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CHEMISTRY

Study of the Reaction of Trinitromethane with Oxiranes

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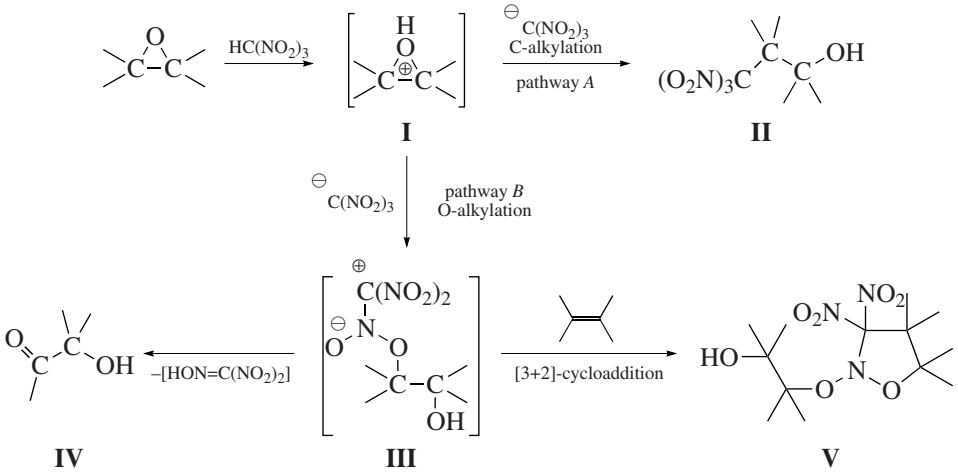
The reaction of olefins with polynitromethanes is a known method for the preparation of 3,3-dinitroisoxazolidines [1, 2]. Previously, we studied reactions of tetranitromethane and halotrinitromethanes with unsaturated compounds containing small rings [3–8]. It was shown that the reactions of polynitromethanes with strained alkenes and acetylenes give a range of N- and O-containing heterocycles (dinitroisoxazolidines, nitroisoxazolines, dinitropiperidones, dinitroaziridines), tetranitropropanes, and *gem*-dinitrocyclopropanes [3–9].

No data on reactions of oxiranes with polynitromethanes have been reported so far, although these reactions can be considered as a new method for generation of alkyl nitronates, which are precursors of diverse heterocycles, and as a possible approach to the synthesis of trinitroalkanols.

The trinitromethyl anion is known to show ambident properties, functioning as either an O- or a C-nucleophile depending on the substrate nature [1, 4, 7]. We suggested two possible pathways for its reaction with epoxides (Scheme 1), namely, pathway *A* including C-alkylation of the oxonium cation **I** to give 3,3,3-trinitropropanols **II** (two-component reaction) and pathway *B* including O-alkylation of the oxonium cation **I** with generation of an unstable nitronic ester **III,** which can either decompose to α-hydroxy ketone **IV** or undergo [3+2]-cycloaddition in the presence of an olefin to give 3,3-dinitroisoxazolidines **V** (three-component reaction).



Scheme 1.

The ratio of C- to O-alkylation of cation **I** with the trinitromethyl anion depends on the positive charge delocalization properties of substituents in the substrate.

This study is devoted to the previously unknown two-component reaction of oxiranes with trinitromethane and aimed at the search for the ways of implementation of C-alkylation of oxonium cation **I** to give type **II** adducts (Scheme 1, pathway *A*).

As the model reaction, we studied the reaction of styrene oxide (**VIa**) with trinitromethane at room temperature in nonpolar and polar solvents (Scheme 2). One could expect that the presence of the phenyl group in the styrene oxide would facilitate C-alkylation of the oxonium cation **I** with trinitromethane.

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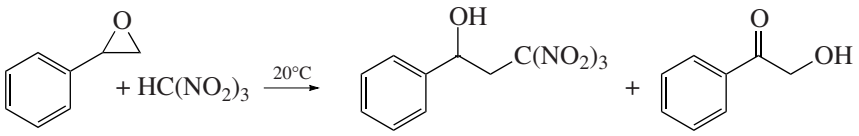


VIa **VIIa** **VIIIa**

Scheme 2.

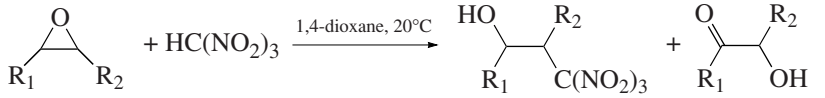
The reaction of styrene oxide (**VIa**) with trinitromethane in benzene was found to follow two pathways, namely, C-alkylation to give γ-trinitropropanol **VIIa** (yield 40%) and O-alkylation to give α-keto alcohol **VIIIa** (yield 55%). The latter results from decomposition of unstable nitronic ester **III** formed from trinitromethane and styrene oxide according to pathway *B*.

The ^{13}C NMR spectrum of the trinitro derivative **VIIa** exhibits signals at δ 38.0 and 74.7 ppm corresponding to the methylene carbon atom of the $CH_2C(NO_2)_3$ fragment and methine carbon atom of the CHOH group, respectively, which attests unambiguously to the formation of the proposed regioisomer. Thus, in this case, the attack by the shielded C-center on the trinitromethyl anion involves only the terminal, spatially more accessible carbon atom of oxirane (**VIa**).

The ^1H and ^{13}C NMR spectra of keto alcohol **VIIIa** correspond to published data [10]. It is obvious that the attack by the O-center of the nucleophile is directed at the benzyl position of oxirane and involves the intermediate formation of thermodynamically more stable benzyl carbocation. These results are in line with published data concerning the effect of steric factors on the regioselectivity of nucleophilic oxirane ring opening [11, 12].

When the reaction of styrene oxide **VIa** with trinitromethane is carried out in dioxane, products **VIIa** and **VIIIa** are formed in 50 and 20% yields, respectively; i.e., C-alkylation becomes the predominant reaction pathway. The reaction of styrene oxide **VIa** with trinitromethane in petroleum ether proceeds exclusively as C-alkylation but trinitropropanol **VIIa** is formed in a low yield (27%) due to partial polymerization of the starting oxide. Note for comparison that the reaction of an aqueous solution of the potassium salt of trinitromethane with styrene oxide **VIa** does not give any identifiable products.

The reaction of trinitromethane with oxiranes **VIb**–**VId** was carried out under conditions optimized for the formation of C-alkylation products using oxide **VIa** (Scheme 3) as an example.



VIa–VId **VIIa–VIId** **VIIIa–VIIIc**

Scheme 3.

The results are summarized in the table.

According to NMR data for the reaction mixture, the reaction of *p*-bromostyrene oxide **VIb** gives trinitro alcohol **VIIb** as the major product, which was formed in 65% yield according to NMR data. However, after chromatographic purification, the yield of alcohol **VIIb** did not exceed 20% due to its low stability against silica gel.

In the reaction of cycloheptene oxide **VIc** with trinitromethane, C- and O-alkylation products **VIIc** and **VIIIc**, respectively, were isolated in approximately equal amounts.

The reaction of propylene oxide **VId** with trinitromethane was carried out in a sealed tube using a fourfold excess of oxirane **VId** with respect to trinitromethane. The reaction affords trinitro alcohol **VIId** in a low yield and 1,2-propanediol **IX** in 40% yield. Note that propylene oxide is substantially polymerized under the reaction conditions under the action of trinitromethane.

1,1-Diphenylethylene oxide proved to be inert with respect to trinitromethane under the selected conditions; this may be due to steric hindrance to the reaction of the trinitromethyl anion with the oxonium cation. An attempt to involve ethylene oxide in the reaction with trinitromethane was also unsuccessful because the reaction under these conditions gave only polymerization products.

Thus, we found that reactions of trinitromethane with oxiranes containing both aryl and alkyl substituents proceed in most cases as competitive C- and O-alkylation to give γ-trinitropropanols **VII** and α-keto alcohols **VIII**, respectively. Trinitro alcohols proved to be rather labile compounds that decompose during storage or during chromatography on silica gel. Nevertheless, these compounds should be classified as rather readily accessible and promising intermediates, for

Reaction conditions and product yields for the reaction of oxiranes **VIa**–**VId** with trinitromethane

Oxirane	R_1	R_2	Products	Time, days	Chromatographic yield, %	
					VII	**VIII**
VIa	Ph	H	**VIIa**, **VIIIa**	1	50	20
VIb	*p*-BrPh	H	**VIIb**, **VIIIb**	7	20	30
VIc	$-(CH_2)_5-$		**VIIc**, **VIIIc**	2	20	23
VId	Me	H	**VIId**, **VIIId**	2	14	–

example, for nitration and preparation of trinitronitratoalkanes, new high-energy compounds.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 and 100 MHz, respectively). Chloroform signals (δ_H 7.28 and δ_C 77.1 ppm) were used as the internal standard. Mass spectra were recorded on an MC Finnigan MAT ITD-700 instrument at an ionization energy of 70 eV. Positive ion MALDI TOF mass spectra were run on a Bruker Daltonics Ultraflex instrument (1,8,9-trihydroxyanthracene was used as the matrix).

The reactions were monitored and the compound purity was checked by TLC (Silufol UV-254). Preparative column chromatography was performed using Acros silica gel (60–200 mesh).

General procedure. Trinitromethane (4 mmol) was added to a solution of oxirane (2 mmol) in 1,4-dioxane (5 ml) at room temperature. The reaction mixture was stirred at 20°C for 1–7 days (table). Then the solvent was evaporated under reduced pressure. The products were isolated by column chromatography on silica gel (elution with petroleum ether–EtOAc, 4 : 1).

3,3,3-Trinitro-1-phenyl-1-propanol VIIa. Yield 270 mg (50%); yellow liquid; R_f 0.63 (petroleum ether–EtOAc, 4 : 1). ^{1}H NMR ($CDCl_3$, δ, ppm): 3.06 (dd, ^2J = 13.9, ^3J = 9.9 Hz, 1 H, CH_2), 3.17 (dd, ^2J = 13.9, ^3J = 2.0 Hz, 1 H, CH_2), 3.45 (br.s, 1 H, OH), 5.14 (dd, ^3J = 2.0, 9.9 Hz, 1 H, CH), 7.28–7.92 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm)[1]: 38.0 (CH_2), 74.7 (CH), 128.8, 129.1 (×2), 129.5 (×2) (CH, Ph), 134.8 (C). MS: *m*/*z* = 271 $[M]^+$.

2-Hydroxy-1-phenylethanone VIIIa [10]. Yield 50 mg (20%); pale yellow liquid; R_f 0.38 (petroleum ether–EtOAc, 4 : 1). ^{1}H NMR ($CDCl_3$, δ, ppm): 3.45 (br.s, 1 H, OH), 4.88 (s, 2 H, CH_2), 7.28–7.92 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 65.3 (CH_2), 127.8 (×2), 127.9 (CH, Ph), 129.0 (2 × CH, Ph), 134.8 (C, Ph), 198.6 (CO).

1-(4-Bromophenyl)-3,3,3-trinitro-1-propanol VIIb. Yield 140 mg (20%); yellow liquid; R_f 0.84 (petroleum ether–EtOAc, 4 : 1). ^{1}H NMR ($CDCl_3$, δ, ppm)[2]: 2.98 (dd, ^2J = 13.7, ^3J = 9.8 Hz, 1 H, CH_2), 3.06 (dd, ^2J = 13.7, ^3J = 1.7 Hz, 1 H, CH_2), 5.09 (dd, ^3J = 1.7, 9.8 Hz, 1 H, CH), 7.08–7.18 (m, 4 H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 37.5 (CH_2), 74.2 (CH), 123.1 [$C(NO_2)_3$], 131.3 (2 × CH, Ph), 131.6 (C, Ph), 132.0 (2 × CH, Ph), 132.7 (C, Ph).

1-(4-Bromophenyl)-2-hydroxyethanone VIIIb [13]. Yield 90 mg (20%); pale yellow liquid; R_f 0.35 (petroleum ether–EtOAc, 4 : 1). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.87 (br.s, 1 H, OH), 3.05 (d, ^2J = 2.0 Hz, 1 H, CH_2), 3.67 (d, ^2J = 2.0 Hz, 1 H, CH_2), 7.49–7.52 (m, 4 H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 65.3 (CH_2), 129.1 (2 × CH, Ph), 131.4 (C, Ph), 132.4 (2 × CH, Ph), 132.9 (C, Ph), 201.3 (CO).

2-(Trinitromethyl)cycloheptanol VIIc. Yield 110 mg (20%); yellow liquid; R_f 0.75 (petroleum ether–EtOAc, 4 : 1). ^{1}H NMR ($CDCl_3$, δ, ppm)[3]: 1.51–1.88 (m, 10 H, CH_2), 3.80–3.85 (m, 1 H, $CHC(NO_2)_3$), 4.91–4.97 (m, 1 H, CHOH). ^{13}C NMR ($CDCl_3$, δ, ppm): 22.4, 26.6, 28.9, 32.9, 33.7 (CH_2), 40.6 [$CH(NO_2)_3$], 70.9 (CHOH), 128.2 [$C(NO_2)_3$].[3]

2-Hydroxyheptanone VIIIc [10]. Yield 60 mg (23%); yellow liquid; R_f 0.58 (petroleum ether–EtOAc, 4 : 1). ^{1}H NMR ($CDCl_3$, δ, ppm)[3]: 1.51–1.88 (m, 10 H, CH_2), 4.31 (dd, ^3J = 3.4, 9.6 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 22.4, 24.9, 28.7, 33.7, 40.1 (CH_2), 77.4 (CH), 203.7 (CO).

4,4,4-Trinitro-2-butanol VIIId [14]. Yield 60 mg (14%); yellow liquid; R_f 0.45 (petroleum ether–EtOAc, 4 : 1). ^{1}H NMR ($CDCl_3$, δ, ppm)[3]: 1.31 (d, ^3J = 5.3 Hz, 3 H, CH_3), 3.64 (dd, ^2J = 12.8, ^3J = 6.7 Hz, 1 H, CH_2), 3.73 (dd, ^2J = 12.8, ^3J = 3.3 Hz, 1 H, CH_2), 4.06–4.12 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 18.9 (CH_3), 41.8 (CH_2), 81.5 (CH), 128.1 [$C(NO_2)_3$]. MALDI TOF MS: *m*/*z* = 209 $[M]^+$.

[1] No signal for the $C(NO_2)_3$ group was observed in the ^{13}C NMR spectrum of **VIIa**.

[2] No signal for the hydroxyl group proton was observed in the ^{1}H NMR spectrum of compound **VIIb**.

[3] No signals for the hydroxyl group protons were observed in the ^{1}H NMR spectra of **VIIc**, **VIIIc**, **VIIId**, or **IX**.

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