

Proceedings of the Iowa Academy of Science

Volume 89 | Number

Article 12

1982

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Recommended Citation

Wawzonek, S.; Hansen, G. R.; and Mudder, T. (1982) "NMR Spectra of 2-p-Nitrophenylindenone," *Proceedings of the Iowa Academy of Science*: Vol. 89: No. 2 , Article 12.
Available at: <https://scholarworks.uni.edu/pias/vol89/iss2/12>

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NMR Spectra of 2-p-Nitrophenylindenone

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Proton and C-13 NMR spectral studies of 2-p-nitrophenylindenone indicate that some polarization is present in this compound which would explain its stability to the dimerization that is observed with 2-phenylindenone. Assignment of frequencies in these spectra was based on intensities of signal and comparison with the spectra of 2-p-nitrophenyl-3-phenyl-2-propenenitrile, 2,3-diphenylindenone and the sodium methoxide addition products of 2-p-nitrophenylindenone and 2-p-nitrophenyl-3-phenyl-2-propenenitrile.

INDEX DESCRIPTORS: 2-Arylindenones, Dimerization, NMR Spectra.

2-p-Nitrophenylindenone (1) is a unique compound in that it is stable in contrast to 2-phenylindenone, which is not known; all attempts to prepare the latter have led to dimerization by a Diels-Alder reaction.¹

The purpose of the present work was to see whether NMR spectral studies could explain the stability of this compound (1). To aid in the interpretation of the ¹H and ¹³C NMR spectra studies were also carried out with the sodium deuteromethoxide adduct of 2-p-nitrophenylindenone (3), 2-p-nitrophenyl-3-phenyl-2-propenenitrile (2), its sodium deuteromethoxide adduct 4 and 2,3-diphenylindenone (7).

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Bruker HX-90 Fourier transform NMR spectrometer operating at 90 MHz and 22.63 MHz.

2-p-Nitrophenylindenone (1) was prepared by the cyclization of 2-p-nitrophenyl-3-phenyl-2-propenenitrile.² NMR(DCON(CD₃)₂) δ 7.32-7.56(m, 4H, 4-, 5-, 6-, 7-Hs), δ 8.12(d, 2H, 2', 6'-Hs, J = 9.4 Hz), δ 8.33(d, 2H, 3', 5'-Hs, J = 9.4 Hz), δ 8.43(s, H, 3-H).

The sodium deuteromethoxide adduct 3 was prepared in an NMR tube by treating the indenone 1 in deuterated dimethylformamide with a slight excess of sodium deuteromethoxide in deuteromethanol. This adduct is stable to water and can be formed even using sodium hydroxide in water. The structure under these conditions would have a hydroxyl group in place of the methoxyl group on the 3-carbon.

NMR δ 5.45(s, 1H, 3-H), δ 7.20-7.70(m, 4H, 4-, 5-, 6-, 7-Hs), δ 7.95(d, 2H, 2', 6'-Hs, J = 9.6 Hz), δ 8.15(d, 2H, 3', 5'-Hs, J = 9.6 Hz).

2-p-Nitrophenyl-3-phenyl-2-propene-nitrile (2) was prepared by the condensation of benzaldehyde with p-nitrobenzylcyanide.³ NMR(DCON(CD₃)₂) δ 8.00-8.19(m, 3H, m and p Hs in 3-phenyl), δ 8.11(d, 2H, 2', 6'-Hs in 2-p-nitrophenyl (J = 9.1 Hz)), δ 8.41(d, 2H, 3', 5'-Hs in 2-p-nitrophenyl (J = 9.1 Hz)), δ 8.00-8.19(m, 2H, o-Hs in 3-phenyl), δ 8.44(s, 1H, 3-H).

The sodium deuteromethoxide adduct 4 was prepared directly in an NMR tube by treating 2 in DCON(CD₃)₂ with a slight excess of sodium deuteromethoxide in deuteromethanol. NMR δ 5.28(s, 1H, 3-H) δ 6.57-6.73(m, 2H, 3', 5'-H in C₆H₅), δ 7.35(d, 2H, 2', 6'-Hs in C₆H₄NO₂, (J = 9.8 Hz)), δ 7.14-7.58(m, 3H, 2', 4', 6'-Hs in C₆H₅), δ 7.56(d, 2H, 3', 5'-Hs in C₆H₄NO₂, (J = 9.8 Hz)).

This adduct is hydrolyzed by water and on standing undergoes decomposition.

2,3-Diphenylindenone (7) was prepared by the cyclization of α,α,β-triphenylacrylic acid with sulfuric acid.⁴

RESULTS AND DISCUSSION

The proton NMR spectrum of 1 (Fig. 1) in deuterated dimethylformamide showed the coupling constant for the

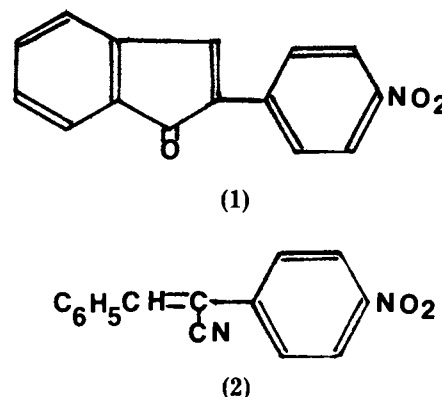


Figure 1. 2-p-Nitrophenylindenone (1) and 2-p-nitrophenyl-3-phenyl-2-propenenitrile (2).

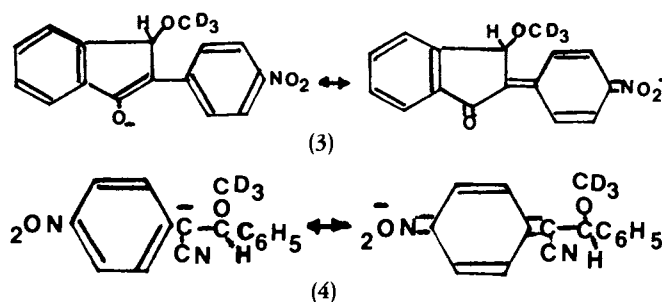


Figure 2. Sodium deuteromethoxide addition products 3, 4, of 2-p-nitrophenylindenone (1) and 2-p-nitrophenyl-3-phenyl-2-propenenitrile (2) respectively.

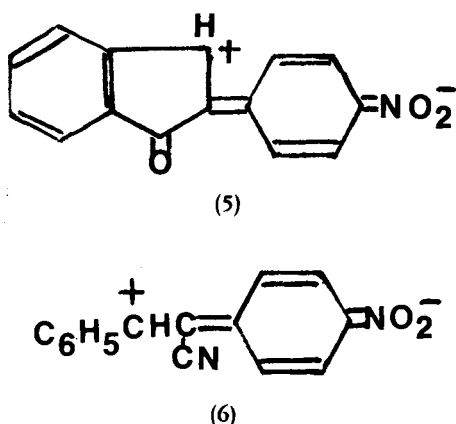


Figure 3. Resonance hybrid contributors (5,6) to the structure of 2-p-nitrophenylindenone (1) and 2-p-nitrophenyl-3-phenyl-2-propenenitrile (2) respectively.

hydrogens in the p-nitrophenyl group at δ 8.12 and 8.33 ppm to be 9.4 Hz. This value is slightly larger than that of 9.1 Hz for the corresponding hydrogens at δ 8.11 and 8.41 ppm in 2-p-nitrophenyl-3-phenyl-2-propenenitrile (2) (Fig. 1). The vinyl hydrogens in both examples have similar chemical shifts (8.43, 8.44 ppm). The latter assignment was based on the proton spectra of the dark red sodium salts (3,4) (Fig. 2) formed by treating 1 and 2 in deuterated dimethylformamide with sodium deuteromethoxide in deuterated methanol. The vinyl hydrogens in 1 and 2 after such treatment become benzylic in nature and resonate at δ 5.45 and 5.28 ppm respectively.

The spectrum for salt 3 showed a coupling constant of 9.6 Hz for the hydrogens in the p-nitrophenyl group at 7.95 and 8.15 ppm and for salt 4 gave a coupling constant of 9.8 Hz for the corresponding hydrogens at 7.35 and 7.56 ppm. The difference of 0.2 Hz between the coupling constant of 1 and 3 is smaller than the difference of 0.7 Hz found for the coupling constants of 2 and the salt 4 and suggests that structure 5 (Fig. 3) is a contributor to the structure of 1. The difference of 0.7 Hz between the coupling constants of 2 and 4 indicates that structure 6 (Fig. 3) is a lesser contributor to the structure of the nitrile 2.

Studies of 1 using C-13 NMR gave results which paralleled those found with proton NMR. Assignment of frequencies to the various carbons, shown in Fig. 4, was based on the intensities of the signals and comparison of the frequencies with values for 2,3-diphenylindenone (7), Fig. 5, and other model compounds.

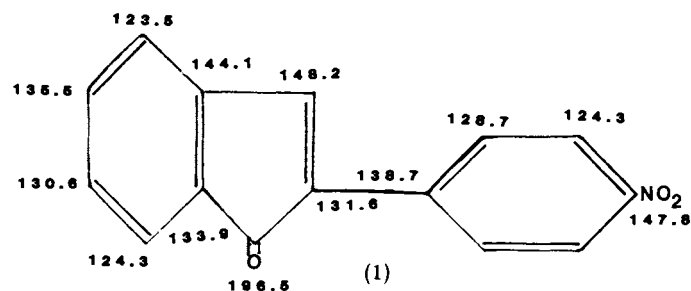


Figure 4. C-13 NMR frequencies of various carbon atoms in 2-p-nitrophenylindenone (1).

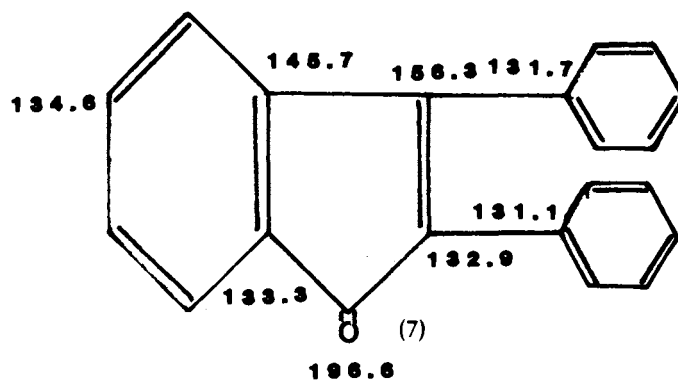


Figure 5. C-13 NMR frequencies of various carbon atoms in 2,3-diphenylindenone (7).

The chemical shift of values for 2,3-diphenylindenone (7) used were assigned on the basis of the intensities of the signals and comparison with related compounds such as 1-indanone and cinnamaldehyde.

The value of δ = 148.2 ppm was assigned to the 3-carbon in 1 and is about the same as the value for the corresponding vinyl carbon in 2 at 147.1 ppm but lower than the value of 156.3 ppm for the 3-carbon in 2,3-diphenylindenone (7) which has a phenyl substituent. The values for the carbon atoms in the cyclopentadienone moiety in 1 are in close agreement with the values for the same component in 7.

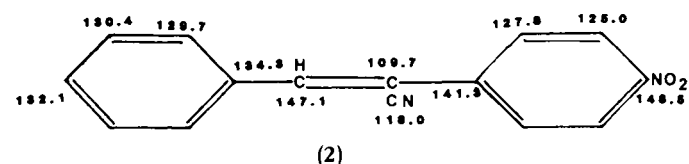


Figure 6. C-13 NMR frequencies of various carbon atoms in 2-p-nitrophenyl-3-phenyl-2-propenenitrile (2).

Assignment of values for the carbon atoms in the 2-p-nitrophenyl group in 1 was based on comparison with the frequencies for the corresponding carbons in the nitrile 2 (Fig. 6). The 1'-carbon in this ring at δ_c = 138.7 ppm and the 4'-carbon (with the nitro group) at 147.8 ppm are at a slightly lower frequency than the values for the corresponding carbons at 141.3 and 148.5 ppm in 2; this shift could be caused by polarization in 1 of the type shown in formula 5.

The C-13 NMR spectrum of the sodium derivative 3a (Fig. 7) gave the values shown. Assignments were based on intensities of the peaks and values reported for model compounds.

The structure is best represented by the resonance hybrids shown in Fig. 3. Evidence for the contribution of the enolate ion is the frequency for the carbonyl carbon at 179.0 ppm. The adjacent 2-carbon atom resonance occurs at 104.5 ppm which is larger than the value of 93 ppm reported⁵ for the corresponding carbon in dibenzoylmethane which is completely enolic. The values of 146.9 and 138.5 ppm were assigned to the bridge carbon in 3a and are higher than the values for the corresponding carbons in 1 and 7 but approach the values of 154.9 and 136.9 ppm reported for these carbons in 1-indanone.⁵

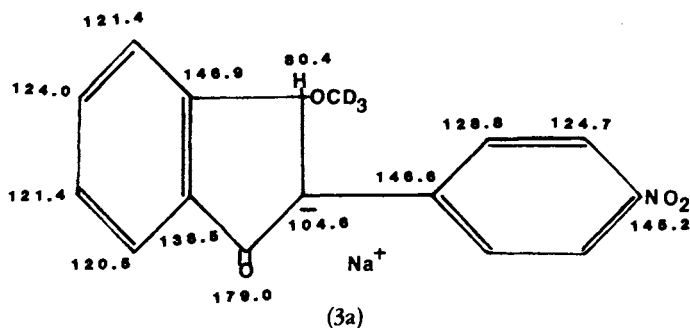


Figure 7. C-13 NMR frequencies of various carbon atoms in the sodium deuteriomethoxide adduct of 2-p-nitrophenylindenone (3a).

The larger polarization of the 2-p-nitrophenyl group in the salt 3a only lowers the frequency of the carbon atom attached to the nitro group to 145.2 ppm. This value is only slightly lower than the value of 147.8 ppm for the corresponding carbon in the ketone 1. The value of 148.8 ppm was assigned to the carbon atom attached to the five-membered ring on the basis of the similarity of this structure to that of p-nitroaniline⁶ which is highly polarized. In the latter the carbon attached to the nitro group resonates at 137.6 ppm and the carbon atom attached to the amino group at 157 ppm.

The frequencies for the 2', 3', 5', 6' carbons in the p-nitrophenyl group at 124.7 and 128.8 ppm in the salt do not vary greatly from the values of 124.3 and 128.7 ppm for the corresponding carbons in 1. This observation is in agreement with the small difference observed between the coupling constants for the hydrogens on these carbons in 1 and 3.

The sodium salt 4 gave a complex C-13 NMR spectrum and must undergo a reverse aldol during the two hours required for the recording of the spectrum.

The NMR results for 2-p-nitrophenylindenone (1) show slight but definite variations from normal expected values. This behavior can be attributed to the contribution of the polarized form 5 to the structure which would prevent involvement of this compound in a Diels-Alder reaction such as that observed with 2-phenylindenone.¹

ACKNOWLEDGMENT

The authors wish to express their appreciation to Dr. W. E. Bennett for his help in interpreting the C-13 NMR spectra.

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