The *ortho*-Claisen Rearrangement of 2-Alloxypyridine. *ortho*-Claisen Rearrangement to Nitrogen[1]

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Received September 27, 1963

Unsymmetrically substituted allylic 2-pyridyl ethers give normal Claisen products on rearrangement to the N-1 and the C-3 atoms when heated in a tertiary amine solvent. Neat rearrangement of a γ-substituted 2-pyridyl ether results in the formation of an abnormal 1-substituted 2-pyridone.

ortho-Claisen rearrangement of 2-substituted 4-alloxypyrimidines was shown recently to give the corresponding 2-substituted 4-hydroxy-5-allylpyrimidines.[3] A subsequent investigation[4] of this reaction showed it to possess the characteristics normally associated with the *ortho*-Claisen rearrangement[5] and established that simultaneous rearrangement to the N-3 atom occurs to nearly the same extent, forming the isomeric 2-substituted 3-allyl-4-pyrimidone. While no investigation of the mechanism of the rearrangement to the N-3 atom was conducted, the lack of formation of the corresponding 1-allyl-4-pyrimidone indicated this rearrangement to be intramolecular.

A number of studies have established that a great deal of specificity is observed in the direction of Claisen rearrangement. Holton[6] recently pointed out that, when two dissimilar *ortho* positions are available, Claisen rearrangement normally takes place predominantly to the position having the higher electron density, the position at which the greater amount of nitration occurs in the corresponding phenol.

In view of these observations, it seems surprising that Claisen rearrangement of a 4-alloxypyrimidine should take place indiscriminately to the markedly different N-3 and C-5 atoms.[7]

Rearrangement of the 2-substituted 4-alloxypyrimidines was accompanied by the formation of considerable amounts of decomposition products. For this reason, and because of the greater simplicity of the system, 2-alloxypyridines were chosen to investigate the *ortho*-Claisen rearrangement to nitrogen.

Mikhant'ev[8] previously had synthesized 2-alloxypyridine (I) by treatment of 2-chloropyridine with sodium alloxide. In our hands, however, this procedure afforded 2-alloxypyridine which was contaminated with a substantial amount of unchanged 2-chloropyridine. A modification of this procedure gave I in higher purity. Rearrangement of I at 255° in dimethylaniline gave two isomeric products, 3-allyl-2-pyridone (II), recovered by crystallization from the reaction mixture, and 1-allyl-2-pyridone (III), obtained by chromatography of the residue (see Scheme I).

Two additional ethers, 2-crotoxypyridine (IV) and 2-(1-methylalloxy)pyridine (V), were prepared. The method by which these compounds were synthesized, nucleophilic substitution of 2-chloropyridine by the sodium salts of the corresponding alcohols, rules out any possible allylic rearrangement. When the crotoxy ether (IV) was heated in dimethylaniline, 3-(1-methylallyl)-2-pyridone (VI) and 1-(1-methylallyl)-2-pyridone (VII) were obtained. The 1-methylallyl ether (V) gave 3-crotyl-2-pyridone (VIII) and 1-crotyl-2-pyridone (IX) on rearrangement in dimethylaniline. In each case the products obtained under these conditions resulted from inversion of the allylic group, indicating that the rearrangements to the N-1 and C-3 atoms are normal intramolecular Claisen rearrangements.

Determination of the Structure of Rearrangement Products.—The n.m.r. spectrum[9] of 2-pyridone was determined and found to show two low-field signals at 2.67 and 2.77 τ due to the 4 and 6 protons. Two additional signals, a doublet at 3.40 (J = 9 c.p.s., relative area = 1) and a triplet at 3.80 τ (J = 7 c.p.s., relative area = 1), can be assigned unequivocally to the 3 and 5 protons, respectively, based on their multiplicity.[10]

The n.m.r. spectra of the 3-substituted 2-pyridones (II, VI, and VIII) all show the presence of the two low-field 4 and 6 protons and the triplet signal assigned to the 5 proton. However, in the three spectra no doublets corresponding to that of the 3 proton of 2-pyridone are present, indicating that the allylic groups of pyridones II, VI, and VIII are attached to the 3 position of the ring.[11] The 1-substituted 2-pyridones (III, VII, and IX) show the presence of four ring protons, thereby indicating that the allylic groups are attached to the ring nitrogen atom.

The spectra of the crotyl pyridones (VIII and IX) show a high-field quartet at 8.37 (J = 3.0, 1.1 c.p.s., relative area = 3) and 8.28 τ (J = 3.3, 1.0 c.p.s., relative area = 3), respectively, due to independent splitting of the methyl signals by the two vinylic protons.[12a] The methyl groups of pyridones VI and VII which are split by a single proton appear as doublets

(1) This investigation was supported in part by Grant CA-02857 from the National Institutes of Health, U. S. Public Health Service.

(2) Allied Chemical Corp. Research Fellow, 1963–1964.

(3) H. J. Minnemeyer, J. A. Egger, J. F. Holland, and H. Tieckelmann, *J. Org. Chem.*, **26**, 4425 (1961).

(4) F. J. Dinan, H. J. Minnemeyer, and H. Tieckelmann, *ibid.*, **28**, 1015 (1963).

(5) For an excellent recent review of the Claisen rearrangement, see S. J. Rhoads, "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 655-683.

(6) P. G. Holton, *J. Org. Chem.*, **27**, 357 (1962).

(7) For a discussion of the characteristics of the pyrimidine ring positions, see D. J. Brown, "The Pyrimidines," Interscience Publishers, Inc., New York, N. Y., 1962, pp. 5–8.

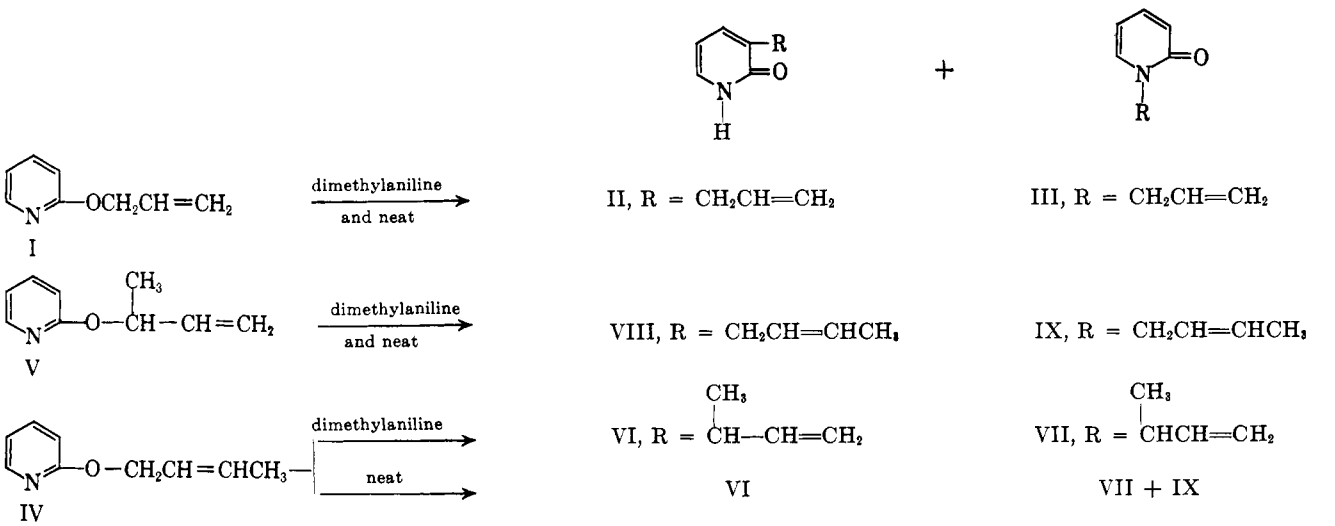
(8) B. I. Mikhant'ev, E. I. Federov, A. I. Kucherova, and V. P. Potapova, *Zh. Obshch. Khim.*, **29**, 1874 (1959).

(9) All n.m.r. spectra were determined using a Varian A-60 spectrometer. Measurements were made in deuteriochloroform solution using tetramethylsilane as an internal standard.

(10) These assignments are consistent with the findings of Elvidge and Jackman who determined the n.m.r. spectrum of 1-methyl-2-pyridone and report a range of 2.69–2.74 for the 4 and 6 protons, 3.43 for the 3 proton, and 3.85 τ for the 5 protons [see J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961)].

(11) It should be mentioned that no signal is observed for the 1 proton in any of the 2-pyridones which are potentially tautomeric. This is not unusual as signals from N–H protons are often broad and indistinguishable from background [see A. R. Katritzky, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **23**, 223 (1962)].

SCHEME I



at 8.69 (J = 7.0 c.p.s., relative area = 3) and 8.55 τ (J = 7.0 c.p.s., relative area = 3), respectively.[12b]

Additionally, the 1-allyl isomer (III) obtained by rearrangement of the alloxy ether (I) is identical with an authentic sample of III prepared by the procedure of Mikhant'ev.[8] The 1-crotyl rearrangement product (IX) was identical with the product obtained when the sodium salt of 2-pyridone was alkylated with crotyl chloride.[13]

Neat Rearrangement of Ethers.—Neat rearrangement of the ethers (I, IV, and V) took place only if these materials were distilled, chromatographed, then redistilled, and rearranged while fresh. Material of lesser purity underwent polymerization when subjected to rearrangement conditions in the absence of solvent.

The composition of the reaction mixtures resulting from the neat rearrangements was investigated by gas chromatography. Neat rearrangement of the allyl ether (I) and the 1-methylallyl ether (V) afforded the same products as were obtained upon rearrangement in dimethylaniline. The amounts of 1 and 3 isomers afforded by the neat rearrangement of I and V were somewhat variable but were comparable to those obtained when these ethers were rearranged in dimethylaniline.

Neat rearrangement of the crotyl ether (IV) at 245° gave the expected 1-methylallyl isomers (VI and VII), and, in addition, afforded the 1-crotyl isomer (IX) but none of the 3-crotyl isomer (VIII). In rearrangements under these conditions, formation of a crotyl product from a crotyl ether is, to our knowledge, previously unreported.[14]

The formation of the 1-substituted products by rearrangement of the crotyl ether (IV) was investigated as a function of time and showed that the normal 1-substituted isomer (VII) is initially formed in greater amount. The ratio of the abnormal 1-crotyl isomer (IX) to the normal isomer (VII) increased as the reaction proceeded and IX accounted for 40–60% of the combined 1-substituted isomers when rearrangement was complete.

Formation of the 1-crotyl isomer (IX) by rearrangement of the crotyl ether (IV) is somewhat analogous to the results observed in the abnormal Claisen rearrangement of 3-ethylallyl phenyl ether. This rearrangement afforded a mixture of the normal product, *o*-(1-ethylallyl)phenol, and an abnormal rearrangement product, *o*-(1,3-dimethylallyl)phenol. The abnormal product has been demonstrated recently to result from isomerization of the initially formed normal product.[15,16]

In the present case, however, isomerization of the normal product (VII) to the abnormal product (IX) does not take place. When a pure sample of the 1-methylallyl isomer (VII) was subjected to rearrangement conditions, none of the abnormal 1-crotyl isomer (IX) formed. Moreover, no reverse rearrangement of VII to form either of the ethers (IV or V) occurred.

Formation of the 1-crotyl isomer (IX) from the crotyl ether (IV) also could result from isomerization of IV to the 1-methylallyl ether (V) prior to rearrangement. However, none of the branched chain ether (V) could be detected by gas chromatography in samples withdrawn during the course of a neat rearrangement of the crotyl ether (IV). The lack of formation of the 3-crotyl isomer (VIII) when the crotyl ether (IV) is rearranged may be taken as additional evidence that no isomerization of IV to V occurs prior to rearrangement, since any V present would form VIII as well as IX on rearrangement.

In summary, ethers I, IV, and V undergo normal Claisen rearrangement when heated in dimethylaniline. The γ-carbon atom of the allylic chain becomes attached to the N-1 and C-3 atoms of the ring. The allyl ether (I) and the 1-methylallyl ether (V) also undergo normal Claisen rearrangement to both the 1 and 3 positions

(12) (a) In the n.m.r. spectra of crotyl alcohol and the crotyl ether (IV), the signals due to the methyl groups have the same general contour as those observed for the 1- and 3-crotyl pyridones (VIII and IX); (b) the same doublet pattern for the methyl groups is observed in the n.m.r. spectra of 1-methylallyl alcohol and the 1-methylallyl ether (V).

(13) An attempt to synthesize the 1-(1-methylallyl) isomer (VII) by alkylating the sodium salt of 2-pyridone with 3-chloro-1-butene also led to the formation of the 1-crotyl isomer (IX). This apparently occurs *via* an S_N2' mechanism.

(14) It should be noted that a similar mixture of crotyl and 1-methylallyl products has been obtained from the acid-catalyzed rearrangement of aliphatic allylic N-phenylformimidates. However, when these rearrangements were run without acid catalysis, only the normal inversion products were obtained [see R. M. Roberts and F. A. Hussein, *J. Am. Chem. Soc.*, **82**, 1950 (1960)].

(15) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1109 (1962).

(16) W. van Philipsborn, *Angew. Chem., Intern. Ed. Engl.*, **2**, 487 (1963).

when rearranged neat. When the crotyl ether (IV) is rearranged neat, normal Claisen rearrangement takes place to the C-3 atom to form the 1-methylallyl isomer (VI). Rearrangement to the nitrogen atom, however, gives both the normal 1-methylallyl isomer (VII) and the abnormal 1-crotyl product (IX).

The formation of a mixture of normal and abnormal products on neat rearrangement of the crotyl ether (IV) could take place by several mechanistic pathways. At present insufficient experimental data is at hand to decide on one of these possibilities. This will be the subject of a forthcoming investigation.

Experimental[17]

2-Alloxypyridine (I).—This material was prepared by a modification of the method of Mikhant'ev.[8] Sodium (4.1 g., 0.18 g.-atom) was dissolved in 40 ml. of allyl alcohol. To this was added 10.2 g. (0.090 mole) of 2-chloropyridine. The mixture was heated on an oil bath at 115° for 8 hr., poured into 50 ml. of water, and extracted with ether. After drying, the solvent was removed under reduced pressure to give crude product which distilled at 62° (12 mm.) to yield 7.9 g. (65%).

This material was shown by infrared analysis to be identical with a sample which had been prepared by the method of Mikhant'ev and was chromatographed to remove the unchanged 2-chloropyridine.

2-Crotoxypyridine (IV).—2-Chloropyridine (10.2 g., 0.090 mole) was added to a solution of 2.30 g. (0.10 g.-atom) of sodium dissolved in 50 ml. of crotyl alcohol. The mixture was heated on an oil bath for 8 hr. at 120°. Work-up of the reaction mixture as for the preparation of I gave 9.2 g. (78%) of IV, b.p. 94° (12 mm.).

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 71.99; H, 7.38; N, 9.79.

2-(1-Methylalloxy)pyridine (V) was prepared in 55% yield by the procedure used for the preparation of IV and had b.p. 86° (20 mm.).

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.39; H, 7.45; N, 9.17.

Rearrangement of 2-Alloxypyridine (I) in Dimethylaniline.—A solution of 11.2 g. of I in 22 ml. of dimethylaniline was heated in a sealed tube for 12 hr. at 255°.

A. **3-Allyl-2-pyridone (II).**—Upon cooling, 2.0 g. of II precipitated from solution and was separated by filtration. Removal of the solvent at reduced pressure and addition of a seed crystal precipitated an additional 1.2 g. of II. The combined solids, 3.2 g. (29%), were recrystallized from petroleum ether–chloroform to give a product with m.p. 124–126°.

Anal. Calcd. for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.13; H, 6.86; N, 10.10.

B. **1-Allyl-2-pyridone (III).**—The filtrate from above was chromatographed on alumina. Initial elution with ligroin removed a mixture of unaltered I and some dimethylaniline. Elution with benzene afforded 2.9 g. (26%) of III which was found to be identical by infrared with an authentic sample of III prepared by the method of Mikhant'ev.[8]

Rearrangement of 2-(1-methylalloxy)pyridine (V) in Dimethylaniline.—V (4.4 g.) in 9 ml. of dimethylaniline was heated in a sealed tube for 4 hr. at 245°.

A. **3-Crotyl-2-pyridone (VIII).**—Crystals of VIII separated from solution on cooling and were collected as described for 3-allyl-2-pyridone (II). Combination of the initially precipitated crystals and those obtained after removal of the solvent gave 1.5 g. (34%) of VIII, m.p. 114–116°, after recrystallization from ligroin–chloroform.

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.31; H, 7.46; N, 9.17.

B. **1-Crotyl-2-pyridone (IX).**—The filtrate from A was chromatographed on alumina as described for 1-allyl-2-pyridone (III) and afforded 1.3 g. (30%) of IX. This material was further purified by preparative scale gas chromatography to obtain an analytical sample.

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.43; H, 7.59; N, 9.53.

1-Crotyl-2-pyridone (IX) by Alkylation of 2-Pyridone.—The procedure used was essentially that of Mikhant'ev.[8] The sodium salt of 2-pyridone (15.3 g., 0.15 mole) was added to a solution of 62.5 g. (0.69 mole) of crotyl chloride in 60 ml. of absolute ethanol. The mixture was refluxed for 2.5 hr. Precipitated sodium chloride was removed by filtration, and the solvent and excess crotyl chloride were removed under reduced pressure to give a light brown oil which distilled to give 7.6 g. (34%) of product, b.p. 94° (0.1 mm.). This was shown by infrared analysis to be identical with IX obtained by rearrangement of the ether V.

Rearrangement of 2-Crotoxypyridine (IV) in Dimethylaniline.—A solution of 3.0 g. of 2-crotoxypyridine in 6 ml. of dimethylaniline was heated in a sealed tube at 250° for 7 hr.

A. **3-(1-Methylallyl)-2-pyridone (VI).**—After cooling, the solvent was removed at reduced pressure; the residue was dissolved in 50 ml. of ether and extracted with 10% sodium hydroxide solution. The aqueous layer was made weakly acidic with 6 *N* hydrochloric acid, and, after filtration, was extracted with chloroform. Evaporation of the chloroform after drying gave 1.1 g. (37%) of crude VI as a light tan oil. This was purified by gradient elution chromatography on alumina but could not be crystallized. Chloroform, ether, ethyl acetate, and methyl alcohol were used with VI being eluted by ethyl acetate–methyl alcohol. This material was further purified by preparative scale gas chromatography to obtain an analytical sample.

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.11; H, 7.46; N, 9.61.

B. **1-(1-Methylallyl)-2-pyridone (VII).**—Evaporation of the ether fraction from A gave 1.8 g. of light brown oil which was chromatographed as described for 1-allyl-2-pyridone (III) and gave 0.9 g. (30%) of VII which was further purified by preparative scale gas chromatography to obtain an analytical sample.

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39 Found: C, 72.21; H, 7.58; N, 9.62.

Neat Rearrangement of 2-Alloxypyridine (I), 2-(1-Methylalloxy)pyridine (V), and 2-Crotoxypyridine (IV).—Distilled samples of the ethers were chromatographed on alumina, redistilled, and rearranged while fresh. The rearrangements were conducted at 245° in sealed tubes.

The composition of the reaction mixtures was investigated by gas chromatography.[18] Peak areas were measured using a K & E 4236 planimeter. Synthetic mixtures were used to obtain correction factors. Positive identifications were established by trapping components, determining their infrared spectra, and comparing these with the spectra of authentic materials.

Neat rearrangement of ethers I and V was shown by this procedure to give the same 1-substituted 2-pyridones (40–55% yield) and 3-substituted 2-pyridones (35–45% yield) as were obtained by rearrangement in dimethylaniline.[19] Relative amounts of 1- and 3-substituted 2-pyridones were found to vary somewhat from batch to batch.

The crotyl ether (IV) gave 3-(1-methylallyl)-2-pyridone (VI) in 30–40% yield. No 3-crotyl-2-pyridone (VIII) was observed at the correct retention time for authentic VIII. Two 1-substituted isomers, 1-(1-methylallyl)-2-pyridone (VII) and 1-crotyl-2-pyridone (IX), were formed when IV was rearranged. The normal isomer (VII) formed in greater amount initially. The amount of abnormal product (IX) increased with respect to VII as the reaction proceeded. The combined yield of the 1-substituted isomers (VII and IX) ranged from 50–60%. The amount of IX formed unaccountably varied from batch to batch but was generally 40–60% of the total yield of 1-substituted isomers when rearrangement was complete.[19]

Attempted Isomerization of 1-(1-Methylallyl)-2-pyridone (VII).—Several sealed tubes containing neat 1-(1-methylallyl)-2-pyridone were heated on an oil bath at 245°. Seven samples were removed at 0.5-hr. intervals and investigated by gas chromatography.[18]

The chromatograms obtained showed that no direct isomerization of VII to the 1-crotyl isomer (IX) takes place. Ethers IV

(17) All melting points are corrected. Microanalyses were performed by Alfred Bernhardt, Mulheim, Germany.

(18) A 2-ft., 20% General Electric XF-1150 on Chromosorb-W column was used. The temperature was programmed from 100–230° at 11°/min. with a helium flow rate of 60 ml./min.

(19) Several unidentified minor components were observed in these chromatograms. These components were present also in samples which were rearranged in dimethylaniline.

and V and the 3-substituted 2-pyridones (VI and VIII) also were shown not to form when neat 1-(1-methylallyl)-2-pyridone (VII) is heated under rearrangement conditions.

Attempted Isomerization of 2-Crotoxypyridine (IV) to 2-(1-Methylalloxy)pyridine (V).—Neat IV was heated in sealed tubes at 245°. Samples were withdrawn at 0.5-hr. intervals for 5 hr. and examined for the presence of the isomerized ether (V) by gas chromatography.[18] The column temperature was maintained at 100° for 8 min. before programming began.

No peak due to V was observed in any of the samples. It was determined that no more than 0.5% of V could be present at any time during the rearrangement.

Aryl Fluoroalkyl Sulfides. I. Preparation by Reaction of Grignard Reagents with Trifluoromethanesulfenyl Chloride[1]

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Received October 18, 1963

The reaction of arylmagnesium halides with trifluoromethanesulfenyl chloride provides a new and convenient synthesis of aryl trifluoromethyl sulfides. The scope and mechanism of this reaction is discussed, and the chemical and physical properties of aryl fluoroalkyl sulfides are described.

Aryl trifluoromethyl sulfides have been synthesized by reaction of antimony trifluoride with aryl trichloromethyl sulfides which were in turn prepared by photo-

$$ArSCH_3 \xrightarrow[h\nu]{Cl_2} ArSCCl_3 \xrightarrow{SbF_3} ArSCF_3$$

initiated chlorination of aryl methyl sulfides.[2] This method is only of moderate utility since the aromatic substituents are limited to inert groups such as nitro or halogens, and the aryl methyl sulfides are not readily available.

Phenyl tetrafluoroethyl sulfide has been prepared by base-catalyzed addition of thiophenol to tetrafluoroethylene.[3] However, this reaction has not been ex-

$$C_6H_5SH + CF_2{=}CF_2 \xrightarrow{base} C_6H_5SCF_2CF_2H$$

tended to substituted thiophenols, and the properties of the tetrafluoroethylthio group have not been studied.

The aryl trifluoromethyl sulfides have been oxidized to the corresponding sulfones by chromic anhydride in sulfuric acid,[2,4] but otherwise the trifluoromethylthio group appears to be inert to normal chemical transformations of the aromatic ring such as reduction of nitro groups,[2] nitration (*ortho–para* orientation),[5] diazotization of amino groups, and hydrolysis of nitriles.[2] Potential dyes[2a,6] and pharmaceutical chemicals[7] containing the SCF_3 and SO_2CF_3 groups have been reported.

Results and Discussion

Synthesis.—The reaction of arylsulfenyl chlorides with Grignard reagents has been reported as a method for preparation of aryl sulfides.[8] This reaction has now been extended to provide a new direct method for preparation of aryl trifluoromethyl sulfides by reaction of aryl Grignard reagents with trifluoromethanesulfenyl chloride (see Table I).[9]

$$ArMgX + CF_3SCl \longrightarrow ArSCF_3 \ (+ ArCl + ArX)$$

The sulfide is obtained in a yield of about 50% by bubbling CF_3SCl into a solution of the Grignard reagent at 0°. In addition, aryl chloride and aryl halide are formed as by-products (5 to 15%) from the Grignard reagent (if X is not Cl). In a search for optimum conditions, it was found that, if CF_3SCl was added to a solution of phenylmagnesium bromide chilled to −40° or if an inverse addition procedure was used (maintaining the reaction mixture at −60° to −80°), the yield of phenyl trifluoromethyl sulfide decreased but that of bromobenzene increased proportionately. The purification of the product by distillation (C_6H_5Cl, b.p. 132°; $C_6H_5SCF_3$, b.p. 142°; C_6H_5Br, b.p. 155°) was simplified by use of arylmagnesium chloride,[10] and yields of products were comparable to yield from reaction of the bromide. Purification also was simplified when arylmagnesium iodide was used, but the yield of aryl trifluoromethyl sulfide was significantly lower.

In order to rationalize the results, consideration was given to the mechanism of the reaction. Although mechanism studies have not been reported on the reaction of arylsulfenyl chlorides with Grignard reagents, a mechanism has been proposed for the reaction of Grignard reagents with alkyl halides.[11] The mechanism suggested is a SN2 or a "push–pull" type which involves

(1) This work was presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961.

(2) (a) French Patent 820,796 (1937); J. Dickey, U. S. Patent 2,436,100 (1948); British Patents 503,920 (1939) and 479,774 (1938); (b) L. M. Yagupolsky and A. I. Kiprianov, *J. Gen. Chem. USSR*, **22**, 2273 (1952); (c) L. M. Yagupolsky and M. S. Marenets, *ibid.*, **24**, 885 (1954).

(3) D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **82**, 5166 (1960).

(4) L. M. Yagupolsky and B. E. Gruz, *J. Gen. Chem. USSR*, **31**, 1219 (1961).

(5) L. M. Yagupolsky and M. S. Marenets, *ibid.*, **26**, 99 (1956).

(6) L. M. Yagupolsky and M. S. Marenets, *ibid.*, **25**, 1725 (1955).

(7) (a) E. A. Nodiff, S. Lipschutz, P. N. Craig, and M. Gordon, *J. Org. Chem.*, **25**, 60 (1960); (b) French Patent 1,245,552 (1960).

(8) H. Lecher, *Ber.*, **58**, 409 (1925); G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, **51**, 1526 (1929); G. Sanna, *Gazz. chim. ital.*, **72**, 305 (1942).

(9) Trifluoromethanesulfenyl chloride was originally reported by R. N. Haszeldine and J. M. Kidd [*J. Chem. Soc.*, 3219 (1953)], who prepared it by reaction of CF_3SSCF_3 or $(CF_3S)_2Hg$ with Cl_2. A convenient synthesis of large quantities of CF_3SCl is the reaction of CCl_3SCl with NaF in tetramethylene sulfone [C. W. Tullock, U. S. Patent 2,884,453 (1959); and C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960)].

(10) Arylmagnesium chlorides are readily prepared in tetrahydrofuran as solvent from aryl chloride and magnesium with isopropyl alcohol or aluminum isopropoxide as initiator [E. T. Blues and D. Bryce-Smith, *Chem. Ind.* (London), 1533 (1960)].

(11) (a) For a general discussion, see M. S. Kharasch and O. Reinmuth "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1048; (b) C. G. Swain, *J. Am. Chem. Soc.*, **70**, 1119 (1948).