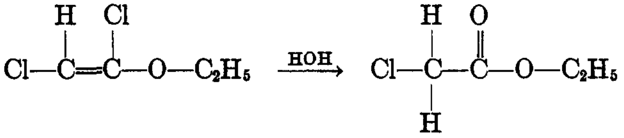
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TORONTO]

THE ACTION OF BROMOCYANOGEN ON FURAN

ALLEN H. KLOPP AND GEORGE F. WRIGHT

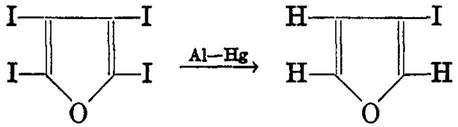
Received January 24, 1939

It is evident from inspection of the commonly accepted furan formula that the reactions of this substance should resemble analogous transformations of divinyl ether and of butadiene. The similarities are more than purely formal; thus, the halogen substituent in β-halovinyl ethers is much less reactive than that in α-halovinyl ethers.

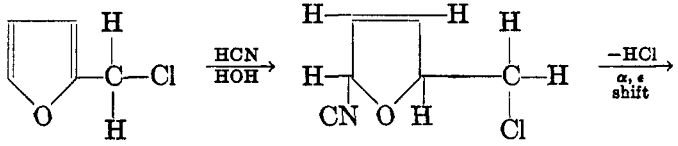


$$\mathrm{Cl{-}\overset{H}{\overset{|}{C}}{=}\overset{Cl}{\overset{|}{C}}{-}O{-}C_2H_5} \xrightarrow{HOH} \mathrm{Cl{-}\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_2H_5}$$

The exact replica of this reaction has not been demonstrated with furans, but a multitude of reactions indicate that the β-substituted furan is always less reactive than the corresponding α-isomer. As one of a number of examples,[1] may be cited the preparation of β-iodofuran by reduction of tetraiodofuran.



The resemblance between furan and butadiene is no less marked. Reichstein[2] has demonstrated that the conversion of furfuryl chloride into 5-methyl-2-furonitrile has its replica in the formation of 2-cyanohexadiene-2,4 (or 2-cyanohexadiene-3,5) from sorbyl chloride. The 1,4 addition characteristic of the conjugated unsaturation satisfactorily explains both systems. This may be formulated as shown here.



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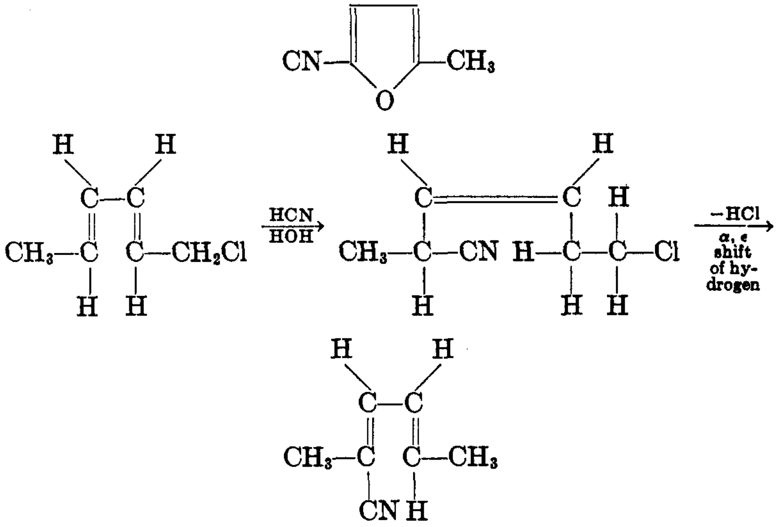
[1] (*a*) HILL AND SANGER, *Proc. Amer. Acad.*, **21**, 135 (1885). (*b*) GILMAN AND WRIGHT, *Rec. trav. chim.*, **53**, 13 (1934). (*c*) GILMAN AND BURTNER, *J. Am. Chem. Soc.*, **55**, 2903 (1933). (*d*) SHEPARD, WINSLOW, AND JOHNSON, *ibid.*, **52**, 2083 (1930).

[2] (*a*) REICHSTEIN, *Ber.*, **63**, 749 (1930); *Helv. Chim. Acta*, **15**, 254 (1932). (*b*) SCOTT AND JOHNSON, *J. Am. Chem. Soc.*, **54**, 2549 (1932).



These analogies must, however, be modified in respect to furan because of its cyclic structure. According to a certain interpretation, the rigidity conferred upon cyclic unsaturated structures causes the substitution reaction to predominate over addition. In the extreme case of structural rigidity (benzene) such a system is unable to dissipate the energy of the activated complex by any means other than reversion to the original reactants or decomposition into the products expected for the substitution reaction.

$$AB + CD \rightleftarrows \begin{bmatrix} AB \\ CD \end{bmatrix} \rightleftarrows AC + BD$$

It has long been known that furan compounds are less prone to absolute substitution reactions than are the corresponding benzene analogues, since frequently the intermediate furan addition compound may be isolated, and this has led Johnson[3] to suggest that furans occupy a classification intermediate between benzene and unsaturated aliphatic compounds. Actually it is doubtful[4] that any other ring system is so aromatic as the benzene nucleus, since only in benzene is the ultimate in structural rigidity realized. All other cyclic unsaturated systems show tendencies toward addition-complex formation prior to, or concomitant with, substitution. It so

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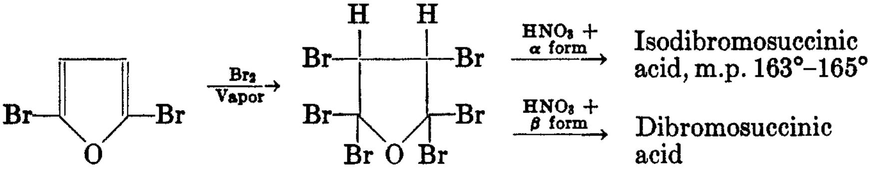
[3] (*a*) Hughes and Johnson, *J. Am. Chem. Soc.*, **53**, 737 (1931). (*b*) Stevenson and Johnson, *ibid.*, **59**, 2525 (1937).

[4] (*a*) Gilman and Wright, *ibid.*, **52**, 3349, (1930). (*b*) Gilman, "Organic Chemistry," John Wiley & Sons, New York, N. Y., 1938, p. 52.

happens that the divinyl ether- and butadiene-like characteristics of furan are modified to such a degree by the cyclic structure that the substitution or addition reaction can be effected at will, depending on the conditions of the reaction and the substituent groups already attached to the furan nucleus.

It has been shown[5] with at least one furan-bromine addition product that the addendum actually saturates the double bonds of the furan ring since diastereomeric forms of the addend were isolated. It is reasonable, therefore, to assume that all addition compounds of furans are substances with normal chemical bonds, and interest naturally turns to the question whether this addition is characteristic of the divinyl ether or the butadiene nature of furan; that is, whether addition is predominantly 1,2 or 1,4. Although 1,4 addition of halogen to a furan was postulated many years before Thiele's exposition of this phenomenon[6], proof of such addition has never been substantiated in a reaction which subsequently leads to the substitution product of a furan.



α modification m.p. 110°–111°
β modification m.p. 55°

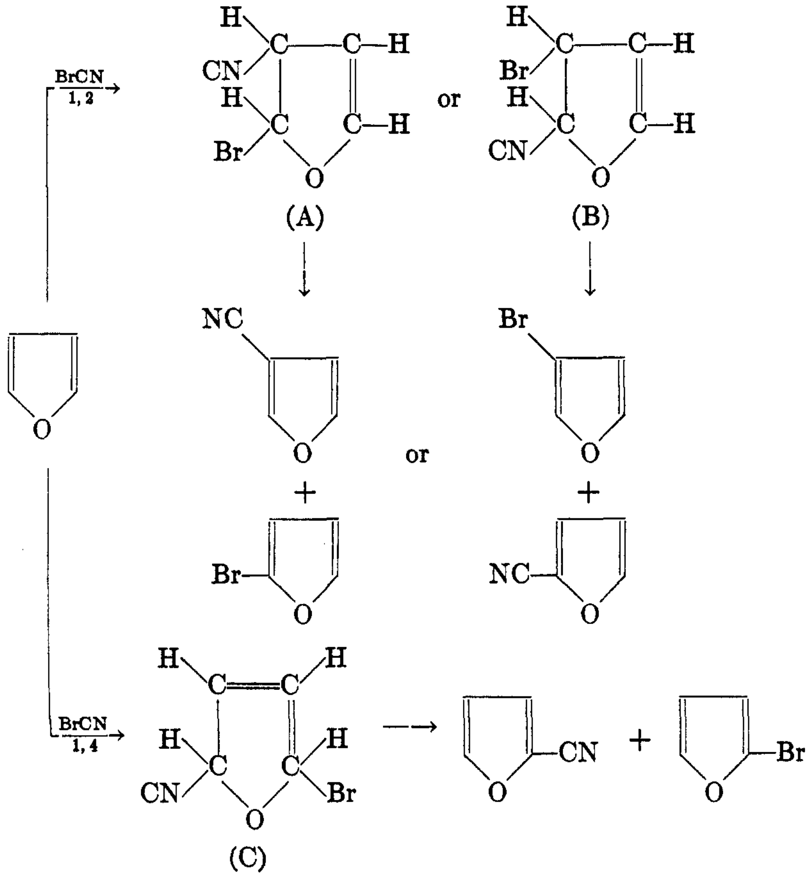
There seems to be no experimental evidence to support an alternative mechanism of substitution involving dissociation of the addition product into its constituents followed by so-called direct substitution. The position of the substituent, therefore, marks the point of attachment of one part of the addendum. This being true, the addition of an unsymmetrical addend like cyanogen bromide should indicate by examination of the pair of substitution products, whether addition occurred in the 1,2 or 1,4 position.

We treated furan with bromocyanogen, following Steinkopf's[7] directions for the similar reaction with thiophene, and obtained 2-furonitrile and 2-bromofuran. The former was identified as 2-furoic acid and the latter as 2-bromofurylmercuric chloride. These results indicate that bromocyanogen adds exclusively 1,4 to furan. We found, however, that furan, unlike

[5] (*a*) Hill and Hartshorn, *Ber.*, **18**, 448 (1885); see also (*b*) Tönnies, *ibid.*, **11**, 1085 (1878).

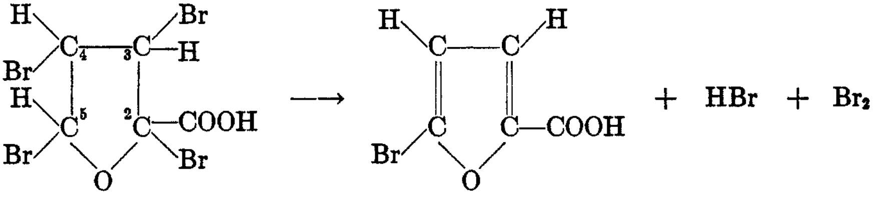
[6] Hill and Cornelison, *Am. Chem. J.*, **16**, 20 (1894).

[7] Steinkopf, *Ann.*, **430**, 78 (1922).



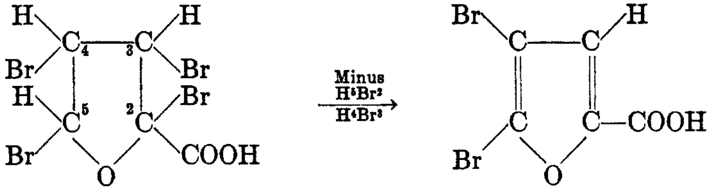
thiophene, gives distressingly low yields (4–5%), the greater part of the furan being destroyed as a green, dense, tarry solid. This is not surprising in view of the unusual sensitivity of furan towards mineral acids. In order to increase the yield we varied solvent and temperature, and used neutralizing agents such as calcium carbonate, but were unsuccessful until dioxane at room temperature was employed as the solvent. Using this medium it was found that yields of 2-bromofuran and 2,5-dibromofuran of 49 per cent. and 5 per cent., respectively, were obtained, but *no trace* of furoic acid could be detected.

This behavior is subject to several interpretations. Firstly, the addition compound C may decompose in dioxane to give hydrogen cyanide exclusively. Secondly, the dioxane environment may encourage 1,2 rather than 1,4 addition, the addition compound A subsequently losing hydrogen cyanide preferentially. In support of the latter mechanism may be mentioned the formation of 2,5-dibromofuran in measurable amount in dioxane medium but not in absence of this solvent. Furthermore, the specific HX elimination required for the second mechanism (namely, H from the α carbon and X from the β carbon) is not an unprecedented phenomenon. When 2,3,4,5-tetrabromotetrahydrofuroic acid is decomposed thermally only 5-bromofuroic acid and neither of the β-bromofuroic acids can be isolated as a recognizable product[8].



Further evidence relating to the two mechanisms would depend on isolation of the furan-bromocyanogen addition product. The addend with furan was too unstable to be isolated and a more stable compound like furoic acid, to which bromine can be added with ease, will not add bromocyanogen.

It is unfortunate that the furan-bromocyanogen addend C cannot be isolated, because the existence of the addition compound as an intermediate in the substitution reaction would confirm the possibility of 1,4-elimination of HX. The existence of this latter mode of elimination is a corollary of the work of Gilman and co-workers[9] which demonstrated that the so-called β,δ-dibromofuroic acid of Hill and Sanger[10] was actually 4,5-dibromofuroic acid. The latter could be formed only by 1,4 elimination of hydrogen bromide from 2,3,4,5-tetrabromotetrahydrofuroic acid.



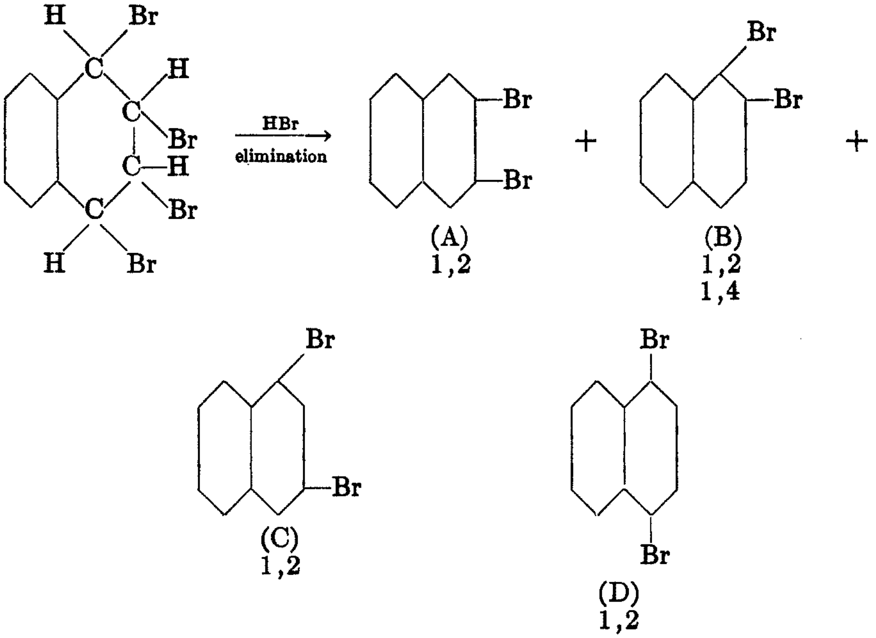
This 1,4 elimination of HX is required by all postulates of 1,4 addition of X_2 to furan or other diene nuclei as a prerequisite of the substitution reaction. Gilman's example is unique since we are aware of no case where such elimination has been demonstrated elsewhere in organic chemistry.

[8] TÖNNIES, *Ber.*, **11**, 1085 (1878).

[9] GILMAN, VANDER WAL, FRANZ, AND BROWN, *J. Am. Chem. Soc.*, **57**, 1146 (1935).

[10] HILL AND SANGER, *Proc. Amer. Acad.*, **21**, 135 (1885); *Ann.*, **232**, 42 (1885).

Indeed this mode of HX elimination is conspicuous by its absence. Thus of the possible dibromo substitution products resulting by elimination of hydrogen bromide from naphthalene tetrabromide, only B (which cannot be formed except by 1,4 elimination of hydrogen bromide) is absent among the reaction products.*



EXPERIMENTAL

Reaction without solvent.—A mixture of 26 g. (0.25 mole) of freshly prepared bromocyanogen and 29 g. (0.43 mole) of furan was refluxed twelve hours on the water bath. To this was added 100 cc. of 10% aqueous sodium hydroxide solution. The resulting mixture was refluxed two to three hours longer and was then steam distilled to yield 0.80 g. of 2-bromofuran (4% of the theoretical) which was identified as 5-bromo-2-furylmercuric chloride, m.p. 172–174°, twice recrystallized from 8:1 ethanol-water to melt at 175°. The melting point of a mixture with the same mercurial prepared from 5-bromofuroic acid showed no depression[11], and oxidation of 1 g. in 3 cc. of acetic acid with 1 cc. of nitric acid (sp. gr. 1.43) gave fumaric acid as the only isolable product. No bromofumaric acid could be detected, although the fumaric acid purified for mixture melting point determination (m.p. 277–278°) still gave a

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*In private communications, Professors Henry Gilman and C. F. H. Allen have noted that this apparent 1,4 elimination can be explained as a successive process, involving 1,2 elimination of hydrogen bromide followed by a 1,3 shift of hydrogen and a subsequent 1,2 elimination of a second molecule of hydrogen bromide. We consider the two processes to be identical on the probability basis.

[11] Gilman and Wright, *J. Am. Chem. Soc.*, **55**, 3302, (1933).

positive Beilstein test for halogen. The same halogen impurity was noted on oxidation of authentic 5-bromofurylmercuric halide.

The steam-distillation residues were evaporated almost to dryness on the steam bath, acidified with hydrochloric acid, and then allowed to evaporate spontaneously to dryness. The residue was sublimed at 100° to yield 0.54 g. (4% of the theoretical) of crude 2-furoic acid m.p. 121–128°. This was dissolved in water to remove 10 mg. of non-acidic constituent melting at 181–182° after crystallization from carbon tetrachloride. This unidentified compound contained halogen and was only slightly soluble in benzene and in ethanol. The aqueous solution of furoic acid was evaporated to dryness and fractionally sublimed at 130° (10 mm.) to yield a first fraction, m.p. 127–128°, and a second fraction, m.p. 120–122°. The first fraction was crystallized from carbon tetrachloride to melt at 129–130°, mixture m.p. with pure 2-furoic acid not lowered. Nine parts of the lower-melting fraction was mixed with one part of pure 2-furoic acid; the mixture melted at 123°. A mixture containing these relative proportions of 3-furoic acid and 2-furoic acid melts at 117–118°. The two sublimates were then recombined and boiled with aqueous mercuric chloride solution for four hours in order to decarboxylate the 2-furoic acid but to leave any 3-furoic acid unchanged. No furoic acid remained in the residue.

Alteration of the above procedure by adding sodium bisulfite to the reaction mixture prior to treatment with alkali did not alter the yield. It was found that a mixture of one equivalent of furan and one equivalent of bromocyanogen with an excess of precipitated calcium carbonate gave results identical with those outlined above. No yields were obtained using carbon tetrachloride, carbon disulfide, or anhydrous ethanol as solvents under otherwise comparable conditions. The pyridine-bromocyanogen complex would not react with furan.

Dioxane as solvent.—A mixture of 6.8 g. (0.10 mole) of furan, 10.6 g. (0.10 mole) of bromocyanogen and 50 cc. of anhydrous peroxide-free dioxane was allowed to stand under efficient reflux at 25° for eight days. To this mixture was added 80 cc. (0.2 mole) of 10% aqueous sodium hydroxide solution containing 12.6 g. (0.1 mole) of sodium sulfite. This mixture was heated to 100° for one hour, then steam-distilled until no more oil came over in the receiver. The bromofuran-dioxane mixture was washed with three 200-cc. portions of water; the volume of oil did not decrease after the second washing. The resultant oil was dried with calcium chloride. It weighed 9.81 g. On distillation two fractions were collected; the first, boiling at 62–65° (210 mm.) weighed 7.18 g. (49% of the theoretical) and was identified as pure 2-bromofuran as follows: b.p. 102–103° (744 mm.); n_D^{20} 1.4980, and by conversion to 5-bromofurylmercuric chloride as before. The second fraction (wt. 1.16 g., 5% of the theoretical) boiled at 51–52° (12 mm.). On redistillation it boiled at 52° (13 mm.); n_D^{25} 1.5419; n_D^{20} 1.5455; d_{20}^{20} 2.27. It would not mercurate, and after oxidation of 0.91 g. in 3 cc. of acetic acid and 1 cc. of nitric acid (sp. gr. 1.42) for four hours at room temperature, evaporation of the solvent under reduced pressure left only fumaric acid, and no bromofumaric acid as an identifiable product. This designates the substance as 2,5-dibromofuran.

The residual steam-distillation liquors were acidified to Congo paper and then continuously extracted with ether. After drying of the ether solution with magnesium sulfate the ether was distilled at 20 mm. pressure. Less than 0.1 mg. of the material remaining did not give a red coloration with ferric chloride and did not have the characteristic odor of furoic acid.†

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†The authors wish to thank the Quaker Oats Company for generous supplies of furoic acid used in this work.

SUMMARY

1. The reaction of bromocyanogen with furan gives small yields of 2-furonitrile and 2-bromofuran, indicating that 1,4 addition and subsequent 1,4 elimination of hydrogen bromide and hydrogen cyanide has occurred.

2. Upon dilution of the reaction mixture with dioxane a good yield of bromofuran, but no furonitrile, is obtained. This solvent causes exclusive elimination of hydrogen cyanide.