Experimental

1,1,4,4-Tetramethoxybutene-2 (I).—A 2-l. three-necked flask was charged with 90.6 g. (1.33 moles) of dry furan, 334 ml. of absolute methanol, and 266 ml. of anhydrous ether. The flask, which was fitted with a mechanical stirrer, thermometer, and addition tube, was cooled to −40° in a Dry Ice–acetone bath. To this stirred solution was slowly added a cooled solution of 214 g. (1.34 moles) of bromine in 666 ml. of absolute methanol. The reaction temperature was allowed to rise to −35°. Reaction temperature was maintained between −40 and −30°. Addition took 1.5 hr. After addition was completed the reaction temperature was maintained at −35° for 30 min. and then it was raised to −19°. Anhydrous ammonia was bubbled through (addition tube removed and gas inlet tube inserted) the reaction. The temperature was kept between −19° and −10°. The clear yellow solution turned opaque and then white in 15 min. (pH 2, universal indicator paper). Ammonia addition was continued until pH 7+ was reached. Total time for ammonia addition was 1 hr.

The reaction mixture was filtered. The precipitate was washed with ether and refiltered. The filtrates were combined and poured into a saturated sodium chloride solution. This was then extracted with ether several times until the ether extract was nearly colorless. The combined ether layers were dried over anhydrous magnesium sulfate, filtered and then distilled (atm.) to remove the ether and methanol. The residue was vacuum distilled. The product distilled at 95–100° (15 mm.) as a pale yellow liquid. N.m.r. gave a correct proton ratio of 1:1:6.

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.5; H, 9.09. Found: C, 54.9; H, 8.88.

1,1,4,4-Tetramethoxy-2,3-dibromobutane (II).—A 1-l. four-necked flask fitted with a stirrer, addition tube, and thermometer was set in an ice–methanol bath. To this was added 100 g (0.560 mole) of the tetramethoxy butene and 110 ml. of carbon tetrachloride. A solution of 102.5 g. (0.640 mole) of bromine in 50 ml. of carbon tetrachloride was slowly added to the reaction maintaining the temperature between 0° to 10°. Addition took 2 hr. after which an opaque red mixture resulted. This was stirred at room temperature for 1.5 hr. and then the reaction mixture was concentrated by blowing with a nitrogen stream. The mixture was then filtered to give 35 g. of a crystalline product and 171 g. of a liquid. After removing the last traces of solvent from the liquid and treating it with cold petroleum ether (b.p. 40–60°), a precipitate formed to give a total of 145 g. (77%) of crystalline product, m.p. 99°–99.5° (n.m.r. confirmed the structure).

Anal. Calcd. for $C_8H_{16}O_4Br_2$: C, 28.5; H, 4.76; Br, 47.6. Found: C, 28.03; H, 4.55; Br, 47.2.

1,1,4,4-Tetramethoxybutyne-2 (III).—A solution of 18.68 g. (0.166 mole) of potassium *t*-butoxide in 120 ml. of *t*-butyl alcohol was prepared in a 500 ml. two-necked flask in a nitrogen atmosphere drybox. The flask was then stoppered and removed from the drybox. The reaction flask was set in a heating mantle in the hood and fitted with a reflux condenser with a calcium chloride drying tube. The crystalline dibromo compound (29 g., 0.083 mole) was added under a nitrogen blanket, and the reaction slurry was magnetically stirred and heated to reflux. Reflux was continued for 6 hr. and then allowed to cool overnight. The reaction mixture was then filtered. It was necessary to slurry the thick paste with ether in order to filter. The yellow brown filtrate was washed with water and then extracted with ether several times. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated by atmospheric distillation to remove the ether and *t*-butyl alcohol. The final traces of solvent were removed by vacuum distillation. The residue distilled as a colorless liquid at 90–98° (6 mm.). This was redistilled to give 10 g. (70%) of tetramethoxybutyne at 83–86° (6 mm.).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.17; H, 8.05. Found: C, 54.78; H, 8.11.

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Cleavage of Cyclopropane by *p*-Toluenesulfonyl Chloride and Aluminum Chloride

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The major product of the cleavage of cyclopropane by acyl chlorides and aluminum chloride is not the expected γ-chloro ketone I (by analogy to the action of hydrogen bromide on cyclopropane) but rather the branched β-chloro ketone II.[2]

$$(CH_2)_3 + RCOCl \xrightarrow[CHCl_3]{AlCl_3} \underset{I}{RCO(CH_2)_3Cl} + \underset{II}{RCOCH(CH_3)CH_2Cl} \text{ with II/I} \cong 2$$

We have found that, in contrast to the action of acyl chlorides, *p*-toluenesulfonyl chloride and aluminum chloride cleave cyclopropane to produce 1-chloro-3-(*p*-toluenesulfonyl)propane (III). Although Hart and Levitt[2b] failed to obtain a reaction of sulfonyl chlorides with cyclopropane and aluminum chloride in chloroform, the change of solvents from chloroform to methylene chloride apparently enables the reaction to proceed. Compound III was obtained in 32% conversion

$$(CH_2)_3 + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow[CH_2Cl_2]{AlCl_3} \underset{III}{p\text{-}CH_3C_6H_4SO_2(CH_2)_3Cl}$$

and was identified by mixture melting point with an authentic sample of sulfone,[3] identical infrared spectra, and identical retention times on the vapor phase chromatogram. The v.p.c. of the reaction mixture indicated the major components to be III and unchanged *p*-toluenesulfonyl chloride. Separation of III from *p*-toluenesulfonyl chloride was effected by column chromatography.

Experimental

Reaction of Cyclopropane with *p*-Toluenesulfonyl Chloride and Aluminum Chloride.—In a 1-l. flask fitted with a stirrer, gas inlet tube, and Dry Ice condenser, were placed 33.3 g. (0.25 mole) of anhydrous aluminum chloride, 450 ml. of dry methylene chloride, and 47.4 g. (0.25 mole) of *p*-toluenesulfonyl chloride. After the solids dissolved, 115 g. (2.74 mole) of cyclopropane was added over a 5-hr. period. The solution was stirred overnight at room temperature (without use of the Dry Ice condenser). The next day 42 g. (1.0 mole) more of cyclopropane was added, and the reaction mixture was again stirred overnight at room temperature. The reaction mixture was poured into 300 g. of water containing 60 ml. of concentrated hydrochloric acid. The methylene chloride was separated and washed with eight equal portions of water. The methylene chloride was dried over anhydrous sodium sulfate, filtered, and the solvent removed under vacuum. The partly-solidified oil was first analyzed by v.p.c. (2 ft. silicon rubber column at 125° in an F and M instrument) using chloroform as the solvent. There were three main peaks corresponding to the solvent, *p*-toluenesulfonyl chloride, and the chlorosulfone III. The retention times corresponded to

(1) National Institutes of Health Predoctoral Fellow, 1962–1963. Supported in part by the National Institutes of Health under grant no. CY-4536.

(2) (a) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **79**, 931 (1957); (b) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959); (c) H. Hart and R. A. Martin, *ibid.*, **24**, 1267 (1959).

(3) W. E. Truce and L. Lindy, *ibid.*, **26**, 1463 (1961).

those for authentic samples of *p*-toluenesulfonyl chloride and III. There were two small peaks, one (1/6 the area of III) before and one (1/25 the area of III) after the appearance of III. These peaks were not identified.

The oil obtained from the methylene chloride evaporation was placed on an aluminum oxide filled chromatograph column and eluted with 80% petroleum ether (b.p. 35–37°) and 20% benzene. The column became heated[4] as the materials moved down. Compound III came through quickly and continued to pass through the column as the eluent was varied to pure benzene. A total of 18.2 g. of III (32% conversion) was obtained and purified by recrystallization from ethanol, m.p. 72–74°, mixed with an authentic sample, m.p. 72–74°. The infrared spectra of the authentic compound and the reaction product were superimposable.

(4) When *p*-toluenesulfonyl chloride in chloroform was placed on an aluminum oxide filled column, the column became heated and the sulfonyl chloride did not pass through the column upon further elution.

Oxygen-to-Nitrogen Rearrangement of Diethyl *N*-(*p*-Tolylsulfonyl)imidocarbonate

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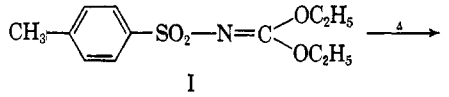
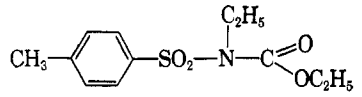
In our work on sulfonylurea derivatives, diethyl N-(*p*-tolylsulfonyl)imidocarbonate (I) was prepared by reaction of *p*-toluenesulfonamide with tetraethyl orthocarbonate in analogy to the known reaction of sulfonamides with triethyl orthoformate to give ethoxymethylenesulfonamides.[1] In a second preparation in which the temperature reached 200° a different product, ethyl ethyl(*p*-tolylsulfonyl)carbamate (II), was obtained in high yield by O → N shift of one ethyl group. The same rearrangement was observed by heating I alone to 200° for about one hour.

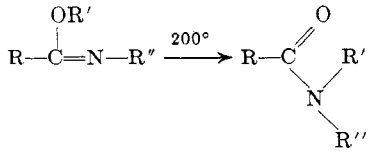


I



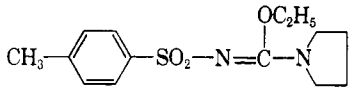
II

This, to my knowledge, novel rearrangement is reminiscent of the Chapman rearrangement[2] which consists in the conversion of alkylimido or arylimido esters into amides by heat.



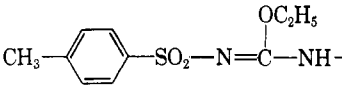
The mechanism of the conversion of I into II is probably similar to that of the Chapman rearrangement.[3] The structure of II, a colorless oil, was established by hydrolysis to N-ethyl-*p*-toluenesulfonamide and infrared data. II showed strong carbonyl absorption at 5.77 μ. On the other hand, I, a solid, m.p. 70–71°, showed very strong absorption at 6.33 μ typical of C=N— stretching.

Aminolysis of I with pyrrolidine gave ethyl N-(*p*-tolylsulfonyl)-1-pyrrolidinecarboximidate (III) which again showed C=N stretching absorption at 6.3 μ.



III

Reaction of I with *n*-butylamine gave the ethyl ether of tolbutamide, namely, 3-butyl-2-ethyl-1-*p*-tolylsulfonylpseudourea.



IV

Its C=N— stretching absorption in the infrared was shifted to 6.18 μ, but n.m.r. clearly established the structure of IV (having the C=N— double bond to the *p*-tolylsulfonyl nitrogen rather than to the butyl nitrogen) by absence of the peak at 4.91 p.p.m. which was present in the n.m.r. spectrum of N-ethyl-*p*-toluenesulfonamide due to the proton on the sulfonamide nitrogen.[4]

Experimental[5]

Diethyl N-(*p*-Tolylsulfonyl)imidocarbonate (I).—A mixture of 85.5 g. (0.5 mole) of *p*-toluenesulfonamide (Eastman) and 144 g. (0.75 mole) of tetraethyl orthocarbonate (Kay Fries) was heated with stirring. At 120–130° ethanol distilled. Within about 2 hr. the temperature of the reaction mixture had reached 160° as distillation of ethanol ceased. It was allowed to cool. Next day the compact crystalline solid was collected and washed with several portions of petroleum ether (b.p. 35–60°). The crude product, 91.2 g. (67%) melted at 69–70°. An analytical sample was prepared by recrystallization from absolute ether, m.p. 70–71°.

Anal. Calcd. for $C_{12}H_{17}NO_4S$: C, 53.12; H, 6.32; N, 5.16. Found: C, 53.06; H, 6.40; N, 5.06.

Ethyl Ethyl(*p*-tolylsulfonyl)carbamate (II).—A mixture of 85.5 g. (0.5 mole) of *p*-toluenesulfonamide and 115 g. (0.6 mole) of tetraethyl orthocarbonate was heated as for I except that the temperature was allowed to reach 200–205° at the end of the reaction. No solid was obtained on cooling. On distillation at 150–152° (0.5 mm.) 124.1 g. (92%) of colorless oil was collected.

Anal. Calcd. for $C_{12}H_{17}NO_4S$: C, 53.12; H, 6.32; N, 5.16. Found: C, 53.37; H, 6.49; N, 5.43.

In a separate experiment a 20-g. sample of I was heated to 200–205° for 1 hr. On distillation 19.1 g. of II was obtained, identified by infrared data.

Either by heating a sample with excess pyrrolidine at reflux for 3 hr. or by warming with an excess of *N* sodium hydroxide on the steam bath after acidification a good yield of N-ethyltoluenesulfonamide, m.p. 64–65°, was obtained, which was identical in every respect to a reference sample.

Ethyl N-(*p*-Tolylsulfonyl)-1-pyrrolidine Carboximidate (III).—A solution of 5.4 g. (0.02 mole) of I in 100 ml. of absolute ether was treated dropwise with 3.5 ml. of pyrrolidine. The solution was evaporated on the steam bath and finally *in vacuo*. The colorless oil crystallized on treatment with 20 ml. of ice–water, yielding 5.8 g. (98%) of a white crystalline solid, m.p. 84–86°. One recrystallization raised the m.p. to 86–87°.

Anal. Calcd. for $C_{14}H_{20}N_2O_3S$: C, 56.73; H, 6.80; N, 9.45. Found: C, 56.97; H, 6.96; N, 9.40.

3-Butyl-2-ethyl-1-*p*-tolylsulfonylpseudourea (IV).—To 20 ml. of *n*-butylamine was added 13.5 g. (0.05 mole) of I. The solution was warmed on the steam bath for 10 min. Excess butylamine

(1) G. Tosolini, *Ber.*, **94**, 2731 (1961).

(2) A. W. Chapman, *J. Chem. Soc.*, **127**, 1992 (1925); 1743 (1927); W. G. Dauben and R. L. Hodgson, *J. Am. Chem. Soc.*, **72**, 3479 (1950).

(3) *Cf.* E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., 1950, pp. 74–75.

(4) N.m.r. values were run in deuteriochloroform. The NH-peak of N-ethyl-*p*-toluenesulfonamide at 4.91 p.p.m. integrated for one proton.

(5) The melting points were taken on a Fisher-Johns block and are corrected.