DINITROSTILBENES IN ELECTRON-TRANSFER REACTIONS

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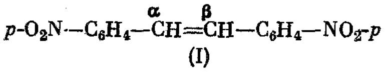
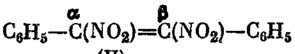
Electron-transfer reactions of compounds of the stilbene series have been reported in [1-4]. Here we report a study of the behavior of the symmetrically substituted dinitrostilbenes (I) and (II) as electron acceptors



$p\text{-}O_2N{-}C_6H_4{-}\overset{\alpha}{C}H{=}\overset{\beta}{C}H{-}C_6H_4{-}NO_2\text{-}p$

(I)



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

(II)

Compounds (I) and (II) contain two types of electrophilic groups, NO_2 and C=C. Our intention in the work reported here was to examine the correlation between the structure of the original dinitrostilbene and the properties of its electron-transfer products. We examined the interaction of electron donors — dipotassium cyclooctatetraene ($C_8H_8K_2$) or potassium naphthalene ($C_{10}H_8K$) — in THF solution with the cis and trans isomers of 4,4'-dinitrostilbene (I) and α,β-dinitrostilbene (II). We chose the ratios of the organopotassium compound and the dinitrostilbene to correspond to one-electron and two-electron transfer [schemes (1)-(3)]. We determined the extent of reaction from the yield of cyclooctatetraene (C_8H_8) [5]; the anionic forms of the nitrostilbenes were quenched with oxidants (oxygen, chlorine, bromine) or proton donors (dilute AcOH or anhydrous NH_4Cl). Control experiments showed that the action of oxygen or other oxidants does not affect the dinitrostilbenes. The same applies to AcOH mixed with AcOK or NH_4Cl.

The cis and trans isomers of (I) are stable and not spontaneously interconvertible. These isomers undergo an electron-transfer reaction with $C_8H_8K_2$. The yield of C_8H_8 is 100% under the conditions of one-electron transfer [1 mole of $C_8H_8K_2$ per 2 moles of (I)] and two-electron transfer [1 mole of $C_8H_8K_2$ per mole of (I)]. Stilbene (I) is converted to the radical anion (III) or the dianion (IV) respectively, the K salts of which are almost insoluble in THF.* The precipitated K salt of the radical anion gives a sharp ESR singlet. The solution above the precipitated radical ion salt contains no paramagnetic species. Addition of dicyclohexyl-18-crown-6 to a suspension of this salt in THF increases its solubility, and the solution above the precipitate has an ESR signal with the characteristic quintuplet of two nitrogen atoms ($a_N^1 = a_N^2 = 3.45$ Oe). The elemental analysis of the precipitated salt of radical anion (III) corresponds to one potassium atom per dinitrostilbene molecule. Treatment of the reaction mixture with oxygen and removal of the solvent under the conditions of one- and two-electron reduction gives trans-(I) in up to 90% yield. The action of the oxidant causes the radical anion (III) or dianion (IV) to lose the extra electrons to form the neutral trans-(I), regardless of the configuration of the original olefin. Treatment of the reaction mixtures with proton donors gives equivalent results. Protonation of (IV) or (III) does not reduce the C=C bond (we detected no 4,4'-dinitrobibenzyl): the interaction of the anionic forms of 4,4'-dinitrostilbene with protons is one-electron or two-electron oxidation (see top, next page.)

Our results imply that the one-electron reduction of (I) causes cis → trans isomerization. Two-electron reduction has the same effect. The degree of electron saturation of the C=C bond in anions (III) and (IV) is not enough for proton addition. Our results are consistent with earlier work [6] on the reduction of (I) by tin in hydrochloric acid: both trans- and cis-(I) form only the trans isomer of 4,4'-diaminostilbene.

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*The insolubility of these salts of the radical anion and the dianion seemingly excludes the possibility that they could interconvert by electron exchange.

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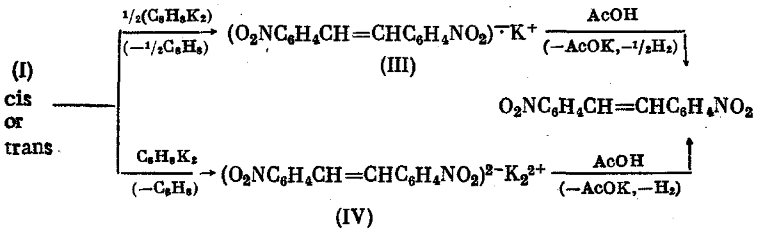
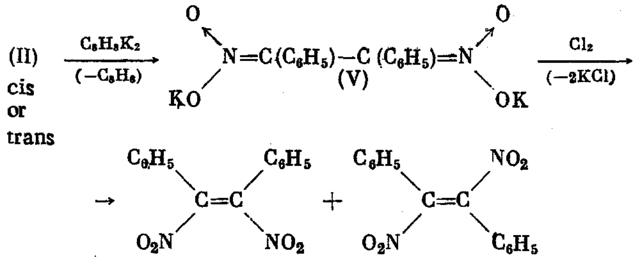


(1)

The cis and trans isomers of (II) also have very different properties and are stable. These isomers undergo irreversible electron transfer with $C_8H_8K_2$. The reaction is quantitative when one or two moles of olefin (II) are used per mole of $C_8H_8K_2$. As a result of electron transfer the acceptor (II) forms the K salt as a gelatinous precipitate. Paramagnetic species cannot be detected when the reaction is carried out under the conditions of one-electron transfer. Addition of dicyclohexyl-18-crown-6 to the reaction mixture generates an ESR signal with unresolved hyperfine structure. When dissolved in water, the precipitate gives a UV spectrum characteristic of the salt of dianion (V) [7]. The yield of dianion (V) is near-quantitative with an equimolar ratio of (II) and $C_8H_8K_2$ and close to 50% when the reactant ratio is 2:1; in the latter case some of (II) remains in solution. The solution precipitates neutral (II) as a mixture of the cis and trans isomers in the ratio 1:4, total yield 40%. This happens when either cis- or trans-(II) is used as electron acceptor. Replacement of $C_8H_8K_2$ by $C_{10}H_8K$ does not alter the outcome of the reactions.

Quenching of dianion (V) with oxidants also regenerates (II) as a mixture of the cis and trans isomers in the ratio 1:4, total yield 85%



(2)

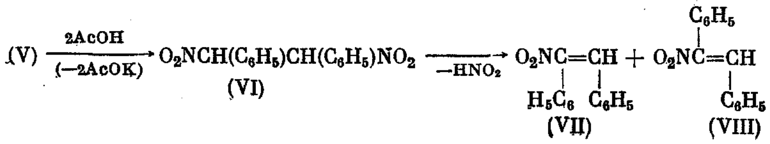
The UV spectra indicate that dianion (V) is common to both cis- and trans-(II). This is plainly the reason why the stereochemical outcome of the oxidation of dianion (V) is independent of the configuration of the original (II) and is the same for the cis and trans isomers. In other words both cis-trans and trans-cis isomerization are possible for (II), unlike (I).

With donor:acceptor ratios appropriate to one-electron transfer, dianion (V) is formed by disproportionation

$$2\,(\mathrm{II}) \xrightarrow[(-\mathrm{C_8H_8})]{\mathrm{C_8H_8K_2}} 2\,[\mathrm{O_2NC(C_6H_5){=}C(C_6H_5)NO_2}]^{\overline{\cdot}}, \qquad \mathrm{K^+} \rightarrow (\mathrm{V}) + (\mathrm{II}) \qquad (3)$$

This is implied by the isomerization of that part of cis- or trans-(II) that is not converted to the insoluble salt of dianion (V) and is recovered from the electron-transfer reaction in the neutral state. This suggests that the isomerization takes place in the radical anions, which then dispropròportionate. The radical anions and dianions of (II) are generated as equilibrium mixtures of the cis and trans forms.

Apart from their differing susceptibility to isomerization, dianions (IV) and (V) also differ in their response to proton donors. Whereas protons cause two-electron oxidation of dianion (IV), dianion (V) adds protons to give α,β-dinitro-α,β-diphenylethane (VI), which is unstable in dilute AcOH and decomposes with the loss of HNO_2. This forms mononitrostilbene in 90% yield as a mixture of the cis-(VII) and trans-(VIII) isomers in the ratio 1:4

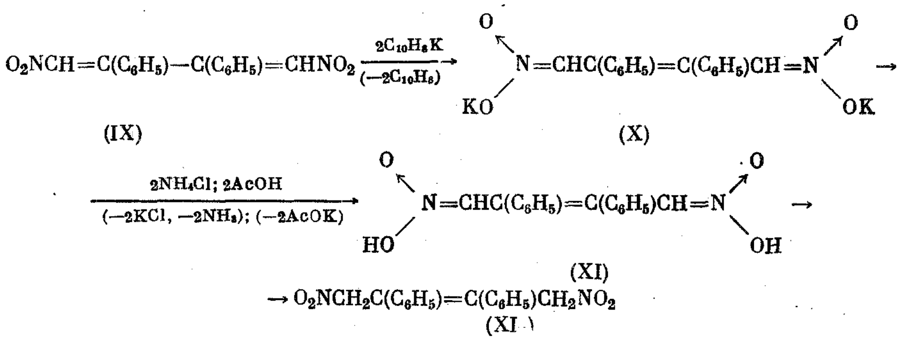


$$(\mathrm{V}) \xrightarrow[(-2\mathrm{AcOK})]{2\mathrm{AcOH}} \underset{(\mathrm{VI})}{\mathrm{O_2NCH(C_6H_5)CH(C_6H_5)NO_2}} \xrightarrow{-\mathrm{HNO_2}} \underset{(\mathrm{VII})}{\mathrm{O_2NC(C_6H_5){=}CH(C_6H_5)}} + \underset{(\mathrm{VIII})}{\mathrm{O_2NC(C_6H_5){=}CH(C_6H_5)}} \qquad (4)$$

Loss of HNO_2 also occurred in the control runs, in which compound (VI) was treated with an aqueous solution of AcOH and AcOK at 0°C in THF. When NH_4Cl was used as the protonating agent, the final product of the reaction was dinitrodiphenylethane (VI) itself, which we obtained in up to 50% yield as a mixture of the meso and D,L isomers.

Electron transfer followed by proton transfer may be considered as a method for the selective hydrogenation of C=C bonds conjugated with two nitro groups. The nitro group remains unaffected: reduction proceeds rapidly without heating.

We established that this method can also be applied to other conjugated dinitro compounds. Thus 1,4-dinitro-2,3-diphenyl-1,3-butadiene (IX) is converted via dianion (X) to trans-1,4-dinitro-2,3-diphenyl-2-butene (XI) in 60% yield



(5)

Schemes (4) and (5) show that two-electron reduction of conjugated dinitro compounds generates the dinitronate dianions. Protonation converts these dianions to the dinitronic acids, isomerization of which affords the hydrogenation products.

In dianion (V) the extra electrons are entirely localized on the nitro groups. The distribution of the extra electrons in dianion (IV) is more intricate: in addition to rather effective localization in the nitro groups, part of their charge is also transferred to the aromatic nuclei and to the carbons of the internuclear C=C bond; protonation of this dianion causes not formation of the dinitronic acid but oxidation, $H^+ + e \rightarrow {}^1/_2H_2$. In the same way treatment of potassium nitrobenzenide in THF with water regenerates nitrobenzene [8].

EXPERIMENTAL

The 4,4'-dinitrostilbenes (I) and α,β-dinitrostilbenes (II) used in the experiments had the melting points: trans-(I) 288-290°C (from acetone) [9]; cis-(I) 183-185°C (from acetone) [6]; trans-(II) 186-187°C (from alcohol) [10]; and cis-(II) 106-107°C (from alcohol) [10].

Two-Electron Reduction of (I) and (II). A solution of (I) or (II) (0.5 mmole) in THF (15 ml) was mixed with a solution of the donor in THF (20 ml) under Ar at −40°C. The donors were the dipotassium salt of the cyclooctatetraene dianion $C_8H_8K_2$ (0.5 mmole) [5] or potassium naphthalenide $C_{10}H_8K$ (1 mmole). The mixture was stirred at −40°C for 30 min. Its temperature was then raised to −5°C and the oxidant (O_2, Cl_2, Br_2) or proton donor (25% solution of AcOH or dry NH_4Cl) was added. In the runs with $C_8H_8K_2$ that ended with protonation the yield of C_8H_8 was determined by GLC [5]; C_8H_8 was obtained in quantitative yield in all runs. The reaction mixture was evaporated under vacuum. The residue was washed with pentene to remove C_8H_8 or dissolved in hexane and passed through a column of Al_2O_3 to remove naphthalene, which was eluted with the first portions of hexane; the other products were eluted with hexane and benzene. In some of the runs naphthalene was removed from the dry residue by vacuum sublimation and the other products were separated by fractional crystallization from alcohol. The products were identified as mixed samples or by TLC with authentic specimens. Treatment of THF solutions of cis- or trans-(I) or (II) with a solution of an equimolar quantity of AcOK in 25% AcOH or with oxidants (O_2, Cl_2, Br_2) did not cause isomerization. In some of the runs the K salts were separated by filtration, washed, dried, and then analyzed.

a) The dipotassium salt of 4,4'-dinitrostilbene (IV) was an unstable cherry red product. Removal of the electrons by an oxidant or AcOH gave (I) (80-90%), mp 288-290°C.

b) Reduction of α,β-dinitrostilbene (II) gave the dipotassium salt of (V) as a gelatinous precipitate. UV spectrum of the salt (H_2O): λ298 nm (ε1.1•10^4). The yield was near-quantitative (based on ε). Quenching of the reaction mixture with an oxidant gave a mixture of the cis and trans isomers in the ratio 1:4 (fractional crystallization from alcohol). The result did not depend on the geometry of the original (II). The total yield was 80-85%. In runs that ended with quenching with 25% AcOH solution, a mixture of cis-(VII) and trans-α-mononitrostilbene (VIII) was isolated by column chromatography (total yield 90%). Compound (VIII) was eluted with hexane (after removal of naphthalene) and (VII) with benzene; they were then purified by crystallization from alcohol. Compounds (VII) and (VIII) were identified as mixed samples with authentic specimens: (VII), mp 71°C [11]; UV spectrum of (VII) ($CHCl_3$): λ318 nm (ε1•10^4); (VIII), mp 126-128°C [12]. PMR spectrum (CCl_4, HMDS, δ, ppm): 7.4 m (10H, C_6H_5), 8.15 s (1H, CH); UV spectrum of (VIII) ($CHCl_3$): λ290 nm (ε1.6•10^4).

The presence of the NO_2^- ion could be detected in the reaction solution treated with AcOH (red coloration on addition of a solution of α-naphthylamine in AcOH [13]). In a control experiment meso-α,β-dinitrodiphenylethane (VI) in THF was treated at 0°C with a solution of an equimolar quantity of AcOK in 25% AcOH; the NO_2^- ion was detected in the solution (qualitative test). α-Mononitrostilbene was isolated quantitatively.

When dry NH_4Cl (0.1 g) was used as protonating agent, loss of HNO_2 did not occur and the product was a mixture consisting of cis- and trans-α,β-dinitrostilbenes in the ratio 1:4 (30% recovery), and meso- and D,L-α,β-dinitro-α,β-diphenylethanes (total yield 50%). The hydrogenation products were identified by TLC with authentic specimens (silica gel, ether–hexane, 4:3) and by comparison of the PMR spectra of these products and dinitrophenylethanes (acetone, HMDS, δ 6.9-7.1).

Selective Hydrogenation of 1,4-Dinitro-2,3-diphenyl-1,3-butadiene (IX). To a suspension of trans,trans-(IX) or cis,cis-(IX) (1.62 mmole) [14] in THF (10 ml) was added at −50°C $C_{20}H_8K$ (3.24 mmole) in THF (10 ml). After 30 min stirring cooled 25% AcOH (20 ml) or dry NH_4Cl (2 g) was added to the mixture at −10°C (all operations in a stream of Ar). The precipitate was filtered off, naphthalene was rinsed off with hexane, and the resulting (IX) was crystallized from CH_3OH (60%), mp 135-138°C [15]. The compound did not depress the melting point of a mixed sample with an authentic specimen.

One-Electron Reduction of (I) and (II). A solution of (I) or (II) (1.0 mmole) in THF (15 ml) was mixed under Ar at −40°C with a solution of $C_8H_8K_2$ (0.5 mmole) or $C_{10}H_8K$ (1 mmole) in THF (20 ml). The mixture was stirred for 30 min while the temperature was allowed to rise to −5°C, and then 25% AcOH (1-2 ml) or an oxidant (O_2, Cl_2, Br_2) was added. When $C_8H_8K_2$ and AcOH were used C_8H_8 was determined (GLC, 100% yield). The reaction products were isolated and freed from cyclooctatetraene or naphthalene by the method described above.

a) When mixed with $C_8H_8K_2$, cis- and trans-(I) gave a dark brown precipitate, which was filtered from THF in Ar, washed with pentane, and dried in a stream of Ar. The ESR spectrum of the precipitate had an intense singlet, while its IR spectrum in KBr or in Vaseline oil (fluorinated or unfluorinated) contained bands at 1300 and 1500 cm^{-1} (neutral nitro group) and 1060, 1170, 1250, and 1455 cm^{-1} (nitro group with an electron [8]). Compounds for elemental analysis were weighed our under Ar. Found: C 53.8; H 3.5; K 14.0% (from the ash). $C_{14}H_{10}NO_4K$. Calculated: C 54.4; H 3.3; K 12.6%.

The one-electron oxidation of 4,4'-dinitrostilbene radical anion (III) was carried out by addition of 25% AcOH to the reaction mixture or by passage of dry O_2. Evaporation of the solvent and separation of the reaction products gave trans-(I). The product was identified via the melting point of a mixed sample; the yield was 85-90%.

b) Reactions of cis- and trans-(II) with electron donors formed the dipotassium salt of the α,β-dinitrostilbene dianion (V) as a gelatinous precipitate. The precipitate was filtered under Ar and dissolved in water. UV spectrum of (V): λ297 nm, ε1•10^4; the yield was 50% (calculated from ε). The filtrate was evaporated; the residue was freed from naphthalene or cyclooctatetraene to give a mixture of cis- and trans-(II) (total yield 40%), which were separated by fractional crystallization from alcohol into the pure cis and trans isomers in the ratio 1:4. In parallel runs the reaction mixture was quenched with an oxidant to give a mixture of cis- and trans-(II) in a total yield of 75%. The isomer ratio was again 1:4. The products were identified by TLC and by the melting point of mixed samples with authentic specimens.

Runs terminated by quenching with AcOH gave as products cis- and trans-(II) in the ratio 1:4 (total yield 40%) and (VII) and (VIII) (total yield 35%). They were identified by TLC and the melting point of mixed samples.

CONCLUSIONS

1. Electron transfer to 4,4'-dinitrostilbenes and α,β-dinitrostilbenes causes isomerization. Isomerization accompanies one- and two-electron transfer.

2. There is a marked difference between the reactions of the dinitrostilbene dianions with protons that depend on the position of the nitro groups: protons induce two-electron oxidation of the nitroaromatic dianion whereas the dinitroethylene dianion adds two protons.

3. The stepwise addition of electrons and protons is a specific method for the selective hydrogenation of an ethylenic bond conjugated with two nitro groups.

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