ELECTRON TRANSFER IN NUCLEOPHILIC VINYL SUBSTITUTION REACTIONS INVOLVING BROMOVINYL SULFONES

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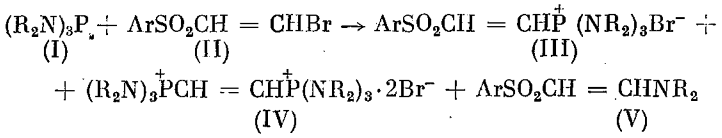
Numerous examples of ion-radical chain reactions for nucleophilic substitution in aliphatic and aromatic compounds are known [1], where the first step is transfer of an electron from the nucleophile as the donor to the acceptor. In some reactions of nucleophilic vinyl substitution (NVS) in the series of inactivated halovinyl compounds [2] it is also assumed that the $S_{RN}1$ mechanism can be realized, although direct proof of electron transfer in these reactions was not obtained.

In the present paper we studied the NVS reactions of a number of β-bromovinyl sulfones, which can be interpreted within the framework of a mechanism that includes the one-electron transfer step.

Previously [3, 4] it was shown by us that when the isomeric β-bromovinyl sulfones are reacted with the full amides of trivalent phosphorus acids (I) the main products are the monosalt (III) and the disalt (IV), accompanied by the formation of the β-dialkylaminovinyl sulfone (V):



$$\underset{(I)}{(R_2N)_3P} + \underset{(II)}{ArSO_2CH = CHBr} \rightarrow \underset{(III)}{ArSO_2CH = CH\overset{+}{P}(NR_2)_3Br^-} + \underset{(IV)}{(R_2N)_3\overset{+}{P}CH = CH\overset{+}{P}(NR_2)_3 \cdot 2Br^-} + \underset{(V)}{ArSO_2CH = CHNR_2}$$

Ar = Ph, p-MeC_6H_4; R = Me, Et

The yield of aminovinyl sulfone (V) depends on the nature of the solvent. Thus, amide (I) (R = Et) when reacted with trans-β-bromovinyl phenyl sulfone (II) (Ar = Ph) in benzene gives β-diethylaminovinyl sulfone (V) (Ar = Ph; R = Et) in less than 5% yield (based on the integral intensity of the doublet in the 5 ppm region in the PMR spectrum of the reaction mixture). In acetonitrile the yield of the aminovinyl sulfone rises to 20%.

When the reaction is run directly in the resonator of the EPR spectrometer in the presence of 2-methyl-2-nitrosopropane (VI) as the spin trap, in either benzene or in acetonitrile, the paramagnetic products (VII) (VIII) (R = Me, Et) were detected. Other radical particles, in particular the arylsulfonylvinyl radical (X),

Fig. 1. EPR spectrum of adduct (VII) (R = Me).

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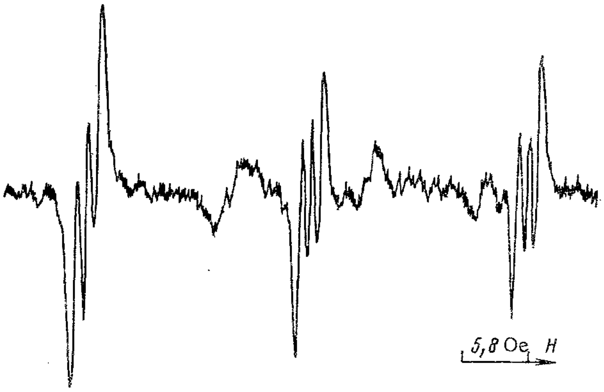

Fig. 2. EPR spectrum of adduct (VIII) (R = Me).

could not be recorded. Adduct (VII) is formed at temperatures of 10-20°C, while (VIII) is formed only at 5° in benzene. The hyperfine structure (hfs) of the EPR spectra of the (VII) adducts (Fig. 1) is caused by the coupling of the unpaired electron with the nuclei of the N and P atoms (a_N = 10.6; a_P = 10.2 Oe). The EPR spectrum of the (VIII) adducts (Fig. 2) consists of nine lines, which is caused by the coupling of the unpaired electron with the nonequivalent N nuclei (a_{N^1} = 18.9, a_{N^2} = 0.9 Oe).

$$\underset{\text{(VII)}}{(R_2N)_3\overset{+}{P} - N(\dot{O})Bu\text{-}t} \quad \underset{\text{(VIII)}}{(R_2N)_2 - \overset{+}{N}R_2{-}N(\dot{O})Bu\text{-}t}$$

Analogous (VII) and (VIII) radicals were recorded previously [5, 7] in the ion-radical reactions of the (I) amides with quinones [5, 6] and diarylbromomethanes [7] in the presence of a spin trap.

p-Dinitrobenzene (DNB) acts as an inhibitor in that it slows up the reaction and lowers the total yield of monosalt (III) and disalt (IV) to 20% in 24 h, whereas in the absence of DNB the yield is 80%.

The presented data can apparently be interpreted within the framework of the ion-radical mechanism for NVS, with the realization of electron transfer from amide (I) to sulfone (II) in the first step.

$$\text{(I)} + \text{(II)} \rightarrow \text{(II)}^{\dot{-}} + [(R_2N)_3\overset{\dot{+}}{P} \leftrightarrow \underset{\text{(IX)}}{R_2\overset{\dot{+}}{N}} - P\,(NR_2)_2] \qquad (1)$$

$$\text{(II)}^{\dot{-}} \rightarrow \underset{\text{(X)}}{ArSO_2CH} = \dot{C}H + Br^- \qquad (2)$$

$$\text{(X)} + \text{(IX)} \rightarrow \text{(III)} + \text{(V)} \qquad (3)$$

The ambident character of cation-radical (IX) explains the formation of the two different spin adducts (VII) and (VIII), the phosphonium compounds (III) and (IV), and also the aminovinyl sulfones (V).

It should be mentioned that the spin trap (VI) itself is an electron acceptor and can generate cation-radicals (IX). It was shown by special experiments that 2-methyl-2-nitrosopropane (VI) actually forms adducts (VII) and (VIII), but in a much lower yield and poorly resolved EPR spectra with a low intensity are observed. In the presence of the (II) sulfones the signals of the (VII) and (VIII) free radicals increase substantially and a more sharply resolved hfs appears.

EXPERIMENTAL

The EPR spectra were recorded on an ER-9 spectrometer (Carl Zeiss, Jena, East Germany) in the temperature range 5-20°.

To a solution of sulfone (II) and nitrosopropane (VI) in either benzene or acetonitrile was added amide (I), and the solution was evacuated.

CONCLUSIONS

It was shown that the reaction of phosphorous hexaalkyltriamides with β-bromovinyl aryl sulfones proceeds via the step of electron transfer with the formation of ion-radicals.

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REACTION OF ACYL(AROYL) ISOCYANATES WITH DIMEDON

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It was shown that the direction of the reactions of trichloroacetyl (I), trifluoroacetyl (II), and benzoyl isocyanates (III) with dimedon (IV) depends on the temperature and nature of the isocyanates. Thus, (I) reacts with (IV) at 18-20°C to give N-trichloroacetyl O-(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl) carbamate (V). The IR spectrum of (V) has the bands (ν, cm^{-1}): 1780 (OCONH), 1735 (C(O)N), 1673 (C=O cycl.), 1650 (C=C), 3280 (NH). PMR spectrum (δ, ppm): 1.00 s (6H, 2Me), 2.50 s (4H, 2CH$_2$), 6.00 s (1H, =CH), 7.40 br. s. (NH). Heating at 65-75° facilitates [4 + 2]-cycloaddition to give 10,10-dimethyl-4,8-dioxo-2-trichloromethyl-1,5,3-dioxazaspiro[5.5]-2-undecene (VI). The IR spectrum of (VI) has the bands (ν, cm^{-1}): 1775 (OCON), 1670 (C(O)C), 1535, 1565 (C=C, C=N).

PMR spectrum of (VI) (δ, ppm): 1.16 s (6H, 2Me), 2.40 s (2H, CH$_2$), 2.50 s (2H, CH$_2$), 7.30 s (2H, CH$_2$). The signal of the protons of the 7-CH$_2$ group is shifted strongly downfield due to the deshielding effects of the C=O group and dioxazinone ring. The reaction of (I) at the C=O group of (IV) resembles the reaction of carbonyl diisocyanate with cyclohexanone (formation of a six-membered spirocyclic product, whose IR spectrum resembles that of (VI) [1]). In addition, a product with mp 104-106° was obtained, which, based on the IR spectral data, has the structure of the trichloroacetamide of 5,5-dimethyl-1-hydroxy-3-oxo-1-cyclohexen-2-oic acid (VII) (ν, cm^{-1}): 1670, 1630, 1595 (C=O, C=C). The low absorption of the C=O groups of the CONHCO fragment is caused by the presence of two intramolecular hydrogen bonds. The absorption bands 2550-2700, 3120, 3280 cm^{-1} correspond to the OH and NH groups.

The main reaction products of (II) with (IV) are 5,5-dimethyl-3-oxo-1-trifluoroacetimino-1-cyclohexene (VIIIa) and 5,5-dimethyl-3-oxo-1-trifluoroacetamido-1-cyclohexene (VIIIb), which, based on the IR and PMR spectral data, are found to be in equilibrium in aprotic solvents (CCl$_4$, CHCl$_3$, CCl$_3$CN). The IR spectra of the (VIII) solutions have the absorption bands (ν, cm^{-1}): 1625-1630 (C=C), 1760-1765 (CF$_3$C(O)N), 1680-1690 (C=O cycl., C=N exocycl.), 2430-2830, 3210, 3330-3370, 3430, 3500-3510 (OH, NH). PMR spectrum (CCl$_4$, δ, ppm): 1.04 s (6H, 2Me), 2.21 s (CH$_2$), 2.51 d ($^{1,4}J$ = 2 Hz (CH$_2$)), 6.10 t ($^{1,4}J$ = 2 Hz (=CH)), 4.60 br. s (OH), 7.30 br s (NH). The signal with δ 4.60 ppm belongs to the labile proton of the OH group, which does not take part in forming a strong H bond [2]. Determination of the pH in aqueous solution (pH 4) disclosed the acid character of (VIII). Evidently, (VIII) is formed by cleaving CO$_2$ from a product that is analogous to (VI). This can be judged by the IR spectrum of a solution of the reaction mixture in CHCl$_3$, recorded at −10°, which has an absorption band at 1760-1765 cm^{-1}, corresponding to the C=O of the dioxazinone ring. The absence of absorption bands in the 3000-3600 cm^{-1} region permits excluding the formation of a substituted urethan. However, it is impossible to exclude the possibility of forming (VIII) via the four-membered spiran intermediate.

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