Brief Communications

The reduction of aromatic nitro compounds by oxiranes

Ya. S. Vygodskii, L. I. Komarova,* and Yu. V. Antipov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, Russian Federation. Fax: +7 (095) 135 5085

Aromatic nitro compounds are reduced to the corresponding amines by epoxides at elevated temperatures (>170 $^{\circ}$ C).

Key words: nitro compounds, amines, epoxides, reduction.

It was expedient in terms of studies on the interaction of epoxides with various heterobonds (ester, amide, and other) and heterocyclic fragments (benzoxazolyl, 1,3,4oxadiazolyl, isocyanurate, and others)¹ to evaluate the stability of imide cycles with respect to similar reactions, taking into account that epoxy resins and oligo- and polyimides are widely used as binders for composites. For this purpose, we have studied the behavior of several imides 1a-d in the presence of glycidyl phenyl ether (GPE), diethylene glycol diglycidyl ether (DEG), and epoxy oligomer based on bisphenol A (ED-20).



b: $X = NO_2$; Y = H; **f**: X = H; $Y = NH_2$; **c**: X = H; $Y = NO_2$; **g**: $X = Y = NH_2$. **d**: $X = Y = NO_2$;

It has been established that the imide cycle in these compounds does not undergo any changes when heated to very high temperatures (270 °C). At the same time, the data of IR spectroscopy show that heating nitroimides **1b**-d with epoxide compounds in an inert atmosphere results in a decrease in the content of nitro groups, beginning at 150 °C (bands at 1520 and 1340 cm⁻¹) until their complete disappearance at 270 °C after 3 h, in a decrease in the content of epoxy groups (865, 915, 3010, and 3060 cm^{-1}) until their complete disappearance as well, and in the simultaneous appearance of primary amino groups (two bands in the range of stretching vibrations of NH₂ groups at 3370-3480 cm⁻¹ and 1615 and a doublet at 1300 and 1100 cm^{-1}). The reaction is accompanied by the liberation of gaseous products containing CO, CO_2 , and water vapor, according to the data of IR spectroscopy.

Aminoimides corresponding to the initial nitroimides (1e-g), glycerol 1-phenyl ether (in the reaction with GPE), and *p*-nitroaniline (from the reaction with nitroimide 1c) were isolated and identified as the reaction products. Judging from the IR spectra, the conversion of the nitro groups in the reaction is close to quantitative. Taking into account the structure of the compounds

obtained and the available data on the insertion reaction of oxiranes at polar heterobonds such as the ester bond,¹ one can suggest a scheme of the reactions (Scheme 1), which results in the reduction of aromatic nitro groups by the protons of the alkylene groups of the epoxide.

This scheme does not cover all of the reactions that can take place in these systems, but makes it possible to imagine probable patterns of the reduction of nitro groups by protons of the oxyrane cycle and the formation of carbon oxides. Perhaps, the process of reduction of nitro groups also involves the alkylene protons of the two epoxy groups. The water formed in the reaction is likely to react with epoxy groups, because glycerol 1-phenyl ether is one of the products of the reaction involving GPE. IR spectroscopy and chromatography





Table 1. Yields of the products of the interaction between aromatic nitro compounds and epoxides at an equimolar ratio of the components

Com- pound ArNO ₂	Epoxide	<i>T</i> /°C ^a	τ/h ^a	Yield of amine (mol %	Found (%) Calculated			Yield of <i>p</i> -nitroaniline (wt %)	Yield of glycerol 1-phenyl ether (mol % of GPE)	$\frac{F_s^{\ b}}{F_{ins}}$	Composition of gaseous reaction
				of ArNO ₂)	С	Н	N ·				products
1a	GPE	260	7	-	-	_	-	_		<u>70</u> 30	
1b	»	260	7	21 ^c (1e)	<u>70.75</u> 70.59	<u>4.15</u> 4.20	<u>11.95</u> 11.76		25 ^d	<u>39</u> 61	H ₂ O, CO ₂ , CO
1c	*	260	7	30 ^e (1 f)	<u>70.36</u> 70.59	<u>4.45</u> 4.20	<u>10.87</u> 11.76	31 ^f	28	<u>32</u> 68	»
1d	»	260	7	12 ^g (1g)	<u>66.51</u> 66.40	<u>4.27</u> 4.35	<u>16.85</u> 16.60		26	<u>30</u> 70	»
p-Nitro- toluene	»	265	6		—	_	_		_	<u>80</u> 20	H ₂ O, CO ₂ , CO, CH ₄
la	DEG	250	7	_					_	<u>52</u> 48	
1b	*	250	7	12 (1e)	<u>70.80</u> 70.59	<u>4.19</u> 4.20	<u>11.80</u> 11.76	_	_	<u>10</u> 90	H ₂ O, CO ₂ , CO
1c	»	250	7	15 (1f)	<u>70.41</u> 70.59	<u>4.22</u> 4.20	<u>11.70</u> 11.76	Traces	_	<u>12</u> 88	»
1d	»	250	7	8 (1g)	<u>66.45</u> 66.40	<u>4.40</u> 4.35	<u>16.20</u> 16.60	_		<u>9</u> 91	»
la	ED-20	250	7	_	<u></u>		-	_	_	<u>39</u> 61	
1b	»	250	7	18 (1e)	<u>70.49</u> 70.59	<u>4.36</u> 4.20	<u>11.71</u> 11.76			<u>29</u> 71	H ₂ O, CO ₂ , CO
1c	*	250	7	20 (1f)	<u>70.62</u> 70.59	<u>4.25</u> 4.20	<u>11.70</u> 11.76	~1		<u>32</u> 68	»
1d	»	250	7	10 (1g)	<u>66.30</u> 66.40	<u>4.41</u> 4.35	<u>16.40</u> 16.60	<u> </u>		<u>28</u> 72	»

^{*a*} Temperature (*T*) and time (τ) of the interaction.

- ^b F_s/F_{ins} is the ratio of the soluble and insoluble fractions. ^c M.p. 205.5 °C (cf. Ref. 3: 205–207 °C). $C_{14}H_{10}N_2O_2$.
- ^d M.p. 64-67 °C (cf. Ref. 3: 69-70 °C).
- $e M.p. 250 \ ^{\circ}C \ ^{4}. \ C_{14}H_{10}N_{2}O_{2}.$
- ^f M.p. 150.5 °C (cf. Ref. 6: 149–151 °C).

^g M.p. 274-276 °C (cf. Ref. 5: 275 °C). C₁₄H₁₁N₃O₂.

show that there are no simple products of the epoxide transformation in the mixtures obtained after the interaction, as would be expected from the scheme presented above. This means that the radicals or charged particles formed in the reaction are consumed in the interaction with the numerous other particles to form large amounts of high-molecular fractions containing fragments of epoxides and imides (Table 1). The small amount of amines (1e-g) is explained by their interaction with epoxides. The presence of *p*-nitroaniline in the reaction products can be explained by transimidation according Scheme 2.

Scheme 2



Actually, aminoimide 1f and p-nitroaniline were isolated as the result of the model transimidation of nitroimide 1c with excess p-phenylenediamine.

It should also be noted that the reduction is accelerated by such compounds as quaternary ammonium salts and alkaline salts of carboxylic acids, which, as is known,¹ catalyze the interaction between oxiranes and esters. For example, the reduction occurs efficiently in the presence of 1 % trimethylbenzylammonium chloride (calculated with respect to the epoxide) at 200–220 °C, which is ~50 °C lower than that without this addition.

The applicability of this high-temperature reduction of aromatic nitro compounds to primary amines was confirmed by the reaction between *p*-nitrotoluene and glycidyl phenyl ether. The disappearance of the nitro and epoxy groups, appearance of amino groups, and formation of a mixture of gaseous products containing CO, CO₂, H₂O, and CH₄ were also observed after 6 h at 265 °C in an inert atmosphere. (The mechanism of the formation of CH₄ should be additionally studied.)

Experimental

IR spectra were recorded on Perkin-Elmer 427, M-80, and Bruker IFS-113v spectrophotometers.

An equimolar mixture of glycidyl phenyl ether (epoxide oligomer) and the corresponding imide (or *p*-nitrotoluene) was heated in a Pyrex tube in argon at 200-270 °C for 7 h. After heating, the tube was frozen with liquid nitrogen, connected to a preliminarily evacuated IR cuvette in which the gas liberated in the reaction was collected. Solid products were treated with diethyl ether, which partially dissolves the reaction product.

The ratio of the soluble and insoluble fractions was (30-40) : (70-60). The soluble fractions were passed through a column filled with Silicagel L-100/1600, using diethyl ether as the eluent. From 7 to 9 fractions were isolated in various experiments. They were individual substances which differed from the initial compounds and mixtures in which there were two or three main substances, according to the data of IR spectroscopy. Judging from IR spectroscopy, the degree of the completeness of the reaction with respect to the nitro compound was close to quantitative. For example, a mixture of gaseous products containing CO, CO2, and water was obtained from 0.4794 g of (4-nitrophenyl)phthalimide 1c and 0.2491 g of glycidyl phenyl ether after heating for 7 h at 260 °C and subsequent treatment (see above). The portion of the solid products (0.28 g) soluble in diethyl ether was chromatographed to give 8 fractions, two of which, namely, fractions 4 and 5, were individual substances, according to the data of LC and IR

spectroscopy. Fraction 4 (0.15 g) was a product of the reduction of nitroimide **1c**: (4-aminophenyl)phthalimide (**1f**), m.p. 250 °C. Found (%): C, 70.36; H, 4.45; N, 10.87. $C_{14}H_{10}N_2O_2$. Calculated: (%): C, 70.59; H, 4.20; N, 11.76. The structure of this compound was also confirmed by its identity with the product obtained from (4-nitrophenyl)phthalimide **1c** and *p*phenylenediamine. Judging from the data of elemental analysis and the IR spectra, fraction 5 (0.07 g) was glycerol 1-phenyl ether. Found (%): C, 64.95; H, 7.51. $C_9H_{12}O_3$. Calculated (%): C, 64.29; H, 7.14. The IR spectrum was completely identical to that of glycerol 1-phenyl ether obtained by counter synthesis according to the known procedure.² According to the data of LC, the other soluble fractions were mixtures of two or three products probably formed as the result of secondary reactions of the formed amine with epoxide, imide, *etc*.

The data on the other reactions of N-arylphthalimides **1f-d** with epoxides are presented in Table 1.

The structures of the isolated compounds were confirmed by elemental analysis, m.p. or b.p. values, and the complete identity of IR spectra with those of the corresponding known compounds.

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