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Reactions of α,β-Dibromo-β-nitrostyrenes with Acetylacetone and Ethyl Acetoacetate

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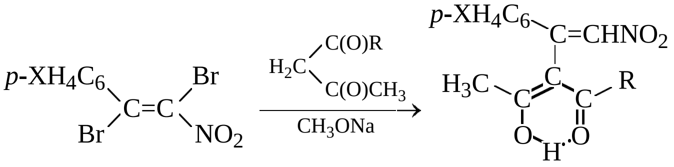
Abstract—The reactions of α,β-dibromo-β-nitrostyrenes with acetylacetone and ethyl acetoacetate were studied. The structures of the products were determined by ^{1}H NMR, IR, and UV spectroscopy. The products derived from acetylacetone were converted into copper chelates.

α,β-Dibromo-β-nitrostyrenes are new representatives of halonitroethenes [1–4]. A combination of a double bond with three functional substituents not only extends the synthetic potential of these compounds but also imparts to them peculiar properties as compared to monohalonitroethenes [5–12].

We found that α,β-dibromo-β-nitrostyrenes **I** and **II** readily react with CH acids (acetylacetone, ethyl acetoacetate) in absolute methanol at –8 to –10°C within 2.5–3 h to form (at the substrate : CH acid : CH_3ONa ratio of 1 : 2 : 2) bright yellow crystalline compounds **III**–**VI**.



I, II **III–VI**

X = H (**I**), Cl (**II**); R = CH_3 (**III, IV**), OC_2H_5 (**V, VI**).

According to the concept of [13–15], the reaction pathway can be considered as initial addition–elimination (S_NVin reaction) followed by substitution of the positively polarized halogen by proton. Such a pathway is nontrivial, although similar examples of halogen “reduction” are known [15–18].

The IR, ^{1}H NMR, and UV spectra confirmed the structure of **III**–**VI** (see table); the physicochemical characteristics of the simplest representatives of this series, **III** and **V**, coincided with those of the same products prepared previously from α-halo-β-nitrostyrenes [13, 14].

The IR spectra of **III**–**VI** contain characteristic absorption bands of antisymmetric and symmetric stretching vibrations of the conjugated nitro group at 1515–1510 and 1335–1330 cm^{-1}. However, the split absorption band of the carbonyl stretching vibrations, characteristic of 1,3-dicarbonyl compounds substituted at the methylene group [19], is absent. Along with a broad band of C–H stretching vibrations at 3020–3010 cm^{-1}, there are weak OH vibration bands at 3120–2830 cm^{-1}. Such a pattern is characteristic of the chelate structure of acetylacetone, acetoacetic acid esters, and their monosubstituted derivatives with an intramolecular hydrogen bond [19]. Conjugated carbonyl and the multiple bond in the spectra of **V** and **VI** are manifested as broad strong bands at 1650 and 1610, 1590 cm^{-1}. In the spectra of **III** and **IV**, the bands of the carbonyl group and double bond overlap, forming a broad strong ill-resolved band at 1610–1585 cm^{-1}. So strong low-frequency shift of the carbonyl band is characteristic of compounds with a very strong intramolecular hydrogen bond [20, 21], considered in some papers [22, 23] as a part of a pseudoaromatic system. Thus, the IR spectra of β-nitroethenyldiacylmethanes **III**–**VI** suggest that these compounds chiefly exist in chloroform solutions in the enol form.

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Spectral characteristics of **III**–**VI**

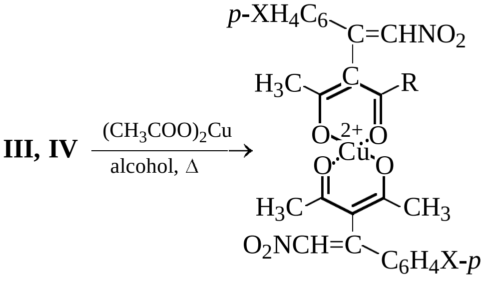
Comp. no.	IR spectrum ($CHCl_3$), ν, cm^{-1}			^1H NMR spectrum ($CDCl_3$), δ, ppm				UV spectrum (CH_3CN), λ, nm (ε, $l\,mol^{-1}\,cm^{-1}$)
	C=O, C=C	NO_2	OH	$CH_3(C_2H_5)$	Ph	=CH	OH	
III	1605, 1590	1510, 1330	3115, 2850	1.93	7.50	7.61	16.78	232 (6830), 287 (13 470)
IV	1610, 1585	1515, 1335	3120, 2850	1.93	7.46	7.59	16.79	220 (9660), 287 (16 150)
V	1650, 1610	1510, 1330	3105, 2830	1.74 (1.12, 4.16)	7.45		13.29	260 (10 100), 294–309 (6300)
VI	1650, 1610, 1590	1515, 1330	3100, 2830	1.75 (1.11, 4.15)	7.40		13.28	260 (12 600), 298–307 (8400)

This is also indicated by the ^1H NMR spectra (see table). For example, in the spectrum of **III** both methyl groups, being magnetically equivalent, give a singlet at 1.93 ppm. A down field signal at 16.78 ppm can be assigned to the hydroxyl proton. A similar spectral pattern is reported [24, 25] for the enol form of acetylacetone. The phenyl and olefinic protons in the spectrum of **III** give singlets at 7.50 and 7.61 ppm, respectively.

The ^1H NMR spectra of **V** and **VI** virtually coincide. The phenyl and olefinic protons in the spectrum of **V** give a signal at 7.45 ppm, and the hydroxyl proton, at 13.29 ppm. The methyl and ethoxyl protons give, respectively, a singlet at 1.74 ppm and multiplets at 1.12 and 4.16 ppm (see table).

The electronic spectra of **III**–**VI** are consistent with the suggested structure. Two absorption bands are observed with $\lambda_{max\,1}$ 220–260 nm (ε 6830–12 600 $l\,mol^{-1}\,cm^{-1}$) and $\lambda_{max\,2}$ 287–309 nm (ε 6300–16 150 $l\,mol^{-1}\,cm^{-1}$).

The enol structure of **III** and **IV** is convincingly confirmed by their tendency to form chelates. Copper chelates **VII** and **VIII** are readily obtained by mixing hot alcoholic solutions of **III** and **IV** with an aqueous solution of copper acetate. Complexes **VII** and **VIII** are green finely crystalline compounds readily crystallizable from ethanol.



VII, VIII

The IR spectra of the copper complexes (see Experimental) contain, along with the absorption bands of the conjugated nitro group, also bands of the carbonyl group and multiple bond, which are strongly shifted toward lower frequencies and form a common broad strong band at 1580–1560 cm^{-1}, and characteristic bands of the chelate ring at 1385 and 1365 cm^{-1}. This pattern is well consistent with the published data for copper β-diketonates [26].

Simple preparation of copper complexes **VII** and **VII** and the possibility of considerably extending their range by varying substituents in the benzene ring of α,β-dibromo-β-nitrostyrene open prospects for the synthesis of a wide range of related chelates which can be of interest for both basic (e.g., examination of the transfer of electronic effects via metal ion) and applied chemistry. It is known that chelates are widely used as polymerization initiators and in analytical chemistry and technology for extraction of metal ions; many β-diketonates exhibit laser activity [27, 28].

To conclude, it should be emphasized that α,β-dibromo-β-nitrostyrenes containing halogen atoms in both geminal and vicinal positions relative to the nitro group behave like *vic*-substituted, rather than *gem*-substituted, monohalonitrostyrenes. Their reactions with CH acids, as those with amines, follow the S_N*Vin* pathway but are additionally accompanied by “reduction” of the geminal halogen. The compounds obtained by the reactions of α,β-dibromo-β-nitrostyrenes with acetylacetone can be recommended as convenient starting agents for preparing nitrovinyl-containing chelates.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in chloroform or in KBr pellets in the working ranges of LiF and NaCl prisms. The ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz, internal reference TMS, solvent $CDCl_3$). The electronic absorption spectra were measured on an SF-46 spectrophotometer in quartz cells, solvent acetonitrile.

1,2-Dibromo-1-nitro-2-phenyl- and -2-(*p*-chlorophenyl)ethenes **I** and **II** were prepared as described in [2].

3-Acetyl-5-nitro-4-phenyl-4-penten-2-one III. A solution of 1.2 g of **I** in 10 ml of absolute methanol was added dropwise at –5 to –10°C to a solution of sodium acetylacetonate prepared from 0.8 ml of acetylacetone and 0.18 g of sodium metal in 10 ml of absolute methanol. The mixture was stirred at –5 to –10°C for 3 h, after which 0.45 ml of glacial acetic acid was added, and the mixture was poured onto crushed ice. The precipitate was filtered off. Yield of **III** 0.44 g (45%); bright yellow crystals, mp 95–96°C (from ethanol) (published data [14]: mp 96°C). Found, %: C 63.24, 63.17; H 5.42, 5.40; N 5.64, 5.69. $C_{13}H_{13}NO_4$. Calculated, %: C 63.14; H 5.30; N 5.67.

3-Acetyl-5-nitro-4-(*p*-chlorophenyl)-4-penten-2-one IV. A solution of 0.68 g of **II** in 5 ml of absolute methanol was added dropwise at –5 to –9°C to a solution of sodium acetylacetonate prepared from 0.4 ml of acetylacetone and 0.09 g of sodium metal in 5 ml of absolute methanol. The mixture was stirred at –5 to –9°C for 2.5 h, after which 0.2 ml of glacial acetic acid was added, and the mixture was poured onto crushed ice. The precipitate was filtered off. Yield of **IV** 0.37 g (66%); bright yellow crystals, mp 113–114°C (from ethanol). Found, %: C 55.61, 55.54; H 4.50, 4.49; N 5.03, 5.04. $C_{13}H_{12}ClNO_4$. Calculated, %: C 55.51; H 4.30; N 4.98.

Ethyl 2-acetyl-4-nitro-3-phenyl-3-butenoate V. A solution of 1.2 g of **I** in 10 ml of absolute methanol was added dropwise at –5 to –8°C to a solution of sodium derivative of ethyl acetoacetate prepared from 1 ml of ethyl acetoacetate and 0.18 g of sodium metal in 10 ml of absolute methanol. The mixture was stirred at –5 to –8°C for 3 h, after which 0.45 ml of glacial acetic acid was added, and the mixture was poured onto crushed ice. The precipitate was filtered off. Yield of **V** 0.48 g (43%); bright yellow crystals, mp 72–73°C (from hexane) (published data [14]): mp 64°C). Found, %: C 60.42, 60.49; H 5.55, 5.51; N 5.01, 5.02. $C_{14}H_{16}NO_5$. Calculated, %: C 60.43; H 5.80; N 5.03.

Ethyl 2-acetyl-4-nitro-3-(*p*-chlorophenyl)-3-butenoate VI. A solution of 1.37 g of **II** in 10 ml of absolute methanol was added dropwise at –5 to –8°C to a solution of sodium derivative of ethyl acetoacetate prepared from 1 ml of ethyl acetoacetate and 0.18 g of sodium metal in 10 ml of absolute methanol. The mixture was stirred at –5 to –8°C for 3 h, after which 0.45 ml of glacial acetic acid was added, and the mixture was poured onto crushed ice. The yellow oily precipitate crystallized on storage, after which it was filtered off. Yield of **VI** 0.4 g (32%); bright yellow crystals, mp 69–71°C (from hexane). Found, %: C 54.03, 54.02; H 4.62, 4.55; N 4.48, 4.50. $C_{14}H_{15}ClNO_5$. Calculated, %: C 53.84; H 4.84; N 4.49.

3-Acetyl-5-nitro-4-phenyl-4-penten-2-one copper chelate VII. A boiling solution of 2 g of copper(II) acetate in 25 ml of distilled water was added to a boiling solution of 0.25 g of **III** in 1 ml of ethanol. The mixture turned dark green, and a finely dispersed precipitate formed. After cooling, the precipitate was filtered off and washed several times with hot water to remove excess copper acetate. Yield of **VII** 0.29 g (52%); green substance, mp 209–210°C (from ethanol) (published data [14]: mp 209–210°C). IR spectrum (KBr), ν, cm^{-1}: 1580, 1520, 1385, 1325. Found, %: C 56.02, 56.14; H 4.32, 4.35; N 5.03, 5.05. $C_{26}H_{24} \cdot CuN_2O_8$. Calculated, %: C 56.11; H 4.32; N 5.04.

3-Acetyl-5-nitro-4-(*p*-chlorophenyl)-4-penten-2-one copper chelate VIII. A boiling solution of 2 g of copper(II) acetate in 25 ml of distilled water was added to a boiling solution of 0.28 g of **IV** in 1 ml of ethanol. The mixture turned dark green, and a finely dispersed precipitate formed. After cooling, the precipitate was filtered off and washed several times with hot water to remove excess copper acetate. Yield of **VIII** 0.3 g (48%); green substance, mp 214–215°C (from ethanol). IR spectrum (KBr), ν, cm^{-1}: 1560, 1510, 1365, 1315. Found, %: C 50.09, 50.12; H 3.65, 3.66; N 4.51, 4.52. $C_{26}H_{22}Cl_2CuN_2O_8$. Calculated, %: C 49.97; H 3.55; N 4.48.

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