SYNTHESIS AND SOME PROPERTIES OF 1,3,5-TRINITROCYCLOHEXANE

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In [1] was described very briefly a method for the synthesis of 1,3,5-trinitrocyclohexane (I) by the reduction of 1,3,5-trinitrobenzene with sodium borohydride. In order to corroborate the structure of (I) only the elemental analysis results were given. In view of the fact that our first attempts to reproduce the method described in [1] proved to be unsuccessful (instead of a crystalline product we obtained a tar, from which (I) could be isolated only with great difficulty), we undertook a more detailed study of the conditions for the synthesis of (I).

It is known [2] that 1,3-dinitrocyclohexane in alkaline medium is unstable. The decomposition goes rapidly in 0.1 N alcoholic NaOH solution, more slowly in 0.01 N solution, while in 0.001 N solution 1,3-dinitrocyclohexane is quite stable (the decomposition was followed spectrophotometrically). In order to ascertain the stability of (I) in alkaline medium a study was made of the change in the absorption with time in the UV spectra of aqueous solutions of (I) at variable NaOH concentration, using an SF-4 instrument. Nitroalkanes form in alkaline medium quite stable nitronate ions, which are characterized by absorption in the 230-250 nm region [2]. The data, obtained in studying aqueous solutions of (I) at variable NaOH concentration, are summarized in Table 1. The concentration of (I) in all of the experiments was $1.78 \cdot 10^{-5}$ mole /liter, and the temperature was 20°.

From Table 1 it can be seen that an alkaline solution of (I) has an intense absorption maximum at $\lambda = 235$ nm, in which connection the intensity of the absorption changes with time, and more rapidly the higher the caustic concentration. The decomposition of (I) was judged by the absence of absorption at λ 235 nm and the appearance of absorption at λ 340 nm.* As a result, (I) is quite stable for 8 h in 0.001 N NaOH solution, and decomposes completely in 2 h in 0.01 N solution, and in 14 min in 0.05 N solution. The results of this work disclosed that it is expedient to run the reduction in the shortest time possible. Thus, if the reduction is run for 40-50 min, and the temperature is kept between −2 and 2°, it becomes possible to obtain (I) in good yield (55%, with 40% given in [1]) and in a crystalline state directly from the reaction mixture (in [1] the compound was isolated as an oil).

The heating curve for (I) when a sample was heated on a NTP-64 instrument (differential-thermal analysis) disclosed that the compound is polymorphous. At 43-46° the low-temperature α-form changes over to the high-temperature β-form. The discussed transformation is enantiotropic. The existence of the transformation was corroborated by microstructure studies (the α-phase is anisotropic, while the β-phase is isotropic).

1,3,5-Trimethylol-1,3,5-trinitrocyclohexane (II) is formed when (I) is reacted with formaldehyde in the presence of catalytic amounts of K_2CO_3. The structure of (II) was confirmed by the elemental analysis data, the IR spectrum, and the preparation of its triacetate and 1,3,5-tri-(bromomethyl)-1,3,5-trinitrocyclohexane (III).

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* Absorption in the 270-280 nm region, corresponding to the non-ionized nitro compound, was not observed.

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TABLE 1

Time, min	0,05 *N* NaOH		0,01 *N* NaOH		0,001 *N* NaOH	
	λ	ε	λ	ε	λ	ε
1	235	32500	235	33700	235	31900
14	340	7300				
90			235 340	17500 6500		
124			340	7000		
480					235	29700

EXPERIMENTAL METHOD

1,3,5-Trinitrocyclohexane (I). To a solution of 9 g of $NaBH_4$ in 200 ml of 50% CH_3OH, with vigorous stirring, at a temperature of −2 to 2°, in 40-50 min, were added in succession a solution of 8 g of 1,3,5-trinitrobenzene (mp 121°) in 40 ml of THF, and then, in drops, in 10-15 min, 100 ml of a 20-25% aqueous solution of tartaric acid. The obtained precipitate of (I) was filtered, washed with water, and dried in the air. Weight 6 g. Recrystallization from isopropanol gave 4.3 g (55%) of (I), mp 121°. From [1]: mp 125°. Found: C 33.22; 33.28; H 4.47; 4.39%. $C_6H_9N_3O_6$. Calculated: C 32.88; H 4.14%. Infrared spectrum (ν, cm^{-1}): 725 med, 808 med, 855 med, 1120 med, 1320 med, 1358 sh, 1275 sh, 1390 s, 1445 med, 1470 med, 1750 med, 2980 med.

1,3,5-Trimethylol-1,3,5-trinitrocyclohexane (II). To a solution of 3.3 g of (I) in 75 ml of ethanol at 40° were added in succession a solution of 0.1-0.15 g of K_2CO_3 in 1 ml of water and 42.8 ml of 38% formalin solution. The mixture was heated at 40° for 15-20 h, cooled, and the obtained precipitate was filtered and washed with ethanol. The yield of (II) was 4.4 g (95%), and it decomposes, without melting, in the range 202-214° (from methylcellosolve). The decomposition point was determined thermographically. Found: C 34.82; 35.20; H 4.86; 5.03; N 12.70%. $C_9H_{15}O_9N_3$. Calculated: C 34.95; H 4.89; N 13.59%. Infrared spectrum (ν, cm^{-1}): 865 w, 1022 w, 1055 w, 1080 med, 1360 med, 1400 med, 1560 s, 3300 s.

The acetyl derivative has mp 195-196° (decompn.) (from glacial acetic acid). Found: C 41.28; 41.51; H 4.90; 4.91; N 8.37; 8.35%; mol. wt. 424.4 (x-ray diffraction). $C_{15}H_{21}O_{12}N_3$. Calculated: C 41.38; H 4.86; N 9.65%; mol. wt. 435.4. Infrared spectrum (ν, cm^{-1}): 933 w, 1052 med, 1090 med, 1233 v.s., 1388 med, 1430 w, 1475 w, 1570 s, 1752 s. Since the constants of (II) and its triacetate differ from those given in [3], then evidently another conformer of the compound was obtained under our conditions.

1,3,5-Tri-(bromomethyl)-1,3,5-trinitrocyclohexane (III). (III) was obtained in the same manner as described in [4] for 1-bromomethyl-1-nitrocyclohexane. The yield of (III) was 7%, mp 240-242° (from nitromethane). Found: C 21.78; 21.81; H 2.62; 2.68; N 8.69; 8.48; Br 48.03; 48.14%. $C_9H_{12}N_3O_6Br_3$. Calculated: C 21.70; H 2.42; N 8.43; Br 48.10%. Infrared spectrum (ν, cm^{-1}): 480 med, 540 w, 580 w, 665 med, 840 w, 855 s, 1045 w, 1065 med, 1220 w, 1275 med, 1360 sh, 1375 med, 1405 med, 1430 med, 1550 sh, 1560 s, 3040 med.

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CONCLUSIONS

A method was developed for the synthesis of 1,3,5-trinitrocyclohexane and some of its properties were studied.

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