acetonitrile at a rotating platinum electrode with 0.1 M tetra-n-propylammonium perchlorate as supporting electrolyte. Reductions were carried out at a dropping mercury electrode in dry (<0.01% water) N,N-dimethylformamide. An aqueous saturated calomel reference electrode was used throughout.

Preliminary fluorescence screening was done by dissolving a few milligrams of the compound in 1 ml of benzene and examining the resulting solution with a Blak-Ray UVL-22 lamp (Ultraviolet Products, Inc.)

Fluorescence spectra, ECL emission spectra, and quantum yield measuremnts were made on a combination radiometer–fluorimeter incorporating a Bausch and Lomb grating monochromator and an Aminco amplifier with a IP21 photomultiplier tube. The details of the fluorescence spectral measurements and quantum yield techniques are described elsewhere.[42] The ECL spectra were measured in a Pyrex cell containing two 80 mesh platinum gauze electrode 1 in. in diameter which were set 2 mm apart. One electrode was set against a flat glass surface of the cell whose total volume was 3.0 ml. Enough fluorescer and tetra-n-butylammonium perchlorate (Southwestern Analytical Co.) were added to make the resulting solution 0.005 M in the former and 0.1 M in the latter. In a nitrogen atmosphere, dry N,N-dimethylformamide was added to fill the cell which was then closed with a Ŧ 14/20 stopper. The cell was placed in the combination radiometer–fluorimeter and approximately 5 v rms was placed across the electrodes with a variable transformer. The voltage setting was adjusted slightly to obtain maximum ECL emission and the spectrum was recorded. The same cell was also used to check the fluorescence spectra although reflection of the excitation light (from a G.E. F4T5/BLB fluorescent tube) by the platinum gauze caused some irregularity and this method could not be employed for accurate fluorescence spectra.

The cyclic voltammetry was carried out using an operational amplifier-based three-electrode electronic polarograph, and polarographic cells of conventional design. The ion-radical lifetimes were measured as the time it takes to go from the polarographic peak of the process in which the ion in question is formed to the peak of the reverse process at a scan rate adjusted so that the reverse peak is just detectable.

Registry No.—1-Methoxynaphthalene, 2216-69-5; 2-methoxynaphthalene, 93-04-9; 1,3-dimethoxynaphthalene, 10075-61-3; 1,4-dimethoxynaphthalene, 10075-62-4; 1,5-dimethoxynaphthalene, 10075-63-5; 1,6-dimethoxynaphthalene, 3900-49-0; 1,7-dimethoxynaphthalene, 5309-18-2; 1,8-dimethoxynaphthalene, 10075-66-8; 2,3-dimethoxynaphthalene, 10103-06-7; 2,6-dimethoxynaphthalene, 5486-55-5; 2,7-dimethoxynaphthalene, 3469-26-9; 1,4,5,8-tetramethoxynaphthalene, 10075-68-0; 1-dimethylaminonaphthalene, 86-56-6; 1,5-bis(dimethylamino)naphthalene, 10075-69-1; 2-dimethylaminonaphthalene, 2436-85-3; 2,6-bis(dimethylamino)naphthalene, 10075-70-4; 2,7-bis(dimethylamino)naphthalene, 10075-71-5; 1-(methylthio)naphthalene, 10075-72-6; 2-(methylthio)naphthalene, 7433-79-6; 1,4-bis(methylthio)naphthalene, 10075-73-7; 1,5-bis(methylthio)naphthalene, 10075-74-8; 1,8-bis(methylthio)naphthalene, 7343-31-9; 2,3-bis(methylthio)naphthalene, 10075-76-0; 2,6-bis(methylthio)naphthalene, 10075-77-1; 2,7-bis(methylthio)-naphthalene, 10075-78-2; 1,4,5,8-tetraphenylnaphthalene, 5710-05-4; 1,5-dimethoxy-4,8-bis(methylthio)-naphthalene, 10075-80-6; 1,5-dimethoxy-4,8-diphenoxynaphthalene, 10075-81-7; 9-methoxyanthracene, 2395-96-2; 9,10-dimethoxyanthracene, 2395-97-3; 9,10-bis(methylthio)anthracene, 10075-83-9; 9,10-bis(2,6-dimethoxyphenyl)anthracene, 10075-84-0; 9,10-bis-(phenylethynyl)anthracene, 10075-85-1; 9,10-diphenoxyanthracene, 10075-86-2; 4-methoxybiphenyl, 613-37-6; 4,4′-dimethoxybiphenyl, 2132-80-1; 3,3′-dimethoxybiphenyl, 6161-50-8; 2,2′-dimethoxybiphenyl, 4877-93-4; 4,4′-bis(methylthio)biphenyl, 10075-90-8; 3,3′-bis(methylthio)biphenyl, 10075-91-9; 2,2′-bis(methylthio)biphenyl, 7343-32-0; N,N′-tetramethylbenzidine, 366-29-0; 10,10′ dimethoxy-9,9′-bianthracenyl, 10294-75-4; 1,6-bis(dimethylamino)pyrene, 10075-93-1; 1,6-dimethoxypyrene, 10103-10-3; 1,6-bis(methylthio)-pyrene, 10075-94-2; naphthalene, 91-20-3; anthracene, 120-12-7; biphenyl, 92-52-4; pyrene, 129-00-0; 9,10-dihydro-9,10-dihydroxy-9,10-bis(2,6-dimethoxyphenyl)-anthracene, 10075-95-3.

Acknowledgment.—We wish to thank W. H. Jura for the polarograms and J. E. Lehnsen for the computations. Thanks are also due to G. W. Kennerly, A. K. Hoffmann, and D. L. Maricle for helpful discussions.

---

[42] *Cf.* M. M. Rauhut, D. Sheehan, R. A. Clarke, B. G. Roberts, and A. M. Semsel, *J. Org. Chem.*, **30**, 3587 (1965).

Nitrocyclopentadiene

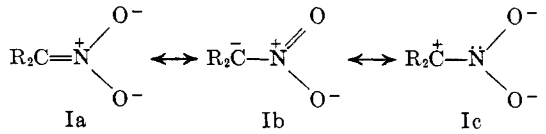
Robert C. Kerber and Marshall J. Chick

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790

Received November 2, 1966

The spectral and chemical properties of the sodium salt of nitrocyclopentadiene have been investigated. Protonation occurs to give the conjugated isomer, 1-nitrocyclopentadiene, as the only simple product.

The structure of salts of nitroalkanes has been extensively studied in recent years by a variety of techniques, including ultraviolet,[1] infrared,[2] and nmr[3] spectroscopy, and, in one case, by X-ray crystallography.[4] These methods uniformly demonstrate that the structure of such salts is best represented by the formula Ia, with only small contributions from Ib and Ic. This is consistent with the chemical properties of



Ia Ib Ic

these salts, which invariably react most rapidly at oxygen with acids and other electrophiles, although thermodynamic control generally favors reaction at carbon.

An exception to the general rule that the carbon-protonated true nitro compound is more stable than

---

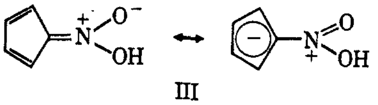
[1] W. Kemula and W. Turnowska-Rubaszewska, *Roczniki Chem.*, **37**, 1597 (1963).

[2] (a) H. Feuer, C. Savides, and C. N. R. Rao, *Spectrochim. Acta*, **19**, 431 (1963); (b) Z. Buczkowski and T. Urbanski, *ibid.*, **18**, 1187 (1962); (c) N. Jonathan, *J. Mol. Spectry.*, **7**, 105 (1961); references therein.

[3] (a) A. A. Griswold and P. S. Starcher, *J. Org. Chem.*, **30**, 1687 (1965); (b) S. Brownstein, *ibid.*, **28**, 2919 (1963).

[4] D. J. Sutor, F. J. Llewellyn, and H. S. Maslen, *Acta Cryst.*, **7**, 145 (1954).

the oxygen-protonated *aci* form is found in the case of 9-nitrofluorene. Nenitzescu and Isacescu[5] showed by bromination studies that protonation of the potassium salt of 9-nitrofluorene occurs only on oxygen to give the stable 9-*aci*-nitrofluorene (II). This has been confirmed by its infrared and ultraviolet spectra.[6,7] The product of protonation of the potassium salt of 1-nitroindene has similarly been ascribed the *aci* structure,[8] for reasons that are unclear.

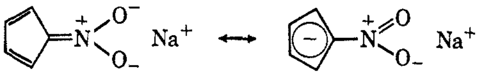


III

The unusual stability of the *aci* form relative to the nitro form in these cases may be a function of the extraordinary acidity of the latter. If so, then *aci*-nitrocyclopentadiene (III), which is tautomeric with the presumably more acidic nitrocyclopentadiene (*cf.* the pK_a values of the hydrocarbons: cyclopentadiene, 15; indene, 18.5; fluorene, 22.9),[9] should be still more stable in this sense. However, III is also closely related in structure to the unstable compound, cyclopentadienone,[10] and may show some of the extraordinary reactivity of that compound.

For these reasons, and because of the current interest in substituted cyclopentadienes and their anions,[11] we thought it worthwhile to reinvestigate the structure of nitrocyclopentadienide ion and its position(s) of protonation.

Sodium nitrocyclopentadienide (IV) was first prepared by Thiele in 1900, by reaction of sodium cyclopentadienide with ethyl nitrate in ethanol.[12] It has also been obtained more recently by reaction of ferrocene with sodium ethoxide and ethyl nitrate[13] and by electroreduction of nitroferrocene.[14]



IVa IVb

Sodium Nitrocyclopentadienide (IV).—The sodium salt was obtained by the method of Thiele,[12] in yields of 16–21%, as an amorphous, red-brown precipitate, which darkened only slightly on standing for 1 month in a desiccator over potassium hydroxide; the spectra remained unchanged over this period.

The ultraviolet spectrum of the salt IV in water shows two peaks, at 232 mμ (ϵ 4300) and at 362 mμ (ϵ 12,200). This is not unlike the spectrum of the isoelectronic 2-nitrofuran, which absorbs at 225 mμ (ϵ 3400) and 315 mμ (ϵ 8100).[15] Similarly, the long-wavelength absorption of 2-nitropyrrole appears at 370 mμ (ϵ 4000); in base, this shifts to 390 mμ (ϵ 15,000).[16]

The infrared spectrum of IV, in Nujol or hexachlorobutadiene mulls, shows a number of strong peaks, (see the Experimental Section). One can assign the 1548-cm^{-1} peak as a C=N stretching frequency (compared with about 1603–1579 cm^{-1} in ordinary nitro salts),[2a] and the strong peaks at 1368 and 1192 + 1175 cm^{-1} (doublet) as the $=NO_2^-$ stretching frequencies. These frequencies are somewhat higher than those in normal secondary nitroalkane salts (1295–1299 and 1164–1168 + 1140–1153 cm^{-1}).[2a] The latter band is frequently split owing to crystal effects,[2a] as it is in IV. If these assignments are correct, they confirm to some extent the lower bond order of the C—N bond and the higher bond order of the N—O bonds to be expected if IVb contributes more to the ground state of IV than Ib does to I in less delocalized salts.

The 60-MHz proton magnetic resonance spectrum of the ion IV in D_2O shows a symmetrical AA'BB' pattern; the low-field component is centered at about τ 3.46, the high-field component being at 3.72. By comparison with a number of model compounds (see Table I), the low-field resonance can be assumed with confidence to be due to the 2 and 5 protons, the higher field resonance being due to those at the 3 and 4 positions. The deshielding of the latter protons, which are too far removed from the nitro group to be subject to its anisotropic effects, with respect to sodium cyclopentadienide (τ 4.38),[17] tends to confirm that the nitro group removes a considerable amount of negative charge from the ring.[18]

Sodium nitrocyclopentadienide (IV) is very soluble in water, dissolving rapidly to give a deep red-brown solution of nearly neutral pH. Quantitative estimation of the pK_a of nitrocyclopentadiene is not possible, but it must be less than 0.

On standing over prolonged periods in D_2O, the 2 and 5 protons of the salt IV slowly exchange with the solvent, as seen by decrease in the size of the downfield multiplet of the nmr spectrum relative to the upfield multiplet. This exchange has a half-life of about 10 days at 5°, and shows that, as between the 2 and 3 positions, *kinetically controlled* protonation of the anion IV occurs at the 2 position.

Nitrocyclopentadiene.—Acidification of an aqueous solution of IV with mineral acid is accompanied by evolution of a colorless gas, and the formation of a voluminous, brown-black precipitate. If the mixture is rapidly extracted with carbon tetrachloride, it is possible to obtain a dilute solution of monomeric nitrocyclopentadiene suitable for spectral study. The

---

[5] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, **63**, 2484 (1930).

[6] J. P. Freeman and K. S. McCallum, *J. Org. Chem.*, **21**, 472 (1956).

[7] More recently, C. D. Nenitzescu and I. G. Dinulescu [*Bull. Acad. Sci. USSR Div. Chim. Sci.*, 1185 (1958); *Izv. Akad. Nauk SSSR, Otd. Khim Nauk*, 1228 (1958)] have claimed that the true nitro form may predominate in nonpolar solvents, although the *aci* form predominates in the crystal and in polar solvents.

[8] W. Wislicenus and K. Pfeilsticker, *Ann.*, **436**, 36 (1924).

[9] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 19.

[10] E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **88**, 3433, 3434 (1966), and references therein.

[11] See, for example: (a) O. W. Webster, *ibid.*, **88**, 3046 (1966); (b) K. Hafner, *et al.*, *Ann.*, **678**, 39 (1964); (c) D. Peters, *J. Chem. Soc.*, 1832 (1960).

[12] J. Thiele, *Ber.*, **33**, 670 (1900).

[13] A. I. Titov, E. S. Lisitsyna, and M. R. Shemtova, *Dokl. Akad. Nauk SSSR*, **130**, 341 (1960); *cf. Chem. Zentr.*, **133**, 6013 (1961).

[14] A. M. Hartley and R. E. Visco, *Anal. Chem.*, **35**, 1871 (1963).

[15] R. F. Raffauf, *J. Am. Chem. Soc.*, **72**, 753 (1950).

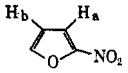
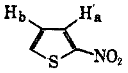
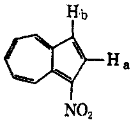
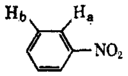
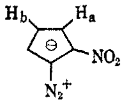
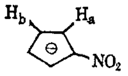
[16] S. S. Novikov, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, 1438 (1959).

[17] S. McLean and P. Haynes, *Can. J. Chem.*, **41**, 1231 (1963).

[18] Assuming a shift of 1 ppm to be equivalent to a change in the π-electron density of about 0.1 electron, and assuming similar ring currents in cyclopentadienide and in IV, one concludes that the 3 and 4 carbons each lose about 0.066 electron on nitration of sodium cyclopentadienide. If the 1, 2, and 5 carbons did likewise, then the negative charge would reside about two-thirds in the ring and one-third on the nitro group. In reality, a greater portion probably goes to the nitro group, owing to its greater electron-attracting influence on the 1, 2, and 5 positions than on the 3 and 4 positions. *Cf.* J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall Co., Inc., Englewood Cliffs, N. J., 1965, pp 88, 89.

TABLE I

NMR DESHIELDING BY THE NITRO GROUP IN SOME UNSATURATED COMPOUNDS

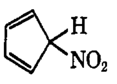
Compd	Deshielding due to nitro group[a] H_a	H_b	Ref
	0.98	0.29	b, c
	0.87	0.10	d, c
	0.60	0.09	e
	0.95	0.15	c
	1.1	0.2	f
	0.92 (assumed)	0.66 (assumed)	This work, g

[a] Difference in chemical shift between nitrated and nonnitrated compound, in parts per million (ppm) to *lower* field. [b] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961). [c] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall Co., Inc., Englewood Cliffs, N. J., 1965, pp 88, 89. [d] S. Gronowitz and R. A. Hoffmann, *Arkiv. Kemi.*, **13**, 279 (1958). [e] D. Meuche and E. Heilbronner, *Helv. Chim. Acta*, **45**, 1965 (1962). [f] D. J. Cram and R. D. Partos, *J. Am. Chem. Soc.*, **85**, 1273 (1963). [g] Reference 17.

material is relatively stable in dilute solution, as evidenced by the fact that the infrared and nmr spectra remained unchanged for at least 24 hr. Attempts to obtain pure material by evaporating the solvent at room temperature were unsuccessful.

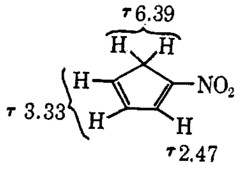
The brown-black precipitate was insoluble in water, alcohols, or nonpolar solvents, but soluble in dipolar aprotic solvents. An infrared spectrum of this material, after drying it in a desiccator, showed hydroxyl, carbonyl, and nitro bands. On the chance that this material derives in part from Nef reaction[19] of IV, which should yield the highly reactive cyclopentadienone[10] and higher molecular weight materials derived therefrom, acidification of the salt IV with acetic acid, which should minimize the Nef reaction[20] was attempted. Only traces of nitrocyclopentadiene were produced, presumably because acetic acid is insufficiently acidic to protonate IV substantially. However, a brown-black precipitate identical with that produced from strong acids slowly formed.

The infrared spectrum of nitrocyclopentadiene in carbon tetrachloride shows strong nitro group absorptions at 1513 and 1365, as well as a weak diene C=C stretch at 1595 and a *cis*-olefin band at 680 cm^{-1}. These features eliminate not only the *aci* structure III,[21] but also the unconjugated structure V, since the nitro group absorptions are more typical of a conjugated nitroalkene than of a secondary nitroalkane.[22]

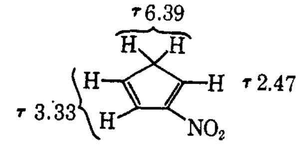


V

Confirmation of this conclusion is obtained from the 60-MHz nmr spectrum, which shows a one-proton triplet (J = 1.9 Hz) at τ 2.47, a two-proton unresolved multiplet at 3.33, and another two-proton unresolved multiplet at 6.39. We feel that this spectrum is more consistent with structure VI than with structure VII because (a) the chemical shift of the methylene group is 0.7 ppm downfield from that in cyclopentadiene itself;[23] this is more consistent with the nitro group being located on the adjacent carbon rather than two carbons removed, as in VII; (b) conversely, the two-proton vinyl multiplet is only slightly downfield from the τ 3.57 of cyclopentadiene,[23] this suggests that the unsubstituted double bond is relatively far removed from the deshielding effect of the nitro group, as in VI; (c) the 1.9-Hz coupling constant between the methylene group and the proton at τ 2.47 is more consistent with the grouping $CH_2C{=}CH$ than the grouping CH_2-$CH{=}C$;[24,25] (d) protonation to form VI is consistent with the observation that the hydrogens adjacent to the nitro group in the salt IV exchange with D_2O, if not exclusively, at least much more rapidly than the remaining protons. An ultraviolet spectrum of VI was obtained by acidifying a 10^{-5} M aqueous solution of IV with 1 drop of acid. No precipitate formed. The solution showed a broad maximum at 327 mμ (ϵ 8300, assuming complete conversion of IV to VI). This is in good agreement with the value 309 mμ (ϵ 10,000) reported for 2-nitro-2,4-hexadiene,[26] especially when allowance is made for the shift to longer wavelength attendant on constraining a diene system within a ring.[27]



VI



VII

In summary, the spectra strongly suggest that the only stable product of protonation of the nitrocyclo-

---

(19) N. Kornblum and R. A. Brown, *J. Am. Chem. Soc.*, **87**, 1742 (1965), and references therein.

(20) N. Kornblum and G. E. Graham, *ibid.*, **73**, 4041 (1951).

(21) 9-*aci*-Nitrofluorene shows no strong NO_2 band in the 1500–1600-cm^{-1} region, but shows instead a C=N absorption at 1652 cm^{-1}; *cf.* ref 6.

(22) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 68.

(23) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

(24) Reference 18, p 99.

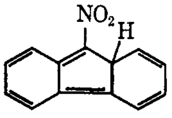
(25) (a) O. W. Webster[11a] has recently reported, principally on the basis of an nmr spectrum very similar to that above, that the product of protonation of cyanocyclopentadienide ion by trifluoroacetic acid is the cross-conjugated 2-cyanocyclopentadiene rather than the linearly conjugated 1-cyanocyclopentadiene, analogous to our VI. For the same reasons as those cited herein, we feel that in fact he has obtained the 1 isomer. This is confirmed by his ultraviolet spectrum, which showed λ_{max} 268 mμ (log ϵ 3.90). 1-Cyanocyclopentadiene had been prepared by Peters[11c] by cracking the Diels–Alder dimer; the 1-cyano assignment was made by comparing the ultraviolet spectrum, λ_{max} 266 mμ (log ϵ 3.81), with that of sorbonitrile, $CH_3CH{=}CHCH{=}CHCN$, λ_{max} 254 mμ (log ϵ 4.43). (b) Dr. Webster has confirmed that his product and that of Peters are identical, and has shown it to be 1-cyanocyclopentadiene by its 100-MHz proton nmr spectrum, with decoupling of the allylic protons: O. W. Webster, personal communication.

(26) A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962).

(27) Reference 18, p 14.

pentadienide ion IV is 1-nitrocyclopentadiene. No direct evidence of the *aci* compound III was obtained, though it may be an intermediate in the production of the voluminous, brown-black precipitate (probably polymeric) which is formed on protonation of solutions of the salt.

The results of this work are not strictly comparable with those in the 9-nitrofluorene system, since, unlike nitrocyclopentadiene, the former cannot give a conjugated nitro compound such as VIII without substantial loss in delocalization energy. However, it is probable that *aci*-nitrocyclopentadiene (III) does not show any extraordinary stability.



VIII

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord Model 137B, calibrated with a polystyrene film. Ultraviolet–visible spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Proton magnetic resonance spectra were obtained on Varian A-60 and HR-100 spectrometers; chemical shifts are reported as τ values relative to tetramethylsilane as internal standard (τ 10.00).

Sodium Nitrocyclopentadienide.—Sodium metal (10.0 g, 0.435 g-atom) was dissolved in 200 ml of absolute ethanol. The solution was cooled to 0°, and nitrogen was bubbled through the solution, then 29.1 g (0.44 mole) of freshly distilled cyclopentadiene and 40.0 g (0.44 mole) of ethyl nitrate were added. The solution was stirred under nitrogen for 2 hr, then stripped to a 100-ml total volume on a rotatory evaporator at less than 40°. The mixture was filtered, and the precipitate was washed with benzene, and vacuum dried for 36 hr. Addition of 100 ml of pentane to the filtrate produced no further precipitate. There was obtained 9.50 g of red-brown sodium nitrocyclopentadienide (16%). A number of preparations of the salt gave yields of 16–21%.

The salt is relatively stable; its color darkens somewhat after 1 month of storage in a desiccator over potassium hydroxide. The infrared and nmr spectra remain unchanged over this period. On heating, it darkens at about 220°, but does not melt below 300°.

The ultraviolet spectrum in water shows absorptions at 232 mμ (ϵ 4300) and 362 mμ (ϵ 12,200). The infrared spectrum in Nujol or hexachlorobutadiene mulls shows peaks at 3333 (w), 3106 (w), 2933 (w), 1618 (m), 1565 and 1548 (s), 1447 (w), 1368 (s), 1255 (s), 1192 and 1175 (s), 1155 (w, sh), 1079 (m), 985 (m), 903 and 892 (m), 735 (m), 694 (m). The 60-MHz nmr spectrum in D_2O shows a symmetrical AA'BB' pattern, the two halves being centered at τ 3.46 and 3.72. The over-all width is about 30 Hz. A 100-MHz spectrum was also obtained in D_2O, and calibrated by use of side bands of the residual water resonance at 473 Hz downfield from TMS; the spectrum approached that of an AA'XX' system, with ten lines detectable in each half of the spectrum; the centers of the two multiplets fell at τ 3.46 and 3.74.

A 0.10 *M* solution of the salt (IV) in water yielded a nearly neutral solution. On standing in D_2O, the intensity of the low-field multiplet in the nmr spectrum decreased relative to that of the high-field multiplet. The data are given in Table II.

TABLE II

EXCHANGE OF PROTONS IN IV BY NMR AT 5°

Time, days	Integral, H_3/H_2
0	1.03
4	1.46
7	1.66
10	1.92
14	2.78

Nitrocyclopentadiene (VI).—A 0.25-g sample of IV was dissolved in 25 ml of water, 2 ml of carbon tetrachloride was added, and the solution was acidified with concentrated HCl. A voluminous, brown-black precipitate formed in the water layer and a colorless gas was evolved. The mixture was shaken, and the carbon tetrachloride layer was removed by pipet after the layers had separated. An infrared spectrum of the carbon tetrachloride layer showed peaks at 3330 (m, b), 1595 (w), 1513 (s), 1490 (s), 1376 (m), 1355 (s), 1292 (m), 990 (w), 952 (w), 895 (w), 680 (m). A 60-MHz proton magnetic resonance spectrum showed a triplet (J = 1.9 Hz, area 1.00) at τ 2.47, a multiplet at 3.33 (area 2.12), and another multiplet at 6.39 (area 1.99).

Similarly, a 9.6×10^{-6} *M* solution of the salt IV in water was acidified with 1 drop of 10% sulfuric acid, and the ultraviolet spectrum was recorded; a broad, featureless peak at 327 mμ was observed. No precipitate appeared. Assuming complete conversion of salt to the protonated form (another drop of acid produced no further spectral change), the ϵ was 8300.

A sample of salt IV (0.140 g) was dissolved in 50 ml of water to give a *ca.* 0.02 *M* solution, and then 0.0860 g of hexamethylbenzene in 5 ml of carbon tetrachloride was added. The solution was acidified with hydrochloric acid. The mixture was shaken, and the lower layer was removed. The ratio between the integrals of the τ 7.85 nmr peak of the standard and the τ 6.39 peak of nitrocyclopentadiene observed in the carbon tetrachloride solution was 8.50; this shows that nitrocyclopentadiene was produced in 53% yield (±5%). The conversion is lower when higher initial concentrations of the salt are used.

Attempted Isolation of Nitrocyclopentadiene.—Solutions of VI in carbon tetrachloride or methylene chloride, prepared by the above procedure, were stripped of solvent at room temperature and reduced pressure. A yellow oil was obtained which rapidly darkened on standing. It did not redissolve in methylene chloride or carbon tetrachloride, and gave a different infrared spectrum from the original solutions.

Precipitate from Acidification of IV.—Attempts to prepare VI by acidification of 1 *M* salt solution, followed by CCl_4 extraction, failed to yield the spectra of VI in the organic layer. A brown-black precipitate, which gave an infrared spectrum identical with that of the sample above, and a colorless gas were the only apparent products. The precipitate was dried in a desiccator over KOH, and the infrared spectrum was determined as a Nujol or hexachlorobutadiene mull. Peaks were observed at 3330 (s), 1710 (w), 1550 (m), 1350 (m), 950 (b, w), and 720 (w) cm^{-1}. The material did not melt below 250°, and was insoluble in water, alcohols, and nonpolar solvents. It was soluble in acetone and dimethyl sulfoxide. An nmr spectrum in acetone showed only a multiplet at τ 6.9, in addition to the solvent resonances.

An attempt to prepare VI by acidification of an aqueous solution of IV with glacial acetic acid also failed to yield the characteristic spectra of VI in the carbon tetrachloride layer. A precipitate similar to the above was slowly produced. Addition of the salt to trifluoroacetic or sulfuric acids also produced only a black precipitate; nmr spectra of the black filtrates revealed only solvent resonances.

Some Further Reactions of IV.—An attempt to prepare bromonitrocyclopentadiene by addition of 1 equiv of bromine to an aqueous solution of IV, followed by carbon tetrachloride extraction, yielded no observable spectra. A brown-black precipitate was produced, which showed an infrared spectrum very similar to those of the precipitate from acidification of IV; this may have been caused by formation of HBr in the initial reaction of bromine with IV.

Aqueous solutions of IV were found to interact with transition metal ions, though IV is alleged not to form 1,1'-dinitroferrocene on treatment with ferrous chloride.[13] Treatment with cupric sulfate produces a deep olive-green color; ferric chloride produces a brown precipitate; mercuric acetate gives a yellow precipitate.

Registry No.—IVa, 10236-20-1; VI, 10236-21-2.

Acknowledgment.—We wish to thank Dr. Peter Wells for his assistance in obtaining the 100-MHz proton magnetic resonance spectrum.