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Thermal Decomposition of Vicinal Dinitroalkanes**

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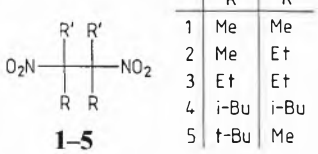
Abstract: Three *sym*-tetraalkyl-dinitroethanes **1**–**3** have been decomposed in solution at 180 to 215°C. The alkylated 1,3-butadienes **10**, **12**, and **13** are formed by elemination of HNO_2. No products could be observed, which were generated by homolytic cleavage of the central C–C bond. Thus the dimers of tertiary α-nitroalkyl radicals (**9**) do not cleave into **9** by heating.

As part of our continuing studies of steric and electronic effects on the thermal decomposition of α,β-disubstituted tetraalkylethanes[1] the behaviour of vicinal dinitro compounds was examined.

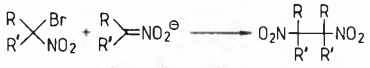


	R	R'
1	Me	Me
2	Me	Et
3	Et	Et
4	i-Bu	i-Bu
5	t-Bu	Me

1–5

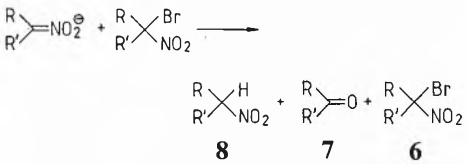
The $S_{RN}1$-reaction between the anion of a secondary nitroalkane and the corresponding α-bromo-nitroalkane (Eq. 1) is the general method to obtain symmetric vicinal dinitro compounds[2]. The derivatives **2** and **3** were prepared in this way in 39% and 25% yield, respectively. Compound **1** was commercially available.

Eq. 1:



	R	R'	yield
2	Me	Et	39%
3	Et	Et	25%

Eq. 2:



	8	**7**	**6**
R=i-Bu, R'=i-Bu:	57%	5%	0%
R=Me, R'=t-Bu:	21%	21%	42%

Attempts to obtain the highly branched derivatives **4** and **5** by the same method did not produce coupling products, but unchanged starting material **6**, the ketones **7**, and the secondary nitroalkanes **8** (Eq. 2). Their formation is attributed to the chain-

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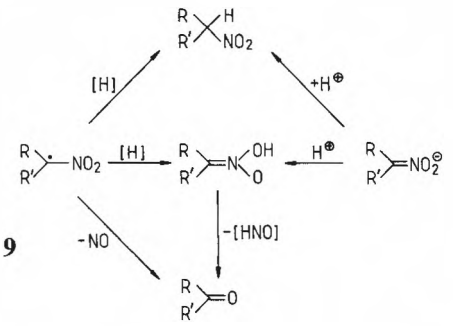
terminating reactions presented in Scheme 1. These processes are the main reactions if the steric demand of the attached groups does not favour the coupling reaction. The ketones and the secondary nitroalkanes could have been formed by protonation of the anion as well.



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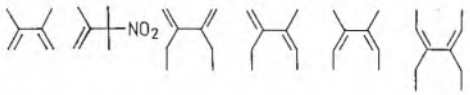
Schema 1. Formation of secondary nitroalkanes and ketones from α-nitroalkyl radicals **9**.

The thermolysis of compounds **1**–**3** under the conditions presented in Table 1 revealed that they do not decompose by cleavage of the central C–C bond, as known for tetraalkylated dimethyl-succinates, succinodinitriles or 1,2-diphenylethanes, but by eliminating nitrous acid. This was shown by the nature of the decomposition products which were exclusively the olefins **10** to **13**. Compound **1** decomposed to the diene **10** and to the allylic nitro compound **11**. In case of the derivatives **2** and **3** *cis*/*trans* isomers of the olefins **12a–c** and **13**, respectively, were formed. They were identified by GC-MS-coupling. Secondary nitroalkanes and ketones, representing the expected products of a C–C bond cleavage reaction, were not found even in trace amounts.



10 **11** **12a** **12b** **12c** **13**

It appears from other work[3–6] that the elimination of nitrous acid does not proceed in a two-step radical mechanism starting with a homolytic cleavage of the C–N bond, followed by the loss of a β-hydrogen atom, but rather via a simultaneous pathway involving a five-centered transition state.

Table 1. Thermal decomposition products of the compounds **1**–**3**.

Substrate	Solvent	T[a] [°C]	t[b] [h]	Product [%][c]	formula
1	mesitylene	215	3	60	C_6H_{10}
				40	$C_6H_{11}NO_2$
2	benzene	200	14	10	C_8H_{14}
				39	C_8H_{14}
				23	C_8H_{14}
				14	C_8H_{14}
				14	C_8H_{14}
3	mesitylene	180	8	18	$C_{10}H_{18}$
				82	$C_{10}H_{18}$

[a] Temperature; [b] time of thermolysis; [c] product composition.

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