Notes

Radicals from 2-Nitrofuran

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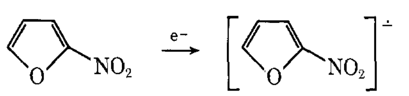
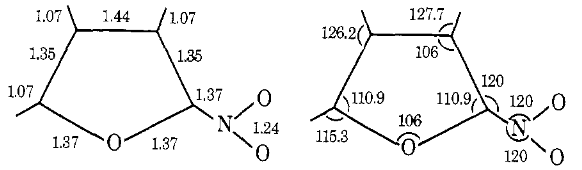
The electrochemical reduction of 2-nitrofuran in acetonitrile affords the corresponding radical anion (I).[1] Its esr



spectrum has been recorded and interpreted in terms of three nonequivalent a_H and one a_N splitting constants (Table I).

Whereas the assignment of a_N is straightforward, some doubt might arise as far as the assignment of the three a_H values is concerned. The 5-methyl-2-nitrofuran radical anion (II) allowed us to show that the 4.12 G splitting belongs to position 5; in fact in II this value is substituted by an a_{Me} splitting of similar magnitude (4.05 G) whereas the other two couplings are almost unaffected.[2] The largest splitting (5.65 G) has been assigned to position 3 and the smallest (1.00 G) to position 4 on the ground that the conjugation of five-membered aromatic rings with substituents in position 2 is expected to be more effective[3] in the 3,5 positions than in the 4 position. To check such an hypothesis theoretical calculations have been carried out by the self-consistent molecular orbital (INDO) method.[4]

The geometrical parameters employed are as follows.



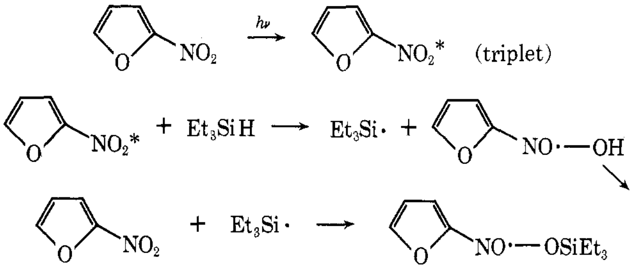
The theoretical splittings for the hydrogen atoms, given in parentheses in Table I, are in agreement with the experiment, thus supporting the tentative assignment for what concerns positions 3 and 4.

This theoretical approach also allowed us to estimate the energy barrier to the internal rotation in the nitrofuran radical anion as a difference between the planar and the 90° twisted structures. The values of the total energies were calculated to be −93.53292 and −93.51702 au, respectively, and the rather large ΔE value (10 kcal mol^{-1}) would indicate that the rotation of the NO$_2$ group is expected to be slow in the esr time scale.

In order to test experimentally such a possibility it would be necessary to differentiate in some way the two oxygen atoms, so that two conformational isomers would appear if the rotation rate around the furan-nitrogen bond is slower than the reciprocal lifetime of the spin of the unpaired electron.

A possible way to reach such a goal is the transformation of the nitrogen group into an alkoxy nitroxide. This modification would completely change the chemical character of the molecule; since, however, the conjugative power of the nitroxide moiety with the aromatic ring is expected to be lower than that of the nitro group, the existence of rotational isomers in the alkoxy nitroxide would be a very strong support in favor of a restricted rotation also in the corresponding nitro derivative.

Sutcliffe, *et al.*,[5,6] demonstrated that the photolysis of nitroaromatics in hydrogen donor solvents affords the corresponding alkoxy nitroxides. Therefore we photolyzed the 2-nitrofuran within the cavity of an esr spectrometer in a solution of triethylsilane. The following reactions are believed[5,6] to occur, yielding the 2-(triethylsiloxy)nitroxyfuran (III).



III

The radical $ArN\dot{O}OH$ decays too fast than required to build up a steady-state concentration allowing the esr detection. That $ArN\dot{O}OH$ is not responsible for the signal reported in Figure 1 is proved by the fact that with hydrogen donor solvents having -CH$_2$- groups (such as tetrahydrofuran) an additional splitting is observed,[5,6] whereas no such a feature is apparent when the solvent has -CH- groups.

Et$_3$SiH was found even more convenient than the previously employed solvents,[5,6] as it affords larger concentrations of radicals and avoids (as the -CH- containing solvents) additional couplings from the -OR moiety in the spectrum.

At room temperature a spectrum analogous to that of

Table I
Hyperfine Splitting Constants (Gauss) of the Radical Anions of 2-Nitrofuran (I), 5-Methyl-2-nitrofuran (II), and the Neutral Radical 2-(Triethylsiloxy)nitroxyfuran (III)[a]

		$a_{H\text{-}3}$	$a_{H\text{-}4}$	$a_{H\text{-}5}$	a_N	a_{Me}
I		5.65 (−5.21)	1.00 (2.06)	4.12 (−3.63)	11.25 (7.28)	
II		6.00	0.85		11.60	4.05
III	70%	5.80	0.90	4.50	13.25	
	30%	5.65	0.85	4.30	13.80	

[a] Values in parentheses refer to the calculated (INDO) splittings of I.

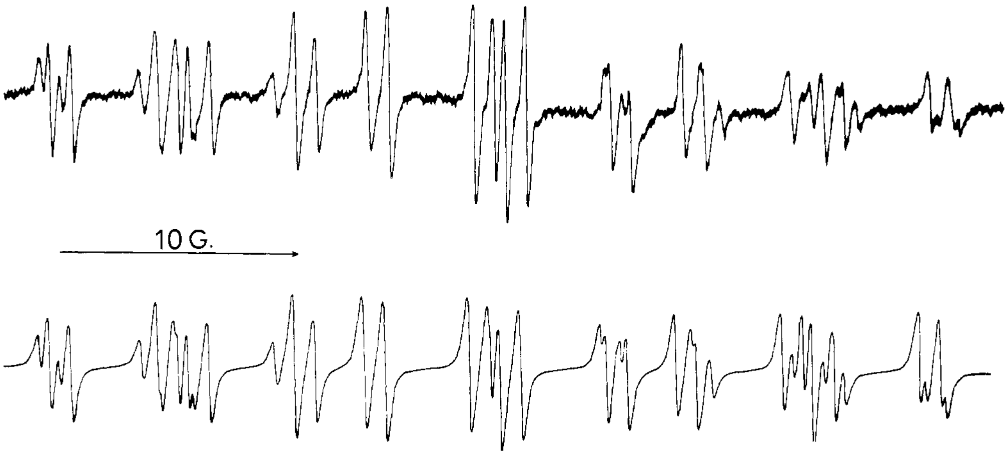
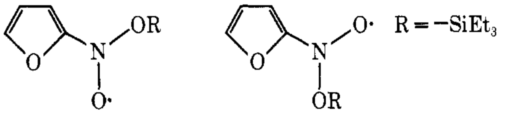


Figure 1. Experimental (upper) and computed esr spectrum of III at −60° showing the existence of two rotational isomers. The hyperfine splitting constants are given in Table I, the intensity ratio of the two species is 7:3, the line width is 0.23 G, and the difference between the two centers of the spectra is 0.10 G.

nitrofuran anion (I) (*i.e.*, one a_N and three a_H couplings) was observed. By lowering the temperature, however, a line width broadening effect was observed and at −60° two well-resolved spectra, corresponding to two different radicals, were detected, their relative intensity being 7:3 (Figure 1).

As the phenomenon appears to be reversible, the two groups of signals were attributed to rotational isomers having respectively the -OR group trans or cis with respect to the heterocyclic oxygen.



trans cis

The two rotamers have rather similar proton splittings and *g* values, the more stable having the center of its spectrum shifted downfield with respect to that of the less stable by only 0.10 G. As the a_H values are not too different from those of the nitro anion (I), the assignment to the various positions has been made assuming af analogous trend.

It is clear that a restricted rotation exists in aromatic alkoxy nitroxides, as already observed in phenyl nitroxide,[7] and that most likely the same can be inferred for the radical anions of nitro aromatics.

The study is being pursued on the more stable thiophene analog which give the same effect.[8]

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Registry No.—I, 34480-16-5; II, 34480-15-4; III, 51108-28-2.

References and Notes

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Vapor-Phase Introduction of Vinyl Ketones in Michael Additions

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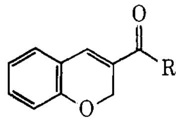
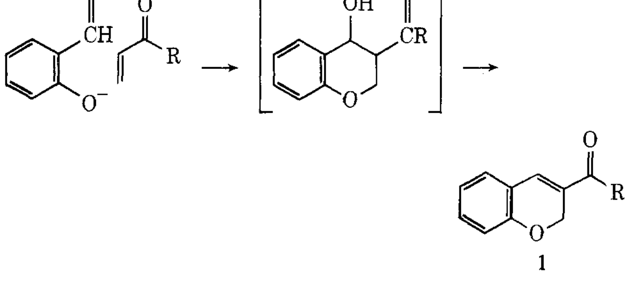
In a study of the photochemistry of some structurally related, unsaturated ketones,[1] the chromenes 1 were needed.



1a, R = H
b, R = CH_3
c, R = Ph
d, R = OH
e, R = OCH_3

Although chromenes **1d** and **1e** have been prepared[2] by the slow addition of sodium hydroxide to a refluxing mixture of salicylaldehyde and acrylonitrile (followed by hydrolysis), **1a–c** have never been reported. Attempts to prepare **1a–c** by the method of Taylor and Tomlinson[2] gave only polymeric mixtures. Attempts to convert **1d** to **1a**, **1b**, or **1c** by conventional reactions (Friedel-Crafts, Grignard, reduction, etc.) also failed, or at best gave poor yields with many side-products. It was then discovered that **1a** and **1b** can be prepared in good yield by stirring a mixture of salicylaldehyde and water with 0.1 equiv of base and introducing 1 equiv of the vinyl ketone (acrolein or methyl vinyl ketone) in the vapor phase in a stream of nitrogen. Apparently this dilution method of adding vinyl ketone prevents polymerization. The chromene is then isolated by simple crystallization or vacuum distillation.



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