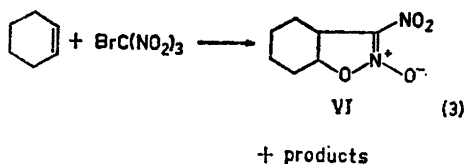
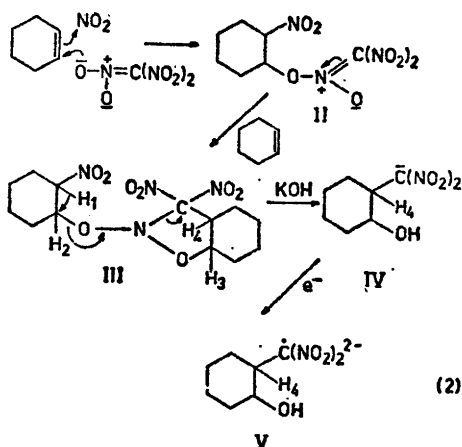
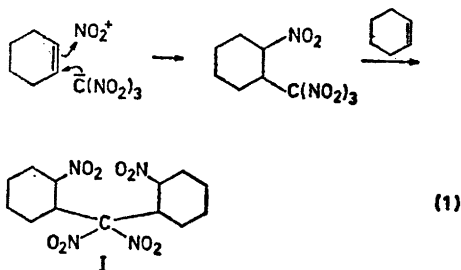


The Structure of the Tetranitromethane-olefin Adduct

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Bradshaw¹ investigated recently the products obtained from the reaction of tetranitromethane with olefins. One of the products I and arises by *C*-alkylation according to eqn. (1). The work by Novikov *et al.*,^{2,3} and our previous experience⁴ of the reaction led us to consider a different structure III, which arises *via* an *O*-alkylation, II, followed by 1,3-dipolar addition, eqn. (2).



The IR spectrum of III showed the presence of an aliphatic nitro group at 1558 cm^{-1} and a geminal dinitro group at 1585 cm^{-1} (CHCl_3), the intensity of which was twice the intensity of the other group. The NMR spectrum revealed the asymmetric nature of the compound. The protons H_1 – H_4 are located at $\delta = 5.0$ ppm (1 H), 4.5 ppm (2 H), and 3.5 ppm (1 H = H_1) as broad multiplets.

Finally the structure III was established by alkaline degradation to the potassium salt IV, which gave a correct analysis. The IR spectrum (KBr) of IV showed the presence of an OH group at 3350 and 3470 cm^{-1} and the geminal dinitro group at 1465, 1240, 1180, and 740 cm^{-1} (*aci*-form). The IR spectrum of protonated IV showed no absorption for an aliphatic nitro group at 1560–1550 cm^{-1} . The geminal nitro group was apparent at 1582 cm^{-1} and the hydroxyl group at 3630 cm^{-1} . The ESR spectrum of V, which further supported the structure IV, had unique characteristics. The two nitrogens are nonequivalent and give rise to 9 lines of alternating line widths ($a_{\text{N}_1} = 9.1$ gauss, $a_{\text{N}_2} = 11.9$ gauss) with secondary splittings from H_4 ($a_{\text{H}_4} = 0.63$ gauss). In agreement with theory nuclei of identical spin moment form sharp lines ($M = +2, -2, 0$); the other lines are broadened.

A crystalline compound was isolated from the reaction between bromotritromethane and cyclohexene, eqn. (3), which analyzed for $\text{C}_6\text{H}_{10}\text{N}_4\text{O}_6$; Mw. 186 from the mass spectrum. The spectral data suggested the structure VI. IR, 1634 (s) $\text{C}=\text{N}$, 1505 (m), 1364 cm^{-1} (m) NO_2 ; UV, λ_{max} 317 $\text{m}\mu$ (8100); NMR, $\delta = 5.01$ (1H), $\delta = 3.80$ (1H), $\delta = 2.5$ –1.3 ppm (8 H), multiplets. This compound has been prepared by a different route⁵ and comparison of the physical data revealed its identity with the reaction product. Compound VI is most probably formed *via* addition of bromotritromethane followed by intramolecular substitution.

None of the compounds mentioned are responsible for the colour of the TNM-olefin test.

Experimental. III. A solution of cyclohexene (1 g) and tetranitromethane (1 g) in chloroform (5 ml) was kept at room temperature for 24 h. Evaporation of the solvent *in vacuo* and chromatography of the yellow oil on silica gave with benzene as eluent a first fraction (discarded) and with chloroform a second fraction as a yellow viscous oil, which crystallized

slowly. Crystallization from cyclohexane afforded III, 0.15 g of light yellow needles, m.p. 107–109°.

Alkaline degradation, IV. III (0.65 g) was dissolved in ethanolic potassium hydroxide solution (100 mg KOH in 2 ml ethanol). A yellow precipitate was formed after a couple of hours. Recrystallization from methanol gave IV, 20 mg, m.p. 180–181° (decomp.). (Found: C 34.92; H 4.32. Calc. for $C_7H_{11}N_2O_4K$ (242.3): C 34.71; H 4.57).

The radical V was prepared as previously described.⁶

VI. Bromotrinitromethane (6 g) and cyclohexene (6 g) in chloroform (15 ml) were left standing for two days at room temperature. The solution was washed with sodium bicarbonate, dried over sodium sulphate and the solvent evaporated *in vacuo*. A yellow oil remained which was extracted once with hexane (25 ml) and chromatographed on silica. After the first eluate (benzene) a second fraction was collected (chloroform), which contained VI, 1.0 g, m.p. 74–75° from methanol. (Found: C 45.03; H 5.74; Calc. for $C_7H_{10}N_2O_4$ (186.2): C 45.14; H 5.41). The gas chromatogram of the hexane solution showed at least 5 components in substantial amounts.

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On the Rotation of Ammonium Ions within Ammonium-Carbanide Ion Pairs*

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It has been proposed that ion pairs containing a carbanion and an ammonium or substituted ammonium ion are involved in hydrogen exchange^{1,2} and tautomeric rearrangements^{3,4} of carbon acids. Some years ago, we showed that the triethylamine catalyzed rearrangement of 1-methylindene to 3-methylindene in pyridine-deuterium oxide occurs without hydrogen exchange.⁵ This intramolecular course of the rearrangement can be interpreted in such a way that the collapse of the ion pair with the formation of 3-methylindene is more rapid than ion pair dissociation. Evidence of the internal rotation of ammonium ions in ammonium-carbanide ion pairs have been found by Cram.^{1,2} An elegant demonstration of this phenomenon is provided by the comparison of the ammonia catalyzed racemization and exchange for a deuterated fluorene derivative in tert-butanol or tetrahydrofuran.⁶ This experiment shows that rotation of the ammonium ion within the ion pair (and collapse of the ion pair) is faster than ion pair dissociation. Thus, comparisons have been made between dissociation and collapse and between dissociation and rotation. From these experiments no comparisons can be made, however, between collapse and rotation rates. This communication will describe some experiments in which internal rotation competes with collapse.

The hexylamine ($R-ND_2$) catalyzed rearrangement of 1-methylindene in pyridine-deuterium oxide was studied by the NMR-technique, and the results of the experiment are given in Fig. 1. The deuterium oxide served as a deuterium pool.

Careful analysis of the NMR-spectrum showed that no deuterium was incorporated into the 1-methylindene, whereas

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