[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

The Structure of β-Amino Derivatives of Nitroölefins[1]

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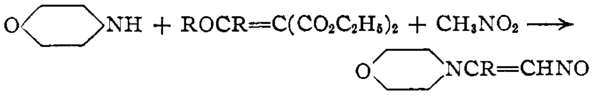
Unsaturated β-aminonitro compounds have been assigned the structure of 1-amino-2-nitroölefins on the basis of their infrared and ultraviolet absorption spectra. The unusual spectral characteristics of these molecules are discussed.

Several references may be found to unsaturated β-aminonitro compounds but in only isolated instances is unambiguous assignment of structure between an enamine or ketimine form possible. Interest in the structure of these substances was stimulated by other studies,[2] and since their spectral characteristics proved to be unusual, a detailed investigation of these compounds was undertaken. As it will be shown that the enamine formula $(\mathrm{RNH{-}\underset{|}{C}=\underset{|}{C}{-}NO_2})$ fits the critical evidence, this formula will be used exclusively for the structures cited in this paper rather than the tautomeric imine formulas $(\mathrm{RN=\underset{|}{C}{-}\underset{|}{C}HNO_2})$ which had been employed earlier.

Preparation and Properties.—There are five routes to these compounds currently recorded in the literature: (1) the condensation of morpholine or piperidine with an alkoxymethylenemalonic ester and nitromethane[3]



(2) the condensation of aromatic amines with α-nitro ketones[4,5]

$$\mathrm{RCOCHRNO_2 + ArNH_2 \longrightarrow ArNHCR{=}CRNO_2}$$

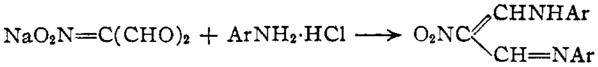
(3) the reaction of *vic*-dinitroölefins[6a] or nitrochloroölefins[6b] with amines

$$\mathrm{O_2NCR{=}CRNO_2 + ArNH_2 \longrightarrow ArNHCR{=}CRNO_2}$$

(4) the reaction of sodium methazonate with aromatic amine salts,[7] and

$$\mathrm{NaO_2N{=}CHCH{=}NOH + ArNH_2{\cdot}HCl \longrightarrow ArNHCH{=}CHNO_2}$$

(5) the condensation of sodium nitromalonaldehyde with primary aromatic amines[8,9]

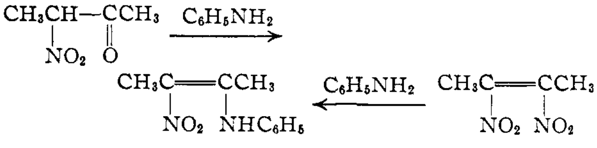


$$\mathrm{NaO_2N{=}C(CHO)_2 + ArNH_2{\cdot}HCl \longrightarrow O_2NC{<}^{CHNHAr}_{CH=NAr}}$$

A sixth method, which involves the reaction of sodium nitromalonaldehyde with secondary aromatic amines, recently has been discovered in this Laboratory.[2]

$$\mathrm{NaO_2N{=}C(CHO)_2 + 2ArNHR{\cdot}HCl \longrightarrow ArNR{-}CH{=}CH{-}NO_2 + ArNR{-}CHO}$$

At least one compound was prepared by each of the methods described and it should be pointed out that where these methods overlap identical materials are obtained. For example, the product obtained from the reaction of 3-nitro-2-butanone with aniline[4] is identical with that prepared from 2,3-dinitro-2-butene and aniline; there was no evidence of any isomeric compound formation. The most general method for the preparation of these compounds appears to be method 4. While originally only primary aromatic amines were employed, it has now been found that secondary amines work equally well. For example, methylaniline may be condensed with sodium methazonate to prepare the same compound obtained from sodium nitromalonaldehyde and methylaniline.



$$\mathrm{CH_3\underset{NO_2}{CH}{-}\underset{O}{\overset{}{C}}CH_3 \xrightarrow{C_6H_5NH_2} CH_3\underset{NO_2}{C}{=}\underset{NHC_6H_5}{C}CH_3 \xleftarrow{C_6H_5NH_2} CH_3\underset{NO_2}{C}{=}\underset{NO_2}{C}CH_3}$$

All these compounds are destroyed by acids and bases. They are resistant to quaternization, and the secondary amine compounds could not be acylated. It has previously been established that these substances can be reduced to diamines,[3,6] but their chemical properties do not distinguish between a ketimine or enamine form. Table I summarizes the spectral characteristics of several of these compounds.

Ultraviolet Absorption Spectra.—The ultraviolet spectra of all the compounds examined except nitromalonaldehyde monoanil and dianil were of the same general shape and were similar to the spectra of conjugated nitroölefins.[10] The similarity of the spectra suggests that all the compounds possess the same fundamental structure. The only structure compatible with all of them is that of a β-aminonitroölefin (I). The long wave length peak at 355–390 mμ may then be associated with the excited structure II. It is probable that the lower wave length peak around 235 mμ is due to the nitroölefin portion of the molecule as it has been demonstrated that nitroölefins absorb at 225–250 mμ and that this band persists even in more conjugated molecules.[10]

$$\underset{\text{I}}{\mathrm{R{-}\underset{NO_2}{C}{=}\underset{NR_2}{C}{-}R}} \qquad \underset{\text{II}}{\mathrm{R{-}\underset{\ominus O_2N}{C}{-}\underset{\oplus NR_2}{C}{-}R}}$$

The compounds fall into two groups according to the position of their long wave length absorption: those which absorb around 355 mμ and those which absorb around 375 mμ. (The stilbene derivatives

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] J. P. Freeman and C. O. Parker, *J. Org. Chem.*, in press.

[3] C. D. Hurd and L. T. Sherwood, Jr., *ibid.*, **13**, 471 (1948).

[4] C. D. Hurd and M. E. Nilson, *ibid.*, **20**, 927 (1955).

[5] C. Harries, *Ann.*, **319**, 254 (1901).

[6] (a) L. B. Clapp, J. F. Brown, Jr., and L. Zeftel, *J. Org. Chem.*, **15**, 1043 (1950); (b) R. Perrot and R. Berger, *Compt. rend.*, **235**, 185 (1952).

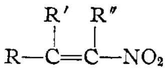
[7] W. Meister, *Ber.*, **40**, 3435 (1907).

[8] H. B. Hill and J. Torrey, Jr., *Am. Chem. J.*, **22**, 89 (1899).

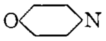
[9] W. J. Hale and E. M. Honan, THIS JOURNAL, **41**, 770 (1919).

[10] E. A. Braude, E. R. H. Jones and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

TABLE I

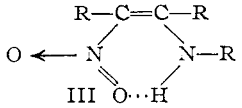
SPECTRAL CHARACTERISTICS OF 1-AMINO-2-NITROÖLEFINS, 

$R{-}\overset{R'}{\overset{|}{C}}{=}\overset{R''}{\overset{|}{C}}{-}NO_2$

R	Compound R′	R″	M.p., °C.	Ultraviolet spectra λmax, mμ	εmax	Infrared bands, cm.⁻¹ 3μ region	6μ region
	H	H	94–95[3,a]	352	13800	..	1625
				234	22000		
$N(CH_3)C_6H_5$	H	H	93.5–94.5[2]	360	23000	..	1625
				238	14500		1585
NH_2	CH_3	CH_3	159–160[6]	355	19000	3280	1620
				234	3200	3120	(1550)[b]
NH_2	C_2H_5	C_2H_5	88–89[6]	358	18000	3300	1612
				235	2000	3150	(1550)[b]
NH_2	C_6H_5	C_6H_5	159–160	361	16000	3280	1608
				245	3000	3130	1572
							(1530)[b]
$NHCH_3$	C_6H_5	C_6H_5	204–205	367[c]	16500	3130	1585
				..	..		1565
$NHCH_2C_6H_6$	C_6H_5	C_6H_5	180–182	368[c]	19900	3150	1587
				..	..		1560
NHC_6H_{11}	C_6H_5	C_6H_5	200.5–201.5	375[c]	20500	..	1588
				..	..		1565
$NHC_6H_4CH_3$-*p*	CH_3	CH_3	107–108	376	20900	..	1608
				237	9800		1580
NHC_6H_5	H	H	96–97[7]	377	23000	3130	1612
				235	14500		1590
NHC_6H_5	CH_3	CH_3	103–104[7]	373	19950	..	1610
				233	8100		1580
NHC_6H_5	C_2H_5	C_2H_5	63–64[6]	375	21600	..	1605 (sh.)
				238	9200		1575
NHC_6H_5	C_6H_5	C_6H_5	156.5–157	390	18000	..	1589
				237	20000		1555
NHC_6H_5	H	$CH{=}NC_6H_5$	94–95[8,a]	390	21000	..	1640
				340	16500		1595
				228	14500		1550
NHC_6H_5	H	$CH{=}O$	146–147[8,a]	357	20500	..	1678
				295	9000		1660
				228	8500		1620
							1580

[a] These compounds were generously supplied by Dr. C. O. Parker. [b] These bands were relatively weak but shifted to shorter wave lengths and greater intensity in solution. [c] The lower wave length band of these compounds was very broad in the region of 235–255 mμ and their exact maxima were indeterminate.

absorbed at somewhat higher wave lengths: 365 mμ for the lower group and 390 mμ for the higher.) All the compounds which absorb at the higher wave length have a hydrogen atom attached to nitrogen in the aminonitroölefin structure. This bathochromic shift can be attributed to the formation of a hydrogen-bonded chelate (III) similar to that found in β-diketones. It is known that such "conjugated chelation" shifts the absorption maxima of β-diketones to higher wave lengths.[11,12] Further discussion of this chelate structure and the factors influencing its formation will be found in the section on the interpretation of the infrared spectra. The spectra of nitromalonaldehyde monoanil and dianil are complicated by the presence of another chromophore in conjugation with the aminonitroölefin moiety. That these compounds are correctly represented by the aminonitroölefin structure is suggested by their long wave length absorption which would not be expected of an unconjugated dianil or anil aldehyde. It is interesting that the aminonitroölefin structure had previously been assigned to the dianil on the basis of chemical evidence.[9]



III

Infrared Absorption Spectra.—Two features of these spectra require explanation if the aminonitroölefin structure (I) is correct. These are the marked lowering of the NH frequency in the compounds containing that group and the absence of bands above 1500 cm.$^{-1}$ which might be attributed to a nitro group. The situation encountered here is quite similar to that found in the β-amino-α,β-unsaturated ketones (IV).[13] In these compounds the carbonyl and NH frequencies were lowered considerably. The lowering of the carbonyl frequency was attributed to the contribution of the ionic resonance structure V to the ground state of

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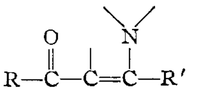
(11) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

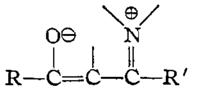
(12) For other examples of the bathochromic effect of chelation, see L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 290.

(13) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, THIS JOURNAL, **71**, 3337 (1949).

these molecules. It is plain that this ionic structure is analogous to the excited structure II written in connection with the interpretation of the ultraviolet spectra of the aminonitroölefins. It thus appears that such an ionic structure also contributes to the ground state of the aminonitroölefins. The NH frequency lowering was attributed to hydrogen bonding.



IV



V

The absence of NH bands in the spectra of many of the compounds and its lowering in many others suggested that these compounds exist in the form of hydrogen-bonded chelates as III. (No shifts of the NH frequency were observed when their spectra were measured in solution indicating intramolecular rather than intermolecular association.) Such chelation would lower the NH frequency by an amount depending upon the strength of the hydrogen bond. In order to verify the presence of an NH group in those compounds which exhibited no NH frequency and to support the suggestion of chelate formation, the N-deutero compound corresponding to 2-(*p*-toluidino)-3-nitro-2-butene was prepared by shaking the hydrogen compound in a dioxane–deuterium oxide mixture. The spectrum of this deuterated compound had a band at 2200 cm.$^{-1}$ attributable to the N–D stretching vibration. It is an interesting but unexplainable fact that this spectrum was remarkably different[14] from that of the hydrogen compound. There were many new bands and bands originally present had undergone major shifts in position. The compounds whose infrared spectra indicated that they were the most strongly hydrogen-bonded absorbed in the region of 375–390 mμ in the ultraviolet (see section on ultraviolet spectra) while the most weakly hydrogen-bonded absorbed in the 355–365 mμ region.

The formation and strength of this hydrogen-bonded chelate appears to be affected by both electronic and steric effects. The strongest chelates were formed when the double bond was completely substituted and an aryl group was attached to the amino nitrogen. When alkyl groups were substituted on the nitrogen atom, the internal association weakened and continued to weaken as the bulk of the alkyl decreased until the unsubstituted amino compounds were almost completely unbonded (see Table I). If the double bond was only partially substituted, the hydrogen bond was also weaker regardless of the substitution on the amino nitrogen atom. The implication of the argument up to this point is that all these compounds are in a *cis* configuration. The possibility exists, of course, that some exist in a *trans* form and it is these that show a weakly-bonded or unbonded NH group. However, 2-amino-3-nitro-2-butene, a compound which appears to be least strongly bonded,[15] exists in the *cis* configuration.[16]

The physical properties of the weakly-chelated compounds are quite suggestive of a high degree of association in their crystal structure. They all possess very high melting points (see Table I) and are soluble only in polar organic solvents. For instance, they are soluble in chloroform but not in carbon tetrachloride. The amino hydrogen atoms of 2-amino-3-nitro-2-butene exchanged readily in heavy water. The infrared spectrum of the deuterium compound exhibited N–D stretching vibrations at 2460 and 2330 cm.$^{-1}$, but otherwise the spectrum was quite similar to that of the hydrogen compound. The vast spectral differences accompanying deuteration of 2-(*p*-toluidino)-3-nitro-2-butene did not occur with this compound. Whether these phenomena are related to the internal association is not known.

The bands in the 6 μ region cannot be assigned unambiguously. In the aromatic compounds studied some of them are undoubtedly associated with the aromatic ring vibrations. Other bands must be associated with the aminonitroölefin group and are probably due to C=C or C=N stretching vibrations. The position of these bands is not fixed within very narrow limits (see Table I) and only poor predictions can be made about their position in the spectrum of a new compound.

Since the lowering of the nitro group frequency below 1500 cm.$^{-1}$ has been attributed to the contribution of the ionic structure II to the ground state of these molecules, any change in structure which would lower its contribution ought to raise the nitro group frequency. In order to test this hypothesis, 1-(*p*-nitroanilino)-2-nitroethylene (VI) was prepared by the reaction of *p*-nitroaniline with sodium methazonate.[7] It was hoped that the *p*-nitro substituent might decrease the aminonitroolefin interaction. The ultraviolet spectrum of this compound was similar to that of the other aminonitroölefins (λ_{max} 395, 233 mμ).[20] Its infrared spec-

VI

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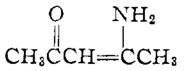
[14] Since these spectra were so different, the deuterium compound was re-exchanged with ordinary water to regenerate the hydrogen compound. This material was identical to that before deuteration.

[15] It is interesting to note that 4-amino-3-pentene-2-one (a) exhibits two bands above 3100 cm.$^{-1}$ in its infrared spectrum indicating only weakly bonded NH groups, whereas all the N-substituted amino ketones showed no free NH groups.[13]

(a) 

$CH_3C(=O)CH=C(NH_2)CH_3$

[16] (a) This assignment of configuration is made on the basis that this compound's reduction product appears to be *meso*-2,3-butanediamine. Assuming *cis*-addition of hydrogen and no rearrangement,[16b] the *cis*-nitroaminoölefin should lead to the *meso*-diamine. The *meso*-diamine configurational assignment was arrived at as follows. The reduction product was isolated as the dibenzamide,[6] m.p. 296–297°. The dibenzamide of *meso*-2,3-butanediamine is reported[17] to melt at 298°. The dibenzamide of the reduction product is different from that obtained from the diamine produced by the action of ammonia on 2,3-dibromobutane,[18] m.p. 238°. That this latter diamine is the DL-isomer is shown by the following comparison; m.p. of ditoluenesulfonamide,[18] 179°; m.p. of authentic DL-2,3-butanedi-*p*-toluenesulfonamide,[19] 178°. (b) However, for a recent indication that this reduction may be non-stereospecific, see N. Kornblum and L. Fishbein, THIS JOURNAL, **77**, 6266 (1955).

[17] E. Strack and H. Schwaneberg, *Ber.*, **67**, 1006 (1934).

[18] G. T. Morgan and W. J. Hickenbottom, *J. Soc. Chem. Ind.*, **43**, 397T (1924).

[19] F. H. Dickey, W. Fickett and H. K. Lucas, THIS JOURNAL, **74**, 947 (1952).

[20] *p*-Nitroaniline itself absorbs at 381 and 226 mμ [L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947)].

trum in Nujol had bands attributable to a bonded NH group (3230 cm.$^{-1}$) and an α,β-unsaturated or aromatic nitro group[21] (1510 cm.$^{-1}$), in addition to bands at 1590 and 1650 cm.$^{-1}$ associated with the nitroaniline moiety. In chloroform the nitro group frequency was shifted to 1522 cm.$^{-1}$. As there is no other band attributable to a nitro group, it appears that both nitro groups absorb at this frequency, and it must be concluded that not only the olefinic nitro group frequency but also that of the aromatic nitro group are affected in this molecule. However, the introduction of the *p*-nitro substituent affected the aminonitroölefin group as predicted.

Conclusions.—From a consideration of their ultraviolet and infrared spectra, unsaturated β-aminonitro compounds are assigned the structure of 1-amino-2-nitroölefins (I and II); the primary and secondary amino compounds exist as hydrogen-bonded chelates (III) of varying strength. The assignment of the enamine rather than the ketimine form to these compounds is consistent with the structures assigned to β-amino-α,β-unsaturated ketones[13] and β-amino-α,β-unsaturated lactones and esters.[22,23] This structure also accounts for the chemical properties of these substances as they are to be regarded as vinylogs of nitramides.

Experimental

2-(*p*-Toluidino)-3-nitro-2-butene.—A solution of 5 g. of *p*-toluidine in 15 ml. of ethanol was added slowly to a solution of 5 g. of 2,3-dinitrobutene[24] in 15 ml. of ethanol. The mixture was cooled in an ice-bath and a bright yellow solid precipitated. This solid was collected and recrystallized from ethanol; m.p. 107–108°, yield 4.5 g. (51%).

Anal. Calcd. for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.59. Found: C, 63.29; H, 6.49; N, 13.29.

α-Anilino-β-nitrostilbene.—One gram of *cis*-dinitrostilbene[25] was dissolved in 5 ml. of acetonitrile and 1 g. of aniline in 5 ml. of ethanol was added. After a few seconds of stirring a bright yellow solid separated. It was collected and recrystallized from ethanol, m.p. 156.5–157°.

Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.92; H, 5.10; N, 8.86. Found: C, 76.00; H, 5.14; N, 9.20.

α-Benzylamino-β-nitrostilbene.—The same directions were followed using benzylamine. The product was obtained by cooling the reaction mixture in a Dry Ice–acetone-bath. The bright yellow solid was recrystallized from ethanol, m.p. 180–182°.

Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.25; H, 4.60; N, 8.58.

α-Cyclohexylamino-β-nitrostilbene.—The directions for the preparation of the aniline compound were followed exactly except for the use of cyclohexylamine. The product was recrystallized from ethanol; m.p. 200.5–201.5°.

Anal. Calcd. for $C_{20}H_{22}N_2O_2$: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.59; H, 6.80; N, 8.47.

α-Amino-β-nitrostilbene.—One gram of *cis*-1,2-dinitrostilbene[25] was dissolved in 5 ml. of acetonitrile and added to 10 ml. of concentrated ammonium hydroxide. This mixture was warmed in hot water for a few minutes and then poured on ice. Bright yellow crystals separated and were collected and recrystallized from aqueous ethanol, m.p. 158–159°.

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.98; H, 5.04; N, 11.66. Found: C, 70.23; H, 5.04; N, 11.60.

α-Methylamino-β-nitrostilbene.—The directions for the preparation of the amino compound were followed with the substitution of 25% aqueous methylamine solution. The product precipitated from the aqueous solution only after acidification with hydrochloric acid. It was recrystallized from ethanol; m.p. 203–204°.

Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.92; H, 5.55; N, 10.75.

1-(N-Methylanilino)-2-nitroethylene.—A solution of 15 g. (0.12 mole) of sodium methazonate[7] in 150 ml. of water was made just acid by the addition of a few drops of 2 *N* hydrochloric acid. A solution of 12.8 g. (0.12 mole) of methylaniline in 200 ml. of water containing 10 ml. of concentrated hydrochloric acid was added all at once. The mixture was stirred for an hour, filtered to remove a dark oily gum and slowly concentrated *in vacuo*. Pale yellow needles separated and were collected on a filter. Three successive evaporations produced 5.8 g. (28%) of the desired compound, m.p. 92–94° (lit.[2] m.p. 93.5–94.5°).

Infrared and Ultraviolet Spectra.—The infrared spectra were measured on a Perkin–Elmer model 21 recording infrared spectrophotometer. The samples were run as Nujol mulls. The ultraviolet spectra were measured on a Beckman DK-1 recording ultraviolet spectrophotometer in absolute ethanol solution. The concentrations of all the solutions were of the order of 10^{-5} to 10^{-5} molar.

Acknowledgments.—We are deeply indebted to Drs. Keith S. McCallum and M. F. Hawthorne for helpful and stimulating discussions of the spectra.

HUNTSVILLE, ALABAMA

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(21) J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955). This author reports 1510 cm.$^{-1}$ for the nitro group frequency of *p*-nitroaniline in chloroform. In Nujol there is no band in the 1500–1550 cm.$^{-1}$ region.

(22) S. A. Glickman and A. C. Cope, THIS JOURNAL, **67**, *1017* (1945).

(23) C. A. Grob, *Helv. Chim. Acta*, **33**, 1787 (1950).

(24) E. M. Nygaard and T. T. Noland, U. S. Patent 2,396,282.

(25) K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, THIS JOURNAL, **75**, 2400 (1953).