[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

2-Trifluoromethylpyridine[1]

BY JOHN M. S. JARVIE, WARREN E. FITZGERALD AND GEORGE J. JANZ

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The formation of 2-trifluoromethylpyridine in 88 mole per cent. yield by reaction of trifluoroacetonitrile and 1,3-butadiene in the homogeneous gas phase at 474° is reported. The synthesis is an example of a generalized cyclization–dehydrogenation reaction between nitriles and dienes leading to the formation of pyridines. The chemical reactivity of trifluoroacetonitrile is comparable to that reported previously for cyanogen in this reaction

The reaction between nitriles and dienes to form 2-substituted pyridines has been reported by Janz and co-workers.[2] The present communication reports the addition of trifluoroacetonitrile to butadiene in the homogeneous gas phase with the formation of 2-trifluoromethylpyridine, a previously unreported compound. The high reactivity of trifluoromethylacetonitrile in this cyclization–dehydrogenation reaction is attributed to the strongly electrophilic properties of the trifluoromethyl group.

Experimental

A continuous flow apparatus of the type described elsewhere[2] was used, modified to be an all glass system. Trifluoroacetonitrile (Peninsular Chemresearch, Inc.) and butadiene (Matheson Co., Inc.) were purified by low temperature distillation and degassed under vacuum prior to use. The reaction system was flushed 30 minutes with nitrogen before and after each experiment. The reactants were passed continuously through the hot zone (475°, 342 cc.) for 4.5 hr. The total material balance was 101%. The data and results are tabulated below. The unreacted nitrile was recovered by low temperature distillation, and the 2-trifluoromethylpyridine by fractional distillation (b.p. 142–144°) using a Podbielniak semi-micro analyser. An experiment with cyanogen and butadiene under comparable conditions was carried out in the same apparatus. The product, 2-cyanopyridine, was estimated polarographically.[3] The data and results are listed for comparison with trifluoroacetonitrile. The lower yield is attributed to loss of cyanogen by side reactions, *e.g.*, polymerization to paracyanogen

	Trifluoro-acetonitrile	Cyanogen
Contact time, sec.	43	82
Mole ratio, RCN/diene	1.7	1.2
Nitrile conversion, mole %	13	47
Pyridinic product, mole %	88	64

2-Trifluoromethylpyridine.—The properties of 2-trifluoromethylpyridine (purified by repeated fractional distillations) were: colorless liquid, b.p. 143.0° (754.5 mm.), $n^{25}\text{D}$ 1.4155. The oil colors yellow on standing and has a characteristic but more pleasant odor than most pyridines. Attempts to prepare the picrate were not successful, indicating that it is, like 2-cyanopyridine, non-basic in properties. The composition was confirmed by micro-chemical analysis. Calcd. for $C_6H_4NF_3$: N, 9.52. Found: N, 9.33.

Its infrared spectrum[4] shows frequencies (cm.$^{-1}$) and intensities of absorption as follows: 3400(m), 3040(w), 2480(v.w), 2237(w), 2117(w), 1955(w), 1920(v.w), 1892(v.w), 1862(m), 1800(v.w), 1744(v.w), 1676(v.w), 1596(s), 1474(w), 1445(s), 1386(v.w), 1338(v.s), 1308(w), 1250(s), 1178(s), 1150(s), 1100(s), 1072(s), 1043(s), 999(s), 969(m), 928(v.w), 901(m), 845(v.w), 795(s), 745(s), 678(s). Comparison of the spectrum with the data available for the trifluoromethyl group and the pyridines appears in the discussion.

Discussion

Examination of the infrared spectrum of 2-trifluoromethylpyridine compared with published spectra is of interest for the recognition of structural units in this compound. Randle and Whiffen[5] have examined the spectra of 21 aromatic compounds with trifluoromethyl substituents for evidence relating to the (CF_3) group frequencies. This led to the assignment of 1321 (±9), 1179 (±7) and 1140 (±9) cm.$^{-1}$ as characteristic of the symmetrical and two antisymmetrical stretching modes, respectively, for this group. 2-Trifluoromethylpyridine shows these characteristic absorptions as strong bands at 1338, 1178 and 1150 cm.$^{-1}$. In the rock salt region the CF_3 deformation[6] absorbs at 760 and 741 cm.$^{-1}$ in CF_3Br and CF_3I, respectively. A strong band in the present compound appears at 745 cm.$^{-1}$. Comparison of the infrared spectrum of 2-methylpyridine,[7] pyridine,[8] and the present compound shows close similarities, the band 1596, 1474, 1445, 1043 and 995 being characteristic of the ring vibrations. Correspondence with the more generalized correlations of Cannon and Sutherland[9] for absorption bands characteristic of pyridines is also readily observed.

The empirical recognition of these structural units, the microchemical analysis, and by analogy with the products isolated in the generalized nitriles–dienes cyclization–dehydrogenation reaction,[2] the identification of the product from the trifluoroacetonitrile–butadiene reaction as 2-trifluoromethylpyridine leaves little doubt.

An estimate of the relative reactivities of trifluoroacetonitrile, cyanogen and acetonitrile in this reaction is possible from a consideration of the space–time yields. If it is assumed that the reaction order is the same in each case, it has been shown[10] that the space–time yield (S.T.Y.) is directly proportional to the rate constant providing the experiments are effected under comparable conditions.

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[1] Part X in the series: The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes.

[2] G. J. Janz and co-workers, THIS JOURNAL, **76**, 6377 (1954); **77**, 3014, 3143 (1955).

[3] J. M. S. Jarvie, R. A. Osteryoung and G. J. Janz, *Anal. Chem.*, **28**, 264 (1956).

[4] Figure 1, supplementary to this article, has been deposited as Document number 4609 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

[5] R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 1311 (1955).

[6] W. F. Edgell and C. E. May, *J. Chem. Phys.*, **20**, 1822 (1952).

[7] A.P.I. Research Project 44, Carnegie Institute of Technology. Catalog of Infrared Spectral Data, Serial No. 743, 2-methylpyridine, contributed by Mellon Institute.

[8] C. H. Kline and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944).

[9] C. B. Cannon and G. B. B. M. Sutherland, *J. Spectrochem Acta*, **4**, 373 (1951).

[10] G. J. Janz and S. C. Wait, Jr., *J. Chem. Phys.*, **23**, 1550 (1955).

Nitrile	CH_3–CN	CF_3–CN	NC–CN
S.T.Y., moles/hr./100 cc. × 10^4	4^a	98	170

[a] G. J. Janz and S. C. Wait, Jr., THIS JOURNAL, **76**, 6377 (1954).

Inspection of the space–time yields accordingly shows that the relative reactivities for acetonitrile, trifluoroacetonitrile and cyanogen are in the ratio of 1:25:43, respectively. The high space–time yield for cyanogen may be attributed in part to the electronic polarizability of the (CN) group and to the fact that there are two potential reaction centers present in this molecule.[11] The enhanced reactivity of trifluoroacetonitrile undoubtedly is due to the influence of the strongly electrophilic (CF_3) group in this molecule. If the higher space–time yield of cyanogen is indeed partly due to the fact that there are two potential reaction centers in each molecule, one may predict that the reactivity of the $(C\equiv N)$ in trifluoroacetonitrile is the same order of magnitude as in cyanogen. A kinetic study of the trifluoroacetonitrile–butadiene reaction is in progress in this Laboratory.

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TROY, N. Y.

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[11] G. J. Janz and associates, THIS JOURNAL, **74**, 1790 (1952); **75**, 1910 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD SCIENCE AND TECHNOLOGY, NEW YORK STATE AGRICULTURAL EXPERIMENT STATION, CORNELL UNIVERSITY]

The Anthocyanin Pigments of Sour Cherries[1]

BY KUANG C. LI AND A. C. WAGENKNECHT

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This paper reports the isolation and identification of antirrhinin and mecocyanin from sour cherries. Crude pigments are obtained through their lead salts, and separation into two individual crystalline pigments is achieved by using silicic acid chromatographic columns. Identities of pigments have been established by means of paper chromatography, color reactions and absorption spectroscopy, including infrared, and by comparison with synthetic specimens.

In connection with the problems of scald formation and discoloration of sour cherries, an investigation of the anthocyanin pigments was made. The chemistry of the anthocyanins of sour cherries has had little attention since the early researches of Rochleder.[2] Willstätter and Zollinger[3] isolated keracyanin from sweet cherries. Robinson and Robinson[4] indicated that the skins of small black cherries (*Prunus avium*) contained cyanidin-3-monoside.

In the present investigation a modified partition chromatographic method involving silicic acid has been devised for the separation and purification of two closely related anthocyanin pigments of sour cherries and, incidentally, the separation also of a diglucoside, a monoglucoside and the aglycone. This method may be extended to handle other types of anthocyanin pigments. The use of infrared spectra for the identification of crystalline anthocyanins represents a simple and discriminating method which had not been employed previously with such highly colored compounds. These analyses can be run on samples as small as 1 mg.

Experimental

Preparation of the Crude Pigments.—The procedure for the preparation of the crude pigments was essentially that of Willstätter and Zollinger[3] in handling sweet cherries. The skins of ripe, fresh sour cherries (*Prunus cerasus* L., var. Montmorency) were extracted with methyl alcohol containing 1% hydrochloric acid. The extracted pigments were precipitated as lead salts, and regenerated by dissolving in methyl alcoholic hydrochloric acid. From the regenerated solution, crude pigments were obtained as a dry red powder by the addition of anhydrous ether.

Separation of the Components in the Crude Anthocyanin Preparation.—A preliminary analysis of the anthocyanin pigments in the skins by paper chromatography has revealed two components of nearly equal concentration, the relative proportions of which remained unchanged in the crude pigment preparation.

Attempts to separate the crude pigments into their individual components by the alumina absorption methods of Karrer and Strong,[5] and of Price and Robinson[6] were unsuccessful. Separation, however, was achieved by a modification of the Spaeth and Rosenblatt[7] method, which had been used for the resolution of microgram quantities of mixtures of synthetic anthocyanidins. In the present modified method, the coarser particles of silicic acid were used instead of the finer particles, and the solvent system was changed from the originally described phenol–toluene–phosphoric acid to *n*-butyl alcohol–acetic acid–water (4:1:5 v./v.).

A typical column 3.5 × 54 cm., prepared from 250 g. of silicic acid, could thus handle 200 mg. of the crude pigments. The chromatogram was developed with the upper layer of the solvent system into two distinct zones (upper zone fraction A, lower fraction B), and elution was complete in about 3 hours at 6.5 ml. per minute.

For ease of handling, each of the anthocyanin fractions in the alcohol-rich eluate was transferred to aqueous solution by shaking with an equal volume of light petroleum ether together with a few ml. of 1% hydrochloric acid. This transfer effected a reduction of about 70% in volume. Crude individual components were obtained dry by evaporation of the aqueous solution under vacuum at room temperature.

Purification and Characterization of Fraction B.—Fraction B was further purified by repeated passage through the

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[1] Journal Paper No. 1011, New York State Agricultural Experiment Station.

[2] F. Rochleder, *Ber.*, **3**, 238 (1870).

[3] R. Willstätter and E. H. Zollinger, *Ann.*, **412**, 164 (1916).

[4] G. M. Robinson and R. Robinson, *Biochem. J.*, **25**, 1687 (1931).

[5] P. Karrer and F. M. Strong, *Helv. Chim. Acta*, **19**, 25 (1936).

[6] J. R. Price and R. Robinson, *J. Chem. Soc.*, 449 (1937).

[7] E. C. Spaeth and D. H. Rosenblatt, *Anal. Chem.*, **22**, 1321 (1950).