in excess of the complex, hydrated at a rate slightly greater than that for butene in pure nitric acid. After about eighteen hours the total butene concentration reached a constant value which was equal to that of the mercuric nitrate. Except in the case of the mercuric nitrate, the metallic salt concentration was a few times that of the initial butene, which was close to 0.005 molal, the approximate saturation value of butene in water.

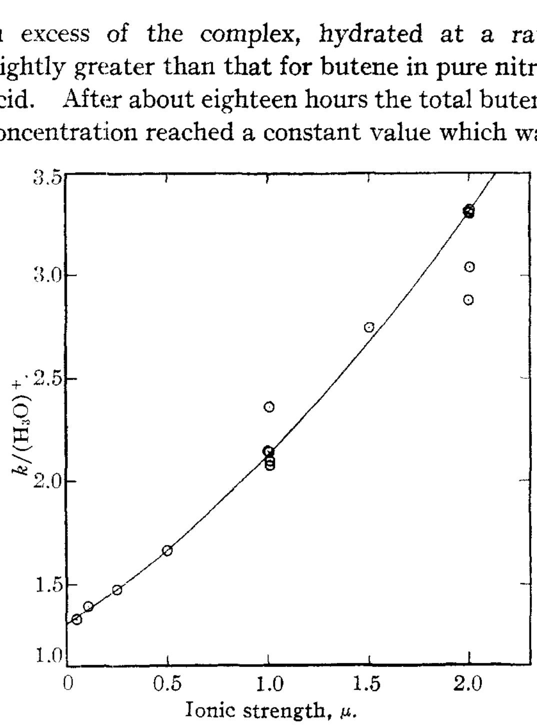

Fig. 6.—Plot of adjusted hydration constant $k/(H_3O^+)$ against the ionic strength.

**Hydration of Mixtures of Normal Butenes.**—The mixture of *cis*- and *trans*-2-butene obtained by the decomposition of 1-butanol with sulfuric acid and the mixture of approximately 70% 1-butene and 30% 2-butene obtained by the decomposition of 1-butanol over alumina[10] were substituted for isobutene in the hydration apparatus. There was no observable decrease in butene concentration at 1 *N* nitric acid in either case, even after several days of standing.

## Summary

The hydration of isobutene is catalyzed by nitric acid and at constant ionic strength the rate is first order with respect to both the butene concentration and the nitric acid concentration. The rate at a given acid concentration is increased on the addition of potassium nitrate. This increase in rate is greater than the increase in the activity of isobutene when determined by means of distribution experiments in carbon tetrachloride.

In the presence of certain metallic ions, some of which have been stated to be catalysts for the hydration of alkenes in more concentrated acids, the specific reaction rate for the hydration of isobutene in 0.20 normal nitric acid is substantially unchanged.

Mixtures of the normal butenes are not hydrated at 25° in 1.0 *N* nitric acid.

(10) Young and Lucas, THIS JOURNAL, **32**, 1964 (1930).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# Super-Aromatic Properties of Furan. III. Nitration

BY HENRY GILMAN AND R. V. YOUNG

## Introduction

Nitration is one of the few substitution reactions essentially characteristic of aromatic compounds. It is not, however, a reaction peculiar to aromatic compounds inasmuch as it is observed also with cycloparaffins[1a] and with saturated[1b] and unsaturated hydrocarbons.[1c] Of more pertinent interest is the fact that compounds like alkylbenzenes[1d] and styrene[1e] can undergo lateral nitration. Rigorous comparisons of these several types and aromatic nuclei may be inadmissible because of differences in experimental conditions. For example, dilute nitric acid and elevated temperatures are generally used in aliphatic nitrations.

If correlations be restricted to benzene as a typical aromatic nucleus, there is no doubt of the more ready nitration of furan. There are several ways for determining relative reaction velocities of nitration. One of these, now reported, involves the nitration of a symmetrical compound containing both the furyl and the phenyl radicals. 2-Furyl phenyl ketone was selected for this purpose, and it has been found that the nitro group replaces a hydrogen of the furan nucleus.

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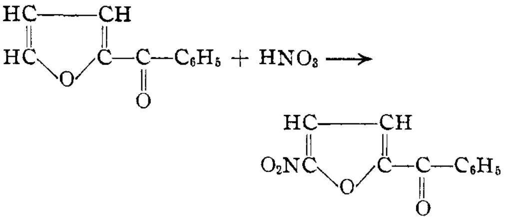
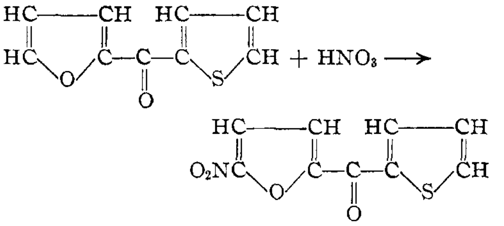
(1) (a) Markownikoff, *Ann.*, **302**, 15 (1898); (b) Worstall, *Am. Chem. J.*, **20**, 202 (1898); Markownikoff, *Ber.*, **33**, 1907 (1900); (c) Wieland and Sakellarios, *ibid.*, **53**, 201 (1920), as well as other citations contained in this paper; (d) Konowalow, *ibid.*, **28**, 1858 (1895); (e) Wieland and Rahn, *ibid.*, **54**, 1770 (1921).



I

On the basis of this experiment it may be concluded that furan is more aromatic than benzene. A similar procedure was employed in the preceding paper of this series wherein it was demonstrated that in the Friedel–Crafts reaction with 2-furyl phenyl ketone the substituent was introduced in the furyl and not in the phenyl nucleus.[2]

**Relative Aromaticities of Furan and Thiophene.**—If the cleavage of mixed organolead compounds by hydrogen chloride[3a] has any validity[3b] in establishing the relative aromaticities of radicals, then the 2-furyl radical is more aromatic than the 2-thienyl radical. This finds support in the nitration of a symmetrical compound containing these radicals: namely, 2-furyl 2-thienyl ketone.



II

The constitution of 5-nitro-2-furyl phenyl ketone (Reaction I) was established by comparison with the product of a Friedel–Crafts reaction between 5-nitro-2-furoyl chloride and benzene. However, 5-nitro-2-furyl 2-thienyl ketone (Reaction II) could not be prepared by a corresponding reaction, and because this nitro ketone is relatively stable to oxidizing agents an indirect procedure was used to establish its structure. Ordinarily, the constitution of a compound with more than one nucleus is proved by introducing a nitro group to stabilize the nucleus holding the nitro group against oxidizing agents. In the present case both nuclei appear to be stabilized in this manner. Accordingly, the nitro group was destroyed by alkali to convert the nucleus holding the nitro group to an aliphatic group which is probably of lactonic structure. The resulting compound was then oxidized, and the acid so formed (2-thenoic acid, $C_4H_3SCOOH$) revealed the nucleus which did *not* contain the nitro group. An α- or 2-nitro group in furan and in thiophene[4] is decomposed by alkali.

## Experimental Part

**Nitration of 2-Furyl Phenyl Ketone.**—To 84 g. (0.82 mole) of acetic anhydride contained in a three-necked flask provided with a thermometer and mercury sealed stirrer, and cooled to −5° by a freezing mixture, was added 36.6 g. (0.57 mole) of fuming nitric acid (sp. gr. 1.5) dropwise so that the temperature did not exceed 0°. Then the temperature was reduced to −10°, and 17.2 g. (0.1 mole) of 2-furyl phenyl ketone in 25 g. of acetic anhydride was added slowly so that the temperature did not rise above −8°. Subsequent to addition, stirring was continued for two hours at −15°. The mixture was then poured upon cracked ice; partially neutralized with 10% sodium hydroxide; and completely neutralized with a sodium bicarbonate suspension. The yellow oil which separated was extracted with ether; and to the combined ether extracts was added 20 g. of pyridine. After standing for fifteen minutes, the ether was removed under reduced pressure and the pyridine solution poured upon ice. The tarry mass which separated soon solidified and, subsequent to ether extraction, the product was recrystallized from an alcohol–water mixture to give 11 g. or a 51% yield of 5-nitro-2-furyl phenyl ketone melting at 111°.

*Anal.* Calcd. for $C_{11}H_7O_4N$: C, 58.73; H, 3.39. Found: C, 58.54 and 58.66; H, 3.47 and 3.45.

The same compound was obtained in a 63% yield from 5-nitro-2-furoyl chloride, benzene and aluminum chloride—reaction setting in immediately with the evolution of hydrogen chloride.

Oxidation of 5-nitro-2-furyl phenyl ketone by acid permanganate yielded 5-nitro-2-furoic acid and a small quantity of benzoic acid.

**5-Nitro-2-furoyl Chloride.**—It was found possible to prepare this nitro acid chloride in excellent yields. Some preliminary experiments revealed that the previous synthesis[5] gave unsatisfactory yields. To 18.8 g. (0.09 mole) of phosphorus pentachloride contained in a flask provided with a reflux condenser holding a tube with calcium chloride, was added 14.2 g. (0.09 mole) of pure 5-nitro-2-furoic acid. The flask was heated gently with a small flame, and hydrogen chloride was evolved rapidly. When the reaction subsided, the mixture was refluxed gently for about five hours. The phosphorus oxychloride was first removed by distillation under the reduced pressure of a water pump, and then the nitro acid chloride was distilled at 119–123° (4 mm.). The yield was 15 g. or 95%. Distillation appears preferable to crystallization[5] for purification.

**Nitration of 2-Furyl 2-Thienyl Ketone.**—Nitration was effected as with 2-furyl phenyl ketone, and the yield of 5-nitro-2-furyl-2-thienyl ketone starting with 2 g. (0.011 mole) or 2-furyl 2-thienyl ketone[6] was 1.3 g. or 48%.

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[2] Gilman and Calloway, THIS JOURNAL, **55**, 4197 (1933).

[3] (a) Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932); (b) Gilman, Towne and Jones, THIS JOURNAL, **55**, 4689 (1933).

[4] The authors are grateful to Dr. I. J. Rinkes for the information on nitrothiophenes.

[5] Marquis, *Ann. chim. phys.*, [8] **4**, 196 (1905).

[6] Gilman, Rowe and Dickey, *Rec. trav. chim.*, **52**, 395 (1933).

After recrystallizing from alcohol and from an acetone–water mixture the compound melted at 161°.

*Anal.* (micro Dumas) Calcd. for $C_9H_5O_4NS$: N, 6.28. Found: N, 6.97 and 6.89.

The semicarbazone of 2-furyl 2-thienyl ketone was prepared from 0.4 g. of ketone, 0.4 g. of semicarbazide hydrochloride and 0.6 g. of sodium acetate. It crystallized slowly from a water–alcohol solution and melted at 150°.

*Anal.* (micro Dumas) Calcd. for $C_{10}H_9O_2N_3S$: N, 17.87. Found: N, 18.40 and 18.32.

In attempted syntheses of the nitro ketone from 5-nitro-2-furoyl chloride and thiophene, the yield of recovered 5-nitro-2-furoic acid varied from 48% (with stannic chloride) to 84% (with titanium tetrachloride). When aluminum chloride was used as the condensing agent, hydrogen sulfide was evolved when heat was applied.

**Oxidation of 5-Nitro-2-furyl 2-Thienyl Ketone.**—The nitro ketone was recovered in amounts varying from 40 to 60% when oxidation was attempted with a 5% solution of permanganate, made acidic with sulfuric acid.

Oxidation was completed successfully by warming the nitro ketone with 10% sodium hydroxide to destroy the nucleus containing the nitro group, and then adding to the cooled solution a slight excess of 5% permanganate solution. After standing overnight, the excess permanganate was removed by ethyl alcohol, the mixture filtered and the filtrate acidified with dilute hydrochloric acid and then extracted with ether. Recrystallization from hot water gave an acid melting at 124–126°. This product contained sulfur and showed no depression in a mixed melting point determination with an authentic specimen of 2-thenoic acid.

**Nitration of 2-Furyl *p*-Phenetyl Ketone, $C_4H_3OCO$-$C_6H_4OC_2H_5$-*p*.**—The purpose of this experiment was to compare the relative aromaticities of furan with phenetole, which has more pronounced aromatic characteristics than benzene.[2,3a] Unfortunately, only tars were obtained on attempted nitration under the conditions used successfully with the ketones previously described in this paper. Oxidation of the tars with permanganic acid gave oxalic acid.

**Nitration of Furoyl-2,4,6-tribromoanilide, 2-$C_4H_3OCO$-$NHC_6H_2Br_3$.**—Raiford and Wickert[7] have shown that Borelli's[8] nitration products from benzoyl-2,4,6-tribromoanilide, $C_6H_5CONHC_6H_2Br_3$, contain the isomeric 2-nitro- and 3-nitrobenzoyltribromoanilides. That is, the nitro group enters the acyl radical and gives as a product a so-called abnormally oriented isomer. Because of the uncommon difficulty of preparing β-substituted furans, and particularly because β-nitrofuran was needed and has not been described, it was considered desirable to attempt the preparation of the abnormally oriented β-nitro-2-furoic acid (and from this the β-nitrofuran) by a reaction analogous with that effected by Borrelli and by Raiford.

The furoyl-2,4,6-tribromoanilide was readily prepared by heating equimolar quantities of furoyl chloride and 2,4,6-tribromoaniline at 120–130° for about four hours until hydrogen chloride was no longer evolved. The yield of crude product was 99%, and this when recrystallized from alcohol melted at 164°.[9]

*Anal.* Calcd. for $C_{11}H_6O_2NBr_3$: Br, 56.54. Found: Br, 56.23 and 56.26.

Several nitrations of this amide were attempted, but only resins resulted and these on acid hydrolysis yielded 2,4,6-tribromoaniline.

One of the expected products of nitration, 5-nitro-2-furoyl-2,4,6-tribromoanilide ($NO_2C_4H_2OCONHC_6H_2Br_3$), was prepared in a 98% yield by heating equimolar parts of 5-nitro-2-furoyl chloride with 2,4,6-tribromoaniline. When recrystallized from alcohol it melted at 191–192°.

*Anal.* Calcd. for $C_{11}H_5O_4N_2Br_3$: Br, 52.37. Found: Br, 52.29 and 52.17.

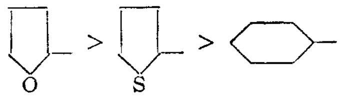
With the thought in mind that nitration might have been interfered with by the presence of a hydrogen on the nitrogen, the related furoyl-N-methylanilide ($C_4H_3$-$OCON(CH_3)C_6H_5$) was prepared with a view to its nitration. The yield of amide from furoyl chloride and methylaniline was 85%. When recrystallized from alcohol the compound melted at 125°.[9]

*Anal.* Calcd. for $C_{12}H_{11}O_2N$: N, 6.96. Found: N, 7.15 and 7.00.

Nitration in the usual manner gave no identifiable product.

## Summary

Nitration of 2-furyl phenyl ketone gave 5-nitro-2-furyl phenyl ketone; and nitration of 2-furyl 2-thienyl ketone gave 5-nitro-2-furyl 2-thienyl ketone. Partly on the basis of these preferential nitrations of symmetrical compounds, the relative aromaticities of these nuclei are as follows



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(7) Raiford and Wickert, THIS JOURNAL, **53**, 3143 (1931).

(8) Borelli, *Gazz. chim. ital.*, **17**, 527 (1887).

(9) This preparation and analysis were carried out by C. R. Buck.