40)  | 234 (2.85)                              | 202 (14.86)                             | 250 (1.83)                              | 15.29                                     |             |            |       |
|               |   | 260 (10.60)  |   | 221 sh (6.02)                           |   |   |             |            |       |
|               |   | 302 (4.65)   |   | 281 (9.52)                              |   |   |             |            |       |
|               |   |  |   | 305 sh (7.41)                           |   |   |             |            |       |
| 4             | NH <sub>2</sub> <sup>b</sup>                  | 232 (24.06)  | 251 (7.13)                              | 225 (19.10)                             | 250 (3.51)                              | 7.30                                      |             |            |       |
|               |   | 260 (7.75)   |   | 278 (7.99)                              |   |   |             |            |       |
|               |   | 331 (4.14)   |   | 338 (4.90)                              |   |   |             |            |       |
|               |   |  |   |   |   |   |             |            |       |
| 8             | N(CH <sub>3</sub> ) <sub>2</sub> <sup>c</sup> | 202 (9.25)   | 213 (4.70)                              | 208 (6.56)                              | 216 (5.76)                              | 4.79                                      |             |            |       |
|               |   | 252 (30.75)  |   | 241 (21.40)                             |   |   |             |            |       |
|               |   |  |   | 279 (7.84)                              |   |   |             |            |       |
|               |   |  |   | 309 (1.23)                              |   |   |             |            |       |
| 6             | Piperidino <sup>d</sup>                       | 205 (9.35)   | 217 (2.94)                              | 211 (5.87)                              | 218 (5.55)                              | 4.79                                      |             |            |       |
|               |   | 256 (32.46)  |   | 246 (24.39)                             |   |   |             |            |       |
|               |   |  |   | 277 (7.41)                              |   |   |             |            |       |
|               |   |  |   | 309 (1.25)                              |   |   |             |            |       |
|               |   |  |   |   |   |   |             |            |       |
| 2             | Cl  | 222 (12.68)  | 239 (2.52)                              | 203 (15.53)                             | 221 (4.62)                              | 35.53                                     |             |            |       |
|               |   | 226 (12.63)  |   | 238 (7.58)                              |   |   |             |            |       |
|               |   | 293 sh (3.05)  |   | 282 (10.05)                             |   |   |             |            |       |
|               | 303 sh (2.11)                                 | 300 sh (9.57)  |   |   |   |   |             |            |       |
|               | CONH <sub>2</sub>                             | 225 (17.10)  |   | 243 (5.33)                              |   |   | 208 (18.51) | 250 (1.60) | 35.53 |
|               |   | 265 (9.70)   |   |   |   |   | 277 (6.02)  |            |       |
| 300 sh (2.02) |   |  |   |   |   |   |             |            |       |
| 1             | CN  | 229 (22.45)  | 246 (3.26)                              | 204 (16.26)                             | 216 (5.19)                              | 29.31                                     |             |            |       |
|               |   | 272 (11.63)  |   | 244 (10.71)                             |   |   |             |            |       |
|               |   | 310 sh (2.16)  |   | 250 sh (9.47)                           |   |   |             |            |       |
|               |   |  |   | 290 (8.91)                              |   |   |             |            |       |
|               |   |  |   | 315 sh (2.98)                           |   |   |             |            |       |

<sup>a</sup> sh = shoulder. <sup>b</sup> The second protonation appears to be complete at 35.53 *N* H<sub>2</sub>SO<sub>4</sub> with λ<sub>max</sub> 221 (20.80), 348 (6.04); λ<sub>min</sub> 270 (0.00). <sup>c</sup> The second protonation appears to be complete at 35.53 *N* H<sub>2</sub>SO<sub>4</sub> with λ<sub>max</sub> 236 (17.57). <sup>d</sup> The second protonation appears to be complete at 35.53 *N* H<sub>2</sub>SO<sub>4</sub> with λ<sub>max</sub> 236 sh (15.63), 244 (16.95).

Table I lists the rate constants for the exchange of H-2 in various pyrazine N-oxides of general structure 1. These constants were obtained in the same manner as we have previously described for the H-D exchange reactions in some polyazaindenes,<sup>4</sup> and are first order in deuterioxide and N-oxide concentration. If we are dealing with the generation of an anion or ylide-like<sup>1,2,4</sup> intermediate such as 2,<sup>5</sup> resulting from a σ bond cleavage, we would expect that there should exist a linear



free-energy relationship between the H-D exchange rates of H<sub>2</sub> and the σ<sub>I</sub> parameters. Figure 1 shows the

(5) Since these reactions occur in aqueous media, the N-oxide function is almost certainly involved in hydrogen bonding with the solvent. This would tend to facilitate the formation of an ylide.

TABLE III  
UV DATA USED IN THE DETERMINATION OF THE  $pK_A$ 's  
FOR SOME 3-X-PYRAZINE 1-OXIDES

| Substituent                      | $\lambda_{used},^a \epsilon \times 10^3$ (solvent) <sup>b</sup>   |
|----------------------------------|---|
| H                                | 263, 12.25 (H <sub>2</sub> O); 4.96 (7.28 N H <sub>2</sub> SO <sub>4</sub> ); 9.77 (0.97 N H <sub>2</sub> SO <sub>4</sub> )   |
| OCH <sub>3</sub>                 | 260, 10.66 (H <sub>2</sub> O); 3.70 (15.29 N H <sub>2</sub> SO <sub>4</sub> ); 6.38 (7.30 N H <sub>2</sub> SO <sub>4</sub> )  |
| N(CH <sub>3</sub> ) <sub>2</sub> | 279, 2.65 (H <sub>2</sub> O); 7.81 (4.79 N H <sub>2</sub> SO <sub>4</sub> ); 6.15 (0.21 N H <sub>2</sub> SO <sub>4</sub> )    |
| Piperidino                       | 280, 3.85 (H <sub>2</sub> O); 7.29 (4.79 N H <sub>2</sub> SO <sub>4</sub> ); 6.27 (0.21 N H <sub>2</sub> SO <sub>4</sub> )    |
| NH <sub>2</sub>                  | 278, 1.99 (H <sub>2</sub> O); 8.03 (7.30 N H <sub>2</sub> SO <sub>4</sub> ); 6.87 (0.21 N H <sub>2</sub> SO <sub>4</sub> )    |
| Cl                               | 260, 11.40 (H <sub>2</sub> O); 3.18 (35.53 N H <sub>2</sub> SO <sub>4</sub> ); 11.25 (0.46 N H <sub>2</sub> SO <sub>4</sub> ) |
| CN                               | 270, 11.56 (H <sub>2</sub> O); 4.43 (29.31 N H <sub>2</sub> SO <sub>4</sub> ); 9.25 (15.29 N H <sub>2</sub> SO <sub>4</sub> ) |
| CONH <sub>2</sub>                | 265, 9.69 (H <sub>2</sub> O); 3.73 (35.53 N H <sub>2</sub> SO <sub>4</sub> ); 5.33 (15.29 N H <sub>2</sub> SO <sub>4</sub> )  |
| CH <sub>3</sub>                  | 262, 12.45 (H <sub>2</sub> O); 4.84 (4.79 N H <sub>2</sub> SO <sub>4</sub> ); 9.63 (0.46 N H <sub>2</sub> SO <sub>4</sub> )   |

<sup>a</sup> The  $\lambda_{used}$  values represent those values where the change in  $\epsilon$  is greatest in going from the nonprotonated to the protonated pyrazine N-oxides. <sup>b</sup> The  $\epsilon$  values given correspond, respectively, to the nonprotonated, totally protonated, and partially protonated species. The totally protonated species was judged to be present when no change in  $\epsilon$  was observed upon further increasing the hydrogen ion concentration of the solvent. Examples of uv spectra of pyrazine and derivatives can be found in ref 6.

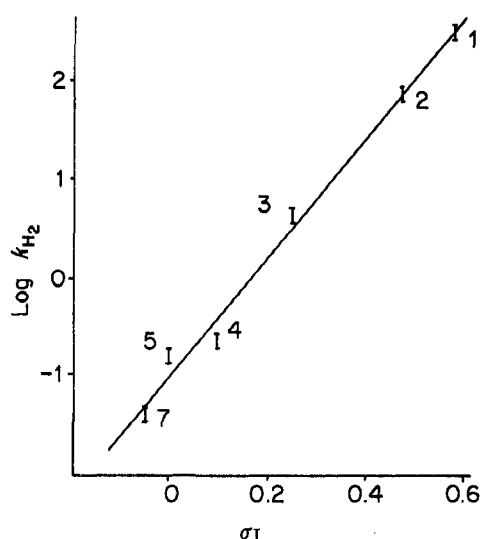
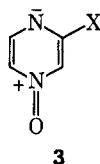


Figure 1.—Hammett correlation for base-catalyzed H<sub>2</sub>-D<sub>2</sub> exchange of some 3-X-pyrazine 1-oxides (see Table I for compound identification).

quite satisfactory correlation obtained with these substituent constants, which take only the inductive effect of the substituent X into account.

A comparison of the equilibria involved in the formation of the anion (2) with that taking place in the N protonation of these pyrazine 1-oxides leads one to suggest that there should also exist a linear correlation between the  $pK$  and the log of the exchange rates of these compounds. If such a correlation does indeed exist, it would offer convincing evidence for the suggested H-D exchange mechanism. Furthermore, a study of the  $pK$ 's of these compounds also would yield some insight into the electronic effects of an N-oxide function in an aromatic system.

The strong base-weakening effect of an N-oxide group upon a *para*-situated  $sp^2$  nitrogen atom is exemplified by a comparison of the  $pK$  of pyrazine ( $pK_A = 0.65$ )<sup>6</sup> with that of pyrazine N-oxide ( $pK_A = 0.05$ ). Thus, there is



(6) A. S. Chia and R. F. Trimble, Jr., *J. Phys. Chem.*, **65**, 863 (1961).

no significant contribution of resonance structures such as 3 to the ground state of pyrazine N-oxide.

The major effect that a 3 substituent has upon the basicity of the nonoxidized nitrogen atom (N<sub>4</sub>) in 3-substituted pyrazine 1-oxides appears to involve the inductive contribution of the substituents only (cf. Figure 1).<sup>7</sup> Thus, a correlation between the exchange rates and the basicities clearly exists. In fact there is a satisfactory linear correlation between the log  $k_{H_2}$  and the  $pK_A$  values of various 3-substituted pyrazine 1-oxides (cf. Figure 2). These correlations offer strong support to the idea that the H-D exchanges in pyrazine N-oxides, and probably also in other related systems (cf. polyazaindenes)<sup>4</sup> occur *via* ylide-like intermediates.

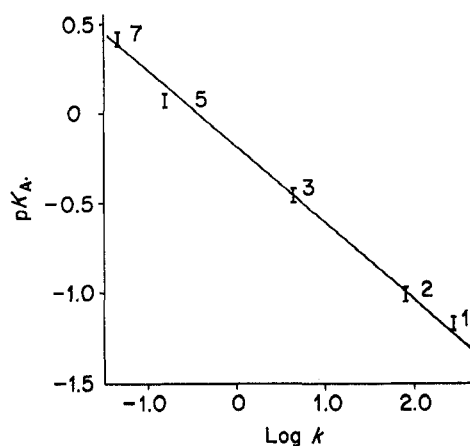


Figure 2.— $pK_A$  correlation for base-catalyzed H<sub>2</sub>-D<sub>2</sub> exchange of some 3-X-pyrazine 1-oxides (see Table I for compound identification).

Because of the distance between H<sub>6</sub> and the substituent X, any effect that X has upon the exchange rate would be considerably muted. An examination of the appropriate rate constants (cf. Table I), shows these considerations to be valid. The factors influencing the exchange rates of H<sub>6</sub> in these derivatives are not yet clear and must await the results of further studies on other heterocyclic ring systems.

(7) These  $pK_A$  effects also confirm that N-4 in pyrazine 1-oxides is more basic than the oxygen atom.

### Experimental Section<sup>8</sup>

**Preparation of the N-Oxides.**—The various N-oxides were prepared by procedures available in the literature.<sup>9-11</sup> The purity of the compounds was ascertained by tlc (alumina plates, developing solvents varied from benzene to benzene-ethyl acetate mixtures), mass spectroscopy, and melting points.

**Determination of pK<sub>A</sub> Values.**—All of the pK<sub>A</sub>'s were determined spectrophotometrically (Cary 14 instrument) using seven different solutions at various H<sub>2</sub>SO<sub>4</sub> concentrations. The procedure used was that described by Chia and Trimble.<sup>6</sup> Tables II and III list some of the pertinent uv data.

**Determination of Rate Constants.**—The appropriate N-oxide was weighed into an nmr tube and 0.4 ml of D<sub>2</sub>O was added.

(8) Nmr spectra were obtained with a Varian HA-100 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E instrument equipped with a solid sample injector. The ionizing voltage employed was 80 V. Elemental analyses were done by Mrs. K. Decker of this department.

(9) H. Shindo, *Chem. Pharm. Bull.*, **8**, 33 (1960).

(10) B. Klein, E. O'Donnell, and J. Auerbach, *J. Org. Chem.*, **32**, 2412 (1967).

(11) A. S. Elina, I. S. Musatova, and G. P. Sirova, *Khim. Geterotsikl. Soedin.*, 725 (1968).

The solution was then allowed to come to 31°, and the HA-100 instrument was adjusted. An initial spectrum and integration was then obtained. Addition of 0.1 ml of the appropriate concentration of aqueous NaOD at 31° was then added with shaking. The total time elapsed between addition of the base until the first spectrum is obtained was between 45 to 60 sec. This, as a referee pointed out, and we are certainly aware of it, allows us to get four points for the rapidly exchanging H<sub>2</sub> of the cyano compound. Nevertheless, the data on five different runs are reproducible within the limits indicated in Table I and cover between two and three half-lives.

In all of the other compounds, 10-15 points, covering at least two-half lives, were obtained.

**Registry No.**—1, 25594-31-4; 2, 6863-76-9; 3, 23902-69-4; 4, 6863-77-0; 5, 2423-65-6; 6, 13134-48-0; 7, 25594-37-0; 8, 13134-49-1.

**Acknowledgment.**—We wish to thank the Petroleum Research Fund administered by the American Chemical Society for supporting this work under Grant No. 2839-A1.

## Bis(trifluoromethyl)thioketene. I. Synthesis and Cycloaddition Reactions

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Received December 10, 1969

Bis(trifluoromethyl)thioketene has been synthesized by cracking its dimer prepared from diethyl malonate, thiophosgene, and sulfur tetrafluoride. It is stable enough to be distilled, handled, and stored without special precautions, yet is highly reactive. A tetramer and polymer have been prepared. Described here are reactions of the thioketene with (a) thiocarbonyl compounds to form dithietanes, (b) olefinic compounds and quadricyclenes to yield thietanes, (c) carbodiimides and azines to give 1,3-thiazetidines, (d) 2,3-dimethylbutadiene to form a 2H-thiopyran, and (e) norbornadienes to yield 2,6 adducts. 1,3-Dipolar additions of the thiocarbonyl group take place with diazomethane, benzonitrile oxide, and nitrones. Like nitrones, aryl oximes also give 1,4,2-oxathiazolidines. Two molecules of the thioketene combine with sulfur to form a dithiolane and tri-thiolane.

Organic chemistry has often been characterized as a mature science; yet some simple types of structures are scarcely known. Monomeric thioketenes have been sought for many years. Thioketene formulas appear in the literature as early as 1877,<sup>1</sup> but such compounds were soon realized to be some multiple of the simple formula.<sup>2,3</sup> Staudinger and coworkers unsuccessfully attempted to prepare a thioketene.<sup>4,5</sup> Dimers of aromatic thioketenes have been reported by Schönberg and coworkers<sup>6</sup> and the desaurins<sup>7</sup> can be regarded as thioketenes dimers. Dicyano- and carbomethoxycyanothioketene have not been isolated, but have been trapped as 1,3-<sup>8a</sup> and 1,4-dipolar<sup>8b</sup> adducts.

Cyanothioketene has been postulated as an intermediate in the formation of dithiafulvenes from thioamides and chlorocycanoacetylene.<sup>9c</sup> Acidification of C<sub>6</sub>H<sub>5</sub>C≡CSNa gave a polymer<sup>9</sup> which may have been derived from phenylthioketene, though this possibility was not mentioned. Subsequently, lithium salts of acetylenic thiols were treated with thiols and with amines to form thio esters and thioamides.<sup>10-12a</sup> Thioketenes were proposed as intermediates in the reaction sequence. Allylbutylthioketene was shown to be an intermediate in the rearrangement of allylthio-1-hexyne by trapping with an amine as a thioamide.<sup>12b</sup> Arylthioketenes have been suggested as intermediates in the photolysis of aryl-substituted 1,2,3-thiadiazoles,<sup>13</sup> and the thermal rearrangement of a dimethylthioketene dimer probably proceeds through the monomer.<sup>14</sup> Attempts to obtain dimethylthioketene by decomposi-

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