[Contribution from the Department of Chemistry, State University of Iowa]

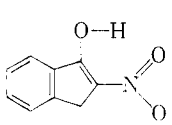
Nitroolefins. II. Derivatives of α-Nitroacetophenone

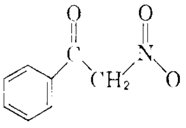
RICHARD D. CAMPBELL and FREDERICK J. SCHULTZ[1]

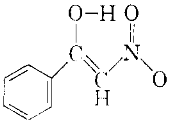
Received April 14, 1960

A number of reactions for the preparation of derivatives of α-nitroacetophenone was studied. A series of sixteen related compounds was prepared. The ultraviolet and infrared spectra of these compounds are reported and discussed.

In the previous paper[2] the 2-nitro-3-hydroxyindene (I) system was discussed. A comparison of the spectra of I and of α-nitroacetophenone (II) showed that tautomerism occurs and that chelate hydrogen bonding occurs in IIE but not in I. It was of interest to study the spectra of analogs of II to look for substituent effects on hydrogen bonding, splitting of the infrared absorption band assigned to symmetrical stretching of the nitro group, tautomerism, and electronic effects causing band displacements.


I


II

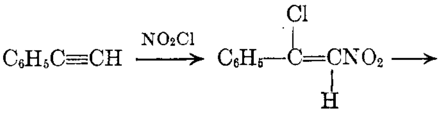

IIE

The reactions of α-nitroacetophenone with ammonia and amines were studied. It was expected that the amine would react with II to give the α-amino-β-nitrostyrene. The analogous reaction in the 1,3-diketone series has been reported.[3] Although II formed a salt readily with ammonia, morpholine, and other bases, the subsequent displacement reaction was not successful. Red oils were formed, suggesting that phenylnitroacetylene[4] might have been produced.

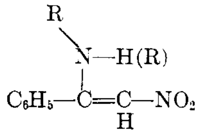
The preparation of the α-amino-β-nitrostyrenes was accomplished by the action of the amines on α-chloro-β-nitrostyrene (XII). This method was reported by Perrot and Berger,[5] but no experimental details were given and no data other than melting points were reported. The preparation of XII by the action of nitrosyl chloride on phenylacetylene gave a 17% yield. A better method employed nitryl chloride and phenyl acetylene to give III in 36% yield. This reaction had variously been reported not to occur[5] and to give α-nitro-β-chlorostyrene.[6] The product obtained by the two methods was identical.

An alternative preparation of XII was attempted. α-Nitroacetophenone was treated with phosphorus pentachloride in methylene chloride. The product which formed is tentatively assigned the structure α-chloro-β-benzoyl-β-nitrostyrene (XIX) on the basis of analytical and spectral data. Under these and other conditions none of the expected product XII was obtained.

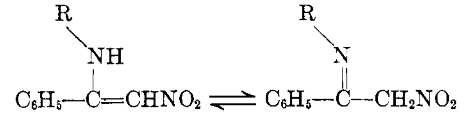
The chloro compound XII reacted readily when treated with primary and secondary amines, *viz.*, morpholine, aniline, benzylamine, and cyclohexylamine. When the amine was used as solvent, decomposition occurred and red oily products formed. The reactions in either solution were rapid and exothermic except in the case of aniline.


$$C_6H_5C\equiv CH \xrightarrow{NO_2Cl} C_6H_5-\overset{Cl}{C}=\underset{H}{C}NO_2 \longrightarrow$$

XII


$$C_6H_5-\overset{R\diagdown N-H(R)}{C}=\underset{H}{C}-NO_2$$

XIII-XVI


$$C_6H_5-\overset{R\diagdown NH}{C}=CHNO_2 \rightleftharpoons C_6H_5-\overset{R\diagdown N}{\overset{\|}{C}}-CH_2NO_2$$

XIV-XVI XIVA-XVIA

The structures of these amine reaction products were established as α-amino-β-nitrostyrenes by acid hydrolysis to α-nitroacetophenone. It has been demonstrated[7] in the amino chalcone analogs that hydrolysis gives the α-, or β-dicarbonyl compound from the respective α- or β-aminochalcone.

The reaction product from morpholine, *viz.*, α-morpholino-β-nitrostyrene (XIII) can exist only in one form. However, tautomerism is possible with the benzylamino (XIV), cyclohexylamino(XV), and anilino (XVI) compounds. More extensive conjugation is present than in the imine forms XIVA and XVA. The imine XVIA is a Schiff base structure with conjugation of both phenyl rings through the azomethine linkage.

In the homologous series, β-methyl-β-nitrostyrene (IX) was treated with excess morpholine to give the addition product 1-morpholino-1-phenyl-

---

(1) Ph.D. Thesis, State University of Iowa, 1960.

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

(3) N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

(4) J. Lovenich and H. Gerber, *Ber.*, **63**, 1707 (1930).

(5) R. Perrot and R. Berger, *Compt. rend.*, **235**, 185 (1958).

(6) W. Steinkopf and M. Kuhmel, *Ber.*, **75**, 1323 (1942).

(7) (a) N. H. Cromwell, D. B. Capps, and S. E. Palmer, *J. Am. Chem. Soc.*, **73**, 1226 (1951); (b) N. H. Cromwell, H. H. Eby, and D. B. Capps, *J. Am. Chem. Soc.*, **73**, p. 1230.

2-nitropropane (XVIII). Numerous attempts to carry out the same reaction with β-nitrostyrene have been unsuccessful. The bromine addition product of IX was prepared.[8] This dibromide (XI) reacted in morpholine to yield α-morpholino-β-methyl-β-nitrostyrene (XVII). This product presumably results from successive dehydrobromination, addition of morpholine, and dehydrobromination. Under the same conditions, the bromine adduct of β-nitrostyrene (III) yields β-bromo-β-nitrostyrene (VIII), and proceeds no further.

Several attempts were made to prepare α-acyloxy-β-nitrostyrenes by acylation of II. Treatment of II with the aroyl chlorides and pyridine in dry benzene yielded 1-phenyl-2-nitroethane-1,1-diol bis-4-nitrobenzoate (XXI) and the corresponding bis-3,5-dinitrobenzoate (XX). The structures of XX and XXI were confirmed by hydrolysis to give nitromethane. Treatment of II with acetyl chloride and pyridine in toluene did not give the expected α-acetoxy-β-nitrostyrene. Instead, a product formed which seems to be α-chloro-β-acetyl-β-nitrostyrene. This product and the corresponding benzoyl compound (XIX) described above are to be studied further.

The ultraviolet spectra of the series with β-nitrostyrene (III) as the reference compound reveal the effect of the substituents on the principal chromophore of β-nitrostyrene at 3110 Å. When the double bond is saturated and conjugation is not possible, the band in the 3000–4000 Å region is absent, as in X, XI, XVIII, XX, and XXI.

The α-hydroxyl and β-bromo substituents cause a bathochromic shift of 410 Å and 130 Å in compounds II and VIII respectively. In compound VII in which both substituents are present the shift is 530 Å demonstrating an additivity of the effect of the two substituents.

The intensity of absorption in compounds II, VII, and the salts of II vary widely in both directions from the reference compound III. This intensity variation indicates concentration variance due to keto-enol equilibrium. The keto form of II is expected to show only the benzoyl chromophore, which absorbs quite weakly in the 3000–4000 Å region. Hence absorption in this range is due to the enol form. The low absorbance in II and VII indicates low enol content. The varying absorption intensity of IV, V, and VII is interesting in that some cations seem to cause higher enol content than would have been expected.

The amino derivatives all seem to be in the enamine form. No other form is possible with the morpholino compound VIII. The other amines show the same direction and almost uniform amounts of shift seen in XVIII. Hydrogen chelation is expected, but does not appear to effect the band locations in these compounds. The aniline compound XVI contains a more extensive conjugation system than is found in the others, hence the more bathochromic band (3780 Å) is to be expected.

The α-halogen and β-methyl groups do not seem to follow a general pattern. The α-chloro group in XII causes a shift (hyposochromic) of −140 Å. In IX the methyl group causes a −40 Å shift. In XVII the methyl group apparently has no effect, as both XVII and XIII absorb at 3560 Å.

The spectrum of α-chloro-β-benzoyl-β-nitrostyrene (XIX) is not what might be predicted.[9,10] The intense band at 2480Å and absence of a band at longer wave length might be explained in terms of extreme steric inhibition of resonance. Further study of this compound is planned.

The infrared spectra provide evidence for the tautomeric forms which are present in the keto-enol alternatives in II and VII. Both have a carbonyl band at 1695 cm.$^{-1}$ (potassium bromide pellet) as expected.[11] A C—C band appears at 1605 cm.$^{-1}$ for II, and as a shoulder at 1600 cm.$^{-1}$ in VII. No C═N absorption was found. The C═C band appears at 1580–1595 cm.$^{-1}$ for these derivatives, and up to 1605 cm.$^{-1}$ for other β-nitrostyrene compounds. These two characteristics establish the structures of XIII–XVII as enamines. No N—H band is observed, again because of hydrogen chelation.[2,11]

The absorption bands for the nitro group appear in the 1550 cm.$^{-1}$ and 1350 cm.$^{-1}$ region for the asymmetric and symmetric modes respectively.[11,12] General patterns for shifts of bands and splitting[13] of bands are difficult to discern. These bands for members of the series may be compared with the values of 1538 cm.$^{-1}$ and 1345 cm.$^{-1}$ for the parent β-nitrostyrene (III). It can be seen that the saturated compounds X, XI, and XVIII have an asymmetric nitro band at a shorter wave length (higher wave number) than does III. (The bands at 1540 and 1525 cm.$^{-1}$ for XX and XII respectively, are due to the aromatic nitro group.) The higher wave number for the unconjugated nitro group and lower wave number for conjugated nitro group is the pattern recognized by Brown.[12]

The asymmetric band for II is high, indicating a saturated nitro group as is found in the keto form. The bromo analog VII fits the same pattern. The amino derivatives XIII–XVII also absorb in the 1545–1572 cm.$^{-1}$ range. For XIII and XVII this band cannot be explained as above since tau-

---

[8] B. Priebs, *Ann.*, **225**, 342 (1884).

[9] R. D. Campbell and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 3456 (1957).

[10] W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **77**, 5134 (1955).

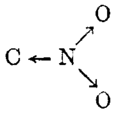
[11] L. J. Bellamy, *Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N.Y. (1958).

[12] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

[13] P. H. Lindenmeyer and P. M. Harris, *J. Chem. Phys.*, **21**, 408 (1953).

tomerism is not possible. It seems that in the electronic ground state the inductive effect of the amino and hydroxyl groups more than balance the conjugative effect.

The symmetric mode band of the nitro group is split in some of the enolic and amino derivatives. This splitting might be explained as evidence of tautomeric equilibrium. The low wave-number bands appear at 1330–1300 cm.$^{-1}$ for II, IV–IX, XII, XV–XVI. However, amines XIII, XIV, and XVII absorb at 1373–1348 cm^{-1}. This shift to higher wave length is anomalous in the above rationale. The higher wave-length components of the split bands in IV, VII, XII, XV, and XVII fall in the same anomalous region. These absorptions may be due to increased bond order of the C—N bond,[12] increasing the force constant of the vibrating system.



The effect of hydrogen chelation and dipole interaction upon the —NO_2 stretching modes is expected to be moderately strong and to be dependent upon configuration of structures, particularly of *cis-trans* isomers, and in structures of fixed configurations.[2] In these cases the dipole effect is expected to cause splitting and anomalous shifts. Further studies are under way to prepare model compounds in an attempt to recognize spectral patterns resulting from these effects.

EXPERIMENTAL

α-Nitroacetophenone (II). This compound was prepared by the method of Long and Troutman[14] with the exception that recrystallization of the product was carried out using petroleum ether (b.p. 60–70°) as the solvent.

Potassium salt of II.[15] A solution of 28 g. of potassium hydroxide in 40 ml. of absolute methanol was added dropwise with stirring to a solution of 8.25 g. of II in 60 ml. of anhydrous benzene. The product, a pale yellow powder, was removed by filtration, washed twice with 25-ml. portions of 50% methanol in benzene, and dried in vacuum. The yield was 8.8 g. (76%).

Ammonium salt of II.[15] A solution of 2.0 g. of II in 200 ml. of anhydrous ether was saturated with anhydrous ammonia by bubbling the dry gas through the solution for 15 min. The white precipitate was removed by filtration and washed with 50 ml. of anhydrous ether. The product was recrystallized from a mixture of 95% ethanol and ether giving 2.1 g. (96%) of yellow platelets which melted at 119°.

Anal. Calcd. for $C_8H_9N_2O_3$: C, 52.8; H, 5.49; N, 15.38. Found: C, 52.52; H, 5.42; N, 15.02.

Morpholinium salt of II.[15] Freshly distilled morpholine (6.13 g.) was added to a solution of 10 g. of II in 30 ml. of warm benzene and the mixture refluxed for 1 hr. The product was removed by filtration after the reaction mixture had cooled to room temperature. After washing with benzene and air drying, the pale yellow crystalline product melted at 138–142° with decomposition to a red oil. The yield was 14.5 g. (94%).

Anal. Calcd. for $C_{12}H_{16}N_2O_4$: C, 57.2; H, 6.35; N, 11.1. Found: C, 56.68; H, 6.25; N, 11.07.

α-Bromo-α-nitroacetophenone (VIII). This compound was prepared as previously described.[16]

1-Phenyl-2-nitroethane-1,1-diol bis-3,5-dinitrobenzoate (XX). 3,5-Dinitrobenzoyl chloride (from 8 g. of 3,5-dinitrobenzoic acid) was dissolved in dry benzene. To this 4.1 g. (0.025 mole) of II was added followed by 2 ml. of dry pyridine. The mixture was refluxed for 2 hr., and the warm solution was filtered. The clear filtrate was then cooled to room temperature. The resulting white needle-like crystals were collected by filtration with suction and recrystallized from acetone. The yield was 11.0 g. (77.4%) of a compound which melted at 187–188°.

Anal. Calcd. for $C_{22}H_{13}N_5O_{14}$: C, 46.3; H, 2.27; N, 12.2. Found: C, 47.65; H, 2.30; N, 11.58.

Hydrolysis of XX. A mixture of 2.0 g. (0.0035 mole) of 1-phenyl-2-nitroethane-1,1-diol bis-3,5-dinitrobenzoate and 25 ml. of 10% sodium hydroxide was warmed on a steam bath for 2 hr. The resulting dark brown solution was cooled to 0° and acidified with 6*M* hydrochloric acid. The acidic solution was extracted with two 30-ml. portions of ether and the combined ether extracts were dried over calcium sulfate.

A small portion of this solution was introduced into the system of a Perkin-Elmer Vapor Fractometer and the resulting chromatograph compared with that of a known solution of nitromethane in ether. On the basis of their similarity it was concluded that the unknown solution contained nitromethane.

1-Phenyl-2-nitroethane-1,1-diol bis-4-nitrobenzoate (XXI). To a solution of 4.1 g. (0.025 mole) of II in 100 ml. of dry benzene, a solution of 5 g. (0.027 mole) of *p*-nitrobenzoyl chloride in 50 ml. of dry benzene was added. Then 2 ml. of dry pyridine was added and the mixture was refluxed for 2 hr. The mixture was filtered while still hot to remove the pyridine hydrochloride which had formed. The filtrate was evaporated to dryness under reduced pressure leaving a yellow crystalline residue which was recrystallized twice from acetone and once from a solution of chloroform in petroleum ether (b.p. 35–60°). The product was pale yellow in color and melted at 168–170°. The yield was 4.8 g. (80%).

Anal. Calcd. for $C_{22}H_{15}N_3O_{10}$: C, 54.88; H, 3.11; N, 8.74. Found: C, 53.91; H, 2.79; N, 8.72.

α-Chloro-β-nitrostyrene (XII), *nitrosyl chloride method.* Ten grams (0.1 mole) of phenylacetylene was dissolved in 75 ml. of anhydrous ether and the solution was cooled thoroughly in an ice-salt mixture. Then 15 g. (0.23 mole) of liquid nitrosyl chloride was added and the reaction vessel was loosely stoppered with a rubber stopper. The mixture was allowed to stand undisturbed, without the addition of ice to the bath, until all evolution of gas had ceased (10 days). During this time the color had faded from deep red to a pale orange. The solvent was removed under vacuum at room temperature leaving a yellow oil which was vacuum distilled. The fraction boiling between 82° and 120° at 1 mm. was collected and redistilled. Three fractions were collected. The first boiled at 82–102° (2 mm.), the second at 102–110° (2 mm.), and the third at 110–120° (2 mm.). After standing for several days, the second fraction crystallized. It was recrystallized from petroleum ether (b.p. 35–60°) giving yellow crystals that melted at 50–52°. This compound was noted to be a strong lachrymator. The yield was 2.1 g. (16.9%).

Anal. Calcd. for $C_8H_6ClNO_2$: C, 52.4; H, 3.28; N, 7.66. Found: C, 52.08; H, 3.28; N, 7.87.

α-Chloro-β-nitrostyrene, nitryl chloride method. Seventy-five milliliters of anhydrous ether contained in a heavy walled tube was thoroughly cooled in a mixture of Dry Ice and acetone. Gaseous nitryl chloride was bubbled into the cold ether until approximately 35 g. (0.43 mole) had been dissolved.

---

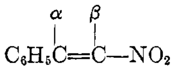
(14) L. M. Long and H. D. Troutman, *J. Am. Chem. Soc.*, **71**, 2471 (1949).

(15) A. Lucas, *Ber.*, **32**, 602 (1899).

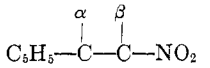
(16) J. Thiele and S. Haeckel, *Ann.* **325**, 11 (1902).

TABLE I

INFRARED AND ULTRAVIOLET ABSORPTION BANDS



$C_6H_5\overset{\alpha}{C}=\overset{\beta}{C}-NO_2$

Compound	Substituents		Ultraviolet			Infrared[a]		
	α	β	Å	$\epsilon \times 10^{-3}$	C=O	C=C	NO_2[b]	NO_2[c]
II	OH	H	2470	11.9	1695	1605	1560	1330
			3520	4.6				
III	H	H	2280	7.8				
			3110	16.6		1642	1538	1348[d]
IV	$O^-NH_4^+$	H	2470	8.4			1563	1350
			3520	18.0				1300
V	O^-K^+	H	2470	4.4				
			3520	10.9			1577	1312[d]
VI	$O^-C_4H_8ON^+$	H	2470	7.3				
			3570	8.6			1570	1325[d]
VII	OH	Br	2570	11.4	1695		1575	1358
			3640	1.4				1325
VIII	H	Br	2290	7.4		1602	1575	
			3240	11.4			1522	1300
IX	H	CH_3	2730	8.5			1518	1323
			3070	10.1				
XII	Cl	H	2290	7.3			1528	1343
			2970	8.9				1313
XIII	$-N(CH_2CH_2)_2O$	H	2440	5.3			1580	1348
			3590	17.8			1558	
XIV	$-NHCH_2C_6H_5$	H	2430	5.9			1572	1373
			3560	23.3			1565	
							1545	
XV	$-NHC_6H_{11}$	H	2300	6.8			1570	1376
			2440	5.7				1355
			3560	17.5				1315
XVI	$-NHC_6H_5$	H	2330	13.7		1595	1565	1362[e]
			2990	6.7				1313
			3780	29.0				
XVII	$-N(CH_2CH_2)_2O$	CH_3	2440	4.9			1554	1353
			3560	24.4				
XIX	Cl	$-\overset{\overset{O}{\|}}{C}C_6H_5$	2480	21.7	1690	1601	1582	1312
	 $C_5H_5-\overset{\alpha}{C}-\overset{\beta}{C}-NO_2$							
X	Br	Br	3230	1.6			1565	1350
								1313
XI	Br	Br,CH_3					1558	1329
XVIII	$-N(CH_2CH_2)_2O$	CH_3	2120	8.5			1550	1360
XX	$[-O_2CC_6H_3(NO_2)_2]_2$	H	2200	45.6				
			2300	42.5	1685		1540	1343
			2500	35.0				
XXI	$[-O_2CC_6H_4NO_2]_2$	H			1682		1588	1345
							1525	1320

[a] Data in cm^{-1}. Medium: Potassium bromide pellet. [b] Asymmetric mode. [c] Symmetric mode. [d] Nujol. [e] Chloroform.

Then 27 g. (0.265 mole) of phenylacetylene was added in a thin stream with stirring. The orange solution was allowed to stand in the cooling mixture for 2 days, then removed and allowed to stand at room temperature for 7 days with the tube loosely stoppered. At the end of this time, the color had faded to yellow. No evolution of gas was noted during the reaction period. The solvent was removed under vacuum at room temperature and the resulting orange oil was distilled under a pressure of 1–2 mm. The portion boiling from 85° to 115° was collected as a yellow oil. The yellow oil was redistilled and the portion boiling from 103–109° (2 mm.) was collected and set aside overnight to crystallize. It was necessary to warm the distillation apparatus gently to prevent crystallization of the product in the condenser and adapter tube. The product was recrystallized from petroleum ether (b.p. 35–60°) and melted at 51–53°. The mixed melting point of this product with that obtained from the reaction of phenylacetylene with nitrosyl chloride was not depressed. The yield was 5.2 g. (35.8%).

α-Morpholino-β-nitrostyrene (XIII). Freshly distilled morpholine (0.19 g., 0.022 mole) was added to XII (1 g., 0.0055 mole) in 25 ml. of anhydrous ether. The reaction was exothermic. The ether-soluble, water-insoluble portion was crystallized from petroleum ether (b.p. 60–70°) to give 0.6 g. (47.5%) of yellow crystals of XIII (m.p. 167–169°).[5]

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.5; H, 5.93; N, 11.96. Found: C, 62.3; H, 5.92; N, 11.48.

α-Anilino-β-nitrostyrene (XVI). Under the above conditions, with a 2-hr. reflux of the reaction mixture, aniline and XII reacted to give XVI (1.2 g., 91.7%) as yellow crystals, m.p. 123–124°.[5]

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 70.0; H, 5.0; N, 11.67. Found: C, 69.74; H, 4.89; N, 11.42.

α-Benzylamino-β-nitrostyrene (XIV). As above, with 2 hr. at room temperature, the reaction of benzylamine and XII gave XIV (1.3 g., 93.8%). The product was recrystallized from carbon tetrachloride–chloroform, m.p. 91°.[5]

Anal. Calcd. for $C_{15}H_{14}N_2O_2$: N, 11.04; Found: N, 10.93.

α-Cyclohexylamino-β-nitrostyrene (XV). As above, XII and cyclohexylamine reacted on standing overnight to give XV (0.8 g., 65%) from ether, melting at 113–114°.[5]

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.3; H, 7.32; N, 11.40. Found: C, 68.31; H, 7.32; N, 11.24.

Hydrolysis of α-amino-β-nitrostyrenes. A mixture of 0.8 g. (0.0033 mole) of α-anilino-β-nitrostyrene (XVI) with 25 ml. of 20% sulfuric acid was refluxed for 45 min. At the end of this time, the reaction mixture was a clear solution containing a small amount of a brown oil. The oil was removed by filtration of the hot solution. The filtrate on cooling to room temperature yielded 0.2 g. (36.5%) of white plates, which, after recrystallization from water, melted at 105°. The mixed melting point with an authentic sample of α-nitroacetophenone was 105–107°. The compound formed a 2,4-dinitrophenylhydrazone which melted at 205° with decomposition. Its mixed melting point with the 2,4-dinitrophenylhydrazone of II was not depressed.

The above procedure was repeated with α-morpholino-β-nitrostyrene (XIII) and α-cyclohexylamino-β-nitrostyrene (XV) with like results.

1-Phenyl-1,2-dibromo-2-nitropropane (XI). This compound was prepared by the method described by an earlier worker.[8]

1-Phenyl-1-morpholino-2-nitropropane (XVIII). One gram (0.0061 mole) of β-methyl-β-nitrostyrene was dissolved in 15 ml. of freshly distilled morpholine and the solution was allowed to stand on the steam bath overnight. After cooling to room temperature, the reaction mixture was diluted with 30 ml. of anhydrous ether, and the solution was washed three times with 50-ml. portions of water to free it of morpholine. The ether solution was freed of solvent by evaporation at room temperature under reduced pressure leaving a light yellow crystalline residue. This was dissolved in hot petroleum ether (b.p. 60–70°), treated with decolorizing carbon, filtered, and cooled. On cooling, a white crystalline product separated which was removed by filtration and recrystallized again from the petroleum ether to give 0.6 g. (39.2%) of a compound which melted at 142–144°.

Anal. Calcd. for $C_{13}H_{18}N_2O_3$: C, 62.2; H, 7.21; N, 11.20. Found: C, 62.36; H, 7.26; N, 10.83.

α-Morpholino-β-methyl-β-nitrostyrene (XVII). A solution of 2 g. (0.0062 mole) of 1-phenyl-1,2-dibromo-2-nitropropane in 20 ml. of freshly distilled morpholine was allowed to stand overnight on a steam bath. The resulting white precipitate was removed by filtration and identified as morpholine hydrobromide by its melting point and by the fact that it was readily soluble in water. The filtrate was poured over 100 g. of ice and the resulting fine suspension was extracted with two 50-ml. portions of ether. The ether solution was evaporated to dryness under reduced pressure at room temperature and the resulting yellow crystalline solid was recrystallized from petroleum ether (b.p. 60–70°) giving a white product. After one additional recrystallization from the petroleum ether the compound melted at 139–141°. The yield was 1.9 g. (91.6%).

Anal. Calcd. for $C_{13}H_{16}N_2O_3$: C, 62.9; H, 6.45; N, 11.30. Found: C, 62.30; H, 7.29; N, 10.83.

α-Chloro-β-benzoyl-β-nitrostyrene (XIX). To a solution of 16.5 g. (0.1 mole) of II in 175 ml. of dry methylene chloride, 20.8 g. (0.1 mole) of phosphorus pentachloride was added. The mixture was refluxed until no more hydrogen chloride was evolved (2 days). The residue was freed of phosphorus oxychloride by vacuum distillation at 70° (12 mm.). The residue from this distillation was extracted twice with 50 ml. portions of petroleum ether (b.p. 60–70°) which were combined and cooled. On cooling, white crystals separated which were removed by filtration and recrystallized from the petroleum ether. The product weighed 3.2 g. (22.3%) and melted at 90°.

Anal. Calcd. for $C_{15}H_{10}ClNO_3$: C, 62.7; H, 3.49; N, 4.88. Found: C, 62.65; H, 3.59; N, 4.89.

1-Phenyl-1,2-dibromo-2-nitroethane (X). This compound was prepared by the method described by an earlier worker.[8]

β-Bromo-β-nitrostyrene (VIII). This compound was prepared by a previously described method.[8]

Spectral determinations. All of the ultraviolet spectra were obtained using a Cary, Model 11, double beam recording spectrophotometer. All samples were run as solutions in 95% ethanol using 1 cm. silica cells.

The infrared spectra discussed were obtained by the use of a Perkin-Elmer, Model 21, double beam recording infrared spectrophotometer. The samples were run as mulls with Nujol or in potassium bromide pellets, as indicated in Table I.

Acknowledgment. The purchase of the infrared spectrophotometer used in this study was made possible by a grant from the National Science Foundation.

IOWA CITY, IOWA