**3-(2,2′,6-Bipyridyl)-*as*-triazino[5,6-f][4,7]-phenanthroline.**—A mixture of 1 g of 6-cyano-2,2′-bipyridine hydrazidine, 1 g of 4,7-phenanthroline-5,6-dione, and 30 ml of ethanol was refluxed 3 hr. The contents of the flask were then poured into water, and the precipitate was removed by filtration, dried, and crystallized from dimethyl sulfoxide, yielding 1.2 g of product melting at 369–370° (57.1%). An analytical sample, melting at 372°, was prepared by crystallization from dimethylformamide.

*Anal.* Calcd for $C_{23}H_{13}N_7$: C, 71.28; H, 3.88. Found: C, 71.66; H, 3.69.

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## The Structure of α-Nitro Ketones

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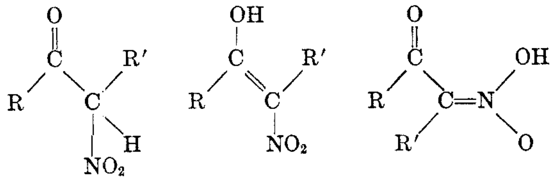
Based on work done in 1914[1] it has been thought that α-nitro ketones could best be represented by three tautomeric structures, Ia, b, and c.[2] This early work done by bromine titration indicated that α-nitroacetophenone existed in solution as a mixture of material of ketonic and enolic structures. The compound was found to be most enolic in toluene (10.3%) and least so in aqueous methanol (2.7%).



Ia Ib Ic

R = alkyl or aryl; R′ = alkyl or H

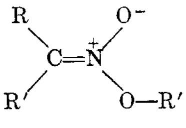
Using spectral techniques Campbell and Pitzer[3] have shown that 2-nitro-1-indanone is isolable as a pure nitro enol. These authors found that the pure enol partially isomerized on standing to a mixture of nitro ketone and nitro enol. Schaub, *et al.*,[4] have determined that 2α-nitro-17β-hydroxy-17α-methyl-5α-androstan-3-one and 2α-nitro-17β-hydroxy-5α-androstan-3-one are mixtures of material of nitro ketone and nitro enol structure. In addition, these workers showed that due to steric interactions the corresponding 4-nitro-3-keto and 16-nitro-17-keto steroids were not enolic. We would like to present data which demonstrates that in general acyclic α-nitro ketones exist in neutral media in the nitro ketone form Ia and that α-nitrocyclohexanone, representative of the cyclic compounds, which was isolatable in the nitro ketone form, isomerizes under mild conditions to a mixture of tautomers.

The proton magnetic resonance (pmr) spectra[5] of 1-nitro-2-pentanone, 2-nitro-3-pentanone, and 3-methyl-3-nitrobutanone in carbon tetrachloride of α-nitroacetophenone and α-nitrocyclohexanone[6] in deuteriochloroform and of α-nitroacetophenone in benzene show only the presence of material of nitro ketone structure. The neat pmr spectra of 1-nitro-2-pentanone, 2-nitro-3-pentanone, and α-nitropropiophenone also give no indication of the presence of enol or *aci*-nitro species in the system. In Table I is given the pmr data on the several α-nitro ketones.

The infrared spectra of the α-nitro ketones also indicated that only material of nitro ketone structure was present. The spectra were run neat and in carbon tetrachloride solution. In neither case was any absorption due to enolic OH observed, no absorption being found below 3.2 $\mu$. The principal absorptions of the compounds occurred at 5.76 $\mu$ ($\epsilon$ ~300) and 6.41 $\mu$ ($\epsilon$ ~800). These bands are assignable to the carbonyl stretching and the asymmetric nitro stretching vibrations of the molecules. The locations and intensities of these bands were unaltered in going from primary to secondary to tertiary α-nitro ketones.

Isomerization of α-nitrocyclohexanone was carried out either by heating [vacuum distillation at ~100° (0.1 mm)] or by passing the compound through a silica gel column. The other nitro ketones were stable to both the distillation and chromatography conditions. In addition, treatment of the acyclic nitro ketones with excess aqueous sodium hydroxide or excess triethylamine in carbon tetrachloride did not cause isomerization. The compounds were recovered unchanged.

In agreement with other workers[3,4] the infrared spectrum of the cyclic enol showed strong absorption at 6.14 $\mu$ and weak absorption at 6.55 $\mu$. Though the 6.14-$\mu$ band has been assigned[3,4] to olefin absorption it is equally consistent with C=N absorption. Kornblum[7] has found that nitronic esters II absorb in the region 6.05–6.2 $\mu$ and therefore no definite conclusion as to enol structure of the α-nitro ketones can be drawn. The pmr spectrum of the tautomeric mixture shows sharp absorption at $\tau$ −3.93. This has been assigned[4] to the OH proton of the nitro enol but is equally consistent with the *aci*-nitro ketone structure; *via* pmr the mixture was determined to be 30.6% enol.



II

R, R′ = H, alkyl or aryl; R″ = alkyl

The isomerization of the cyclic α-nitro ketone to an enolic structure is best interpreted in terms of the instability of the cyclic α-nitro ketone rather than to the stability of the enol. Stuart–Briegleb models indicate that there is severe crowding of the nitro and carbonyl groups in the boat and both chain conformers of the molecule; enolization alleviates this. Enolization also decreases the unfavorable electrostatic interactions between the two polar functionalities.

That the acyclic α-nitro ketones do not substantially exist in a stable enolic form is interpretable in terms of the known weak hydrogen bonding ability of aliphatic nitro compounds. It has been shown *via* infrared and ultraviolet spectra that aliphatic nitro groups form

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[1] K. H. Meyer and P. Wertheimer, *Ber.*, **47**, 2374 (1914).

[2] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p 633.

[3] R. D. Campbell and C. L. Pitzer, *J. Org. Chem.*, **24**, 1531 (1959).

[4] R. E. Schaub, W. Fulmor, and M. J. Weiss, *Tetrahedron*, **20**, 373 (1964).

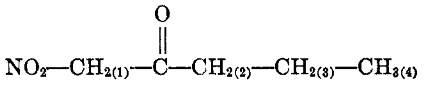
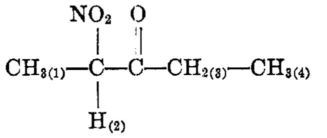
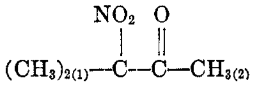
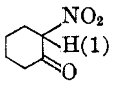
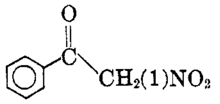
[5] It is estimated that an enol concentration of >1% would have been observable in both the pmr and infrared spectra. We have determined by neat pmr spectra that ethyl acetoacetate contains 7.5% enol. This is in excellent agreement with Burdett and Rogers [J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964)] who determined the compound to be 8% enolic.

[6] The pure nitro ketone isomer.

[7] N. Kornblum and R. A. Brown, *J. Am. Chem. Soc.*, **86**, 2681 (1964).

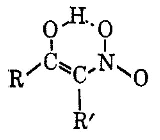
TABLE I

THE PROTON MAGNETIC RESONANCE SPECTRA OF α-NITRO KETONES

| Compound | Solvent | $\tau$[a] | Relative areas |
|---|---|---|---|
|  $NO_2-CH_{2(1)}-\overset{O}{\overset{\|}{C}}-CH_{2(2)}-CH_{2(3)}-CH_{3(4)}$ | $CCl_4$ | (1) 4.72, (2) 7.49<br>(3) 8.35, (4) 9.06 | ... |
|  | Neat | ... | (1) 2.00, (2) 1.96<br>(3) 2.16, (4) 2.88 |
|  $CH_{3(1)}-\underset{H_{(2)}}{\overset{NO_2}{C}}-\overset{O}{\overset{\|}{C}}-CH_{2(3)}-CH_{3(4)}$ | $CCl_4$ | (1) 8.32, (2) 4.73<br>(3) 7.40, (4) 8.89 | ... |
|  | Neat | ... | (1) 2.93, (2) 1.01<br>(3) 2.00, (4) 3.05 |
|  $(CH_3)_{2(1)}-\overset{NO_2}{C}-\overset{O}{\overset{\|}{C}}-CH_{3(2)}$ | $CCl_4$ | (1) 8.31, (2) 7.83 | (1) 5.95, (2) 3.06 |
|  | $DCCl_3$[b] | (1) 4.66 (multiplet)<br>(ring protons) multiplet<br>main peaks at<br>7.42 and 7.97 | (1) 0.95<br>(ring protons) 8.05 |
|  | $DCCl_3$[b] | (1) 4.08<br>(ring protons) multiplet<br>main peaks at<br>2.18 and 2.37 | (1) 2.05<br>(ring protons) 4.94 |

[a] All the signals had multiplicities and coupling constants consistent with the structural assignments. [b] The compound was insoluble in carbon tetrachloride.

weak hydrogen bonds[8] to proton donors. Schleyer[9] has suggested, to account for this weak hydrogen-bonding ability, that the nitro group is an electron-demanding rather than an electron-rich function. In light of this it is reasonable to expect that a hydrogen-bonded nitro enol (III) would not be stable relative to material of *trans* nitro ketone[10] structure and that this structure would not significantly contribute to the ground state of the molecule.



III, R = alkyl or aryl
R′ = alkyl or H

## Experimental Section

The alkyl α-nitro ketones were prepared by the method of Hurd and Nilson[11] and were purified by column chromatography on silica gel using 1:1 (v/v) methylene chloride–isohexane as eluent; see Table II for physical data. α-Nitrocyclohexanone,[6] mp 37.5–38.5° (lit.[12] mp 37°), was synthesized by chromic acid oxidation[11] of 2-nitrocyclohexanol prepared by the method of Levy and Scarfe.[13] It was purified by recrystallization from ether–pentane at −70°. Partial isomerization was effected by vacuum distillation[14] or column chromatography through silica gel using methylene chloride–isohexane as eluent. No attempt was made to determine the thermodynamic equilibrium composition.

TABLE II

| Compound | Bp or mp, °C | Found, %[a] C | H | N |
|---|---|---|---|---|
| 1-Nitro-2-pentanone | 31–31.5 | 45.72 | 6.85 | 10.47 |
| 2-Nitro-3-pentanone | 88 (10.5 mm)<br>lit.[11]<br>82–85 (8 mm)[b] | 45.91 | 6.94 | 10.49 |
| 3-Methyl-3-nitrobutanone | 29.5–30 | 45.90 | 7.02 | 10.61 |

[a] Calcd for $C_5H_9NO_3$: C, 45.80; H, 6.92; N, 10.68. [b] 2,4-DNPH mp 102–103° (lit.[11] mp 105–106°).

*Anal.* Calcd for $C_6H_9NO_3$: C, 50.35; H, 6.29; N, 9.79. Found: C, 50.18; H, 6.40; N, 9.83.

The aromatic α-nitro ketones, α-nitroacetophenone and α-nitropropiophenone, were prepared from benzoyl cyanide by the method of Bachman and Hokama[15]: α-nitroacetophenone, mp 106–106.5° (lit.[16] mp 105–106°); α-nitropropiophenone, bp 124° (2 mm) (lit.[15] bp 124° (2 mm)).

The pmr spectra were run on a Varian Associates Model V-4311 spectrometer operated at 60 Mcps. The $\tau$ values were determined using tetramethylsilane ($\tau$ 10) as internal standard. No determinations of peak locations were made in the neat spectra. The infrared spectra both neat and in solution were run on a Beckman IR 4 equipped with sodium chloride optics.[17] Molar extinction coefficients were determined in carbon tetrachloride solution.

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[8] M. Kuhn, W. Luttke, and R. Mecke, *Z. Anal. Chem.*, **57**, 680 (1963); T. Urbanski, *Bull. Acad. Polon. Sci., Class III*, **1**, 239 (1953); **4**, 87, 381 (1956); Z. Eckstein, T. Urbanski, and W. Sobotka, *ibid.*, **5**, 679 (1957); T. Urbanski, *Tetrahedron*, **6**, 1 (1959); T. Urbanski and D. Ciercierska, *Roczniki Chem.*, **29**, 11 (1955); T. Urbanski, *ibid.*, **31**, 37 (1957); W. F. Baitinger, P. von R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron*, **20**, 1635 (1964); H. E. Ungnade, E. M. Roberts, and L. W. Kissinger, *J. Phys. Chem.*, **68**, 3225 (1964).

[9] W. F. Baitinger, P. von R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron*, **20**, 1635 (1964).

[10] In the acyclic compound a *trans* juxtaposition of the carbonyl and nitro groups eliminates both the unfavorable steric and electronic interactions.

[11] C. D. Hurd and M. E. Nilson, *J. Org. Chem.*, **20**, 927 (1955).

[12] H. Wieland, P. Garbsch, and J. J. Chavan, *Ann.*, **461**, 295 (1928).

[13] N. Levy and C. W. Scarfe, *J. Chem. Soc.*, 1093 (1946).

[14] "Kugelrohr" distillation at ~100° (0.1 mm).

[15] A. B. Bachman and T. Hokama, *J. Am. Chem. Soc.*, **81**, 4882 (1959).

[16] A. J. Jakubowitsch, *J. Prakt. Chem.*, **142**, 37 (1935).

[17] The authors are indebted to Mr. E. Poti and Mr. G. Taylor, Jr., respectively, for their assistance in the determination of the infrared and pmr spectra.