Reactions of Tetraalkyl-2-tetrazenes with Tetranitromethane

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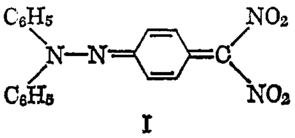
Tetraalkyl-2-tetrazenes react with tetranitromethane in inert solvents to give dipolar ions of trialkyl-(β,β-dinitrovinyl)-2-tetrazenes. The predominant resonance structure associated with these dipolar ions has a cationic portion derived from the 2-tetrazene and a 1,1-dinitrocarbanionic portion stabilized through charge separation and conjugation.

Tetraalkyl-2-tetrazenes, derivatives of an unsaturated hydronitrogen with type formula N_4H_4,[1] are decomposed photolytically or pyrolytically to give dialkylamino radicals[2] which are initiators for radical polymerization.[3] Although pyrolysis of tetramethyl-2-tetrazene has been accomplished in organic solvents at 145°,[4] 2-tetrazenes in the presence of peroxy compounds are polymerization catalysts at temperatures as low as $-20°$.[5] At this temperature neither the tetrazene nor the peroxy compound alone can promote polymerization. Oxidants such as iodine or silver(I) react with tetraalkyl-2-tetrazenes to form products which have not been fully characterized.[6] A scheme for the characteristic decomposition of the 2-tetrazenes in acidic media has been proposed.[7]

The facile elimination of a nitro group in the reaction of tetranitromethane with bases usually leads to the formation of dinitromethanenitronate salts; products of nitration or nitrosation of the base may be produced in conjunction with the salt formation.[8] Although the reduction of tetranitromethane by phenylhydrazine proceeds beyond the trinitromethane stage to nitromethane,[9] its reduction by 1,1,2-triphenylhydrazine gives 4-(dinitromethylene)-2,5-cyclohexadien-1-one diphenylhydrazone (I),[10] the product of a coupling reaction involving the hydrazine and tetranitromethane. Recently free-radical species derived from tetranitromethane were detected when it was reduced in basic media.[11]



I

In this work we have found that the reaction of tetranitromethane with 1,1,4,4-tetramethyl-2-tetrazene, 1,4-diisopropyl-1,4-dimethyl-2-tetrazene, and 1,4-dicyclohexyl-1,4-dimethyl-2-tetrazene yields crystalline yellow solids which are stable for several months at room temperatures after recrystallization from diethyl ether, even in the presence of air and moisture. They are insensitive to impact, ignite with a yellow flame on a hot plate at 300°, and decompose near their melting points with the evolution of gas. The compounds are sparingly soluble in *n*-hexane; somewhat soluble in water; moderately soluble in benzene, ethanol, ether, and carbon tetrachloride; and are quite soluble in chloroform and acetone. Ultraviolet absorption spectra of freshly prepared solutions of the yellow solids in the above solvents have absorption maxima near 390 mμ; chloroform solutions seem to be the most stable, but light causes decomposition of all the solutions. This appears to be a characteristic of aliphatic nitro compounds.[12] Characteristic infrared absorption maxima for the solids occur near 1630, 1530, 1450, and 1180 cm^{-1} with a broad band near 1260 cm^{-1}.

Proton nmr spectra of deuteriochloroform solutions of solids derived from 1,4-diisopropyl- or 1,4-dicyclohexyl-1,4-dimethyl-2-tetrazene possess peaks associated with one N-methyl unit, two nonequivalent N-isopropyl or N-cyclohexyl units, and a single vinylic proton. The derivative of tetramethyl-2-tetrazene at $-20°$ had spectra corresponding to three N-methyl units (τ 6.40, 6.56, and 7.06) and a vinylic proton (τ 1.83); at 60° the two methyl peaks at higher field coalesced, the spectra then corresponding to two equivalent N-methyl units (τ 6.89), a single N-methyl unit (τ 6.47), and the vinylic proton (τ 1.96). When tetramethyl-2-tetrazene and tetranitromethane are mixed at $-78°$, an intense reddish violet color develops and the proton nmr lines are greatly broadened. When the temperature is raised, the color gradually changes to yellow; sharp peaks characteristic of the above-described product appear which persist on recooling the solution to $-78°$.

The solid reaction product of tetranitromethane and tetramethyl-2-tetrazene is decomposed in concentrated aqueous solutions of hydrogen chloride or potassium hydroxide. In each case methyl azide and dimethylammonium chloride or dimethylamine were identified as decomposition products. Decomposition with potassium hydroxide also gave potassium nitromethanenitronate.

A coupling reaction involving tetranitromethane and 1,1-dimethylhydrazine yields the yellow solid, 1,1-dinitro-2,3-diaza-3-methyl-1-butene (II, R = CH_3), which is analogous to 1,1-dinitro-2,3-diaza-3,3-diphenyl-1-propene (II, R = C_6H_5) prepared by Matevosyan and Ikrina[13] from the reaction of 1,1-diphenylhydrazine and tetranitromethane.

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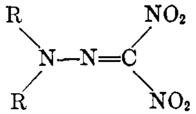
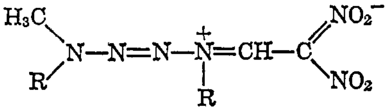


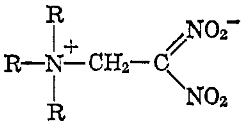
II

Discussion

Ultraviolet and infrared spectra, solubility behavior, and crystallinity suggest a high degree of polarity for the homologous compounds, III, obtained from the reaction of tetranitromethane and tetraalkyl-2-tetrazenes. For example, the reaction of tetranitromethane and tetramethyl-2-tetrazene yields the dipolar ion, 1,1,4-trimethyl-4-(β,β-dinitrovinyl)-2-tetrazene (for simplicity compounds are named as if they were nonpolar). These dipolar ions (or internal salts) have a betaine-like structure in that the nitrogen with the positive charge is completely substituted; they exhibit solubility in various solvents and stability toward intramolecular rearrangement characteristic of this type compound.[14] The formation of betaine-like dipolar ions which possess a substituted ammonium cationic portion and a 1,1-dinitrocarbanionic portion, IV, has been reported.[15,16]



III



IV

Ultraviolet spectra of the compounds support the assignment of structure III. In aqueous solution, most salts of 3-substituted 1,1-dinitro-2-propene exhibit two ultraviolet maxima, 313–326 mμ (log ϵ 4.20–4.29) and 395–410 mμ (log ϵ 3.92–4.00).[17] These salts contain the chromophore group $^{-}C(NO_2)_2$—CH=CH—, isoelectronic with the group $^{-}C(NO_2)_2$—CH=N^{+}R— found in the dipolar ions, III. The spectrum of an aqueous solution of 1,1,3-trinitro-2-propene is an exception; a single intense maximum at 395 mμ (log ϵ 4.33) was observed and the dipolar ions appear to be more closely related to this salt, $\lambda_{\max}^{\mathrm{EtOH}}$ 389–393 mμ (log ϵ 4.36–4.37). The single maximum in the spectrum of the 1,1,3-trinitro-2-propene salt has been ascribed to the presence of a single rotomeric conformation in which resonance interaction is important.[17,18] In contrast with III, spectra of compounds I and II (R = CH_3) do not display maxima in this region.

Spectra of ethanolic solutions of the dipolar ions exhibit another maximum near 250 mμ (log ϵ 3.84). The positions and intensities of the spectral maxima vary only slightly when solvents of widely different polarity are employed. Spectra of solutions of tetramethyl-2-tetrazene display a shoulder in the region near 250 mμ which is more intense in polar than nonpolar media and which has been attributed to a protonated or solvated form of the tetrazene.[19] Spectra of III then are in agreement with a betaine-like structure which retains its dipolar character in solvents of widely varying polarity,[20] and which is similar to that of a protonated tetrazene.

Infrared spectra also support the structure III. The strongest absorption in the infrared is located in the region 1280–1250 cm^{-1} and another strong band is observed at 1180–1175 cm^{-1}. Salts which have the structure $^{-}C(NO_2)_2$—CH=CH— have absorptions in the regions 1280–1260 and 1180–1160 cm^{-1} due to the asymmetric and symmetric stretching modes of the nitro group, respectively.[21,22] This contrasts with absorption of dinitroalkanes, 1590–1575 and 1340–1325 cm^{-1},[23] and salts of dinitroalkanes, ~1480, 1210, and 1120 cm^{-1}.[24] The second most intense absorption band exhibited by the infrared spectra of the dipolar ions, III, is in the region 1640–1620 cm^{-1} and may be due to the C=N^{+} bond since absorption of immonium salts has been observed in the region 1700–1645 cm^{-1}.[25] In contrast, the spectrum of II (R = C_6H_5) has absorption near 1590 cm^{-1} due to the C=N stretching vibration.[13] Compounds I and II (R = CH_3) also show absorption in this region.

The nmr spectra of solutions of the dipolar ion III (R = CH_3) show two methyl proton signals which are temperature dependent. This suggests some double-bond character of the 1,2-N-N bond[26] arising from delocalization of π electrons along the nitrogen chain of the tetrazene. Some contribution from an azomethinimine-type dipolar ion, —N^{-}—N^{+}R=C<,[27] is possible.

Molecular weights corresponding to a monomer were obtained for solutions of III (R = CH_3) in acetone and benzene. This is in agreement with previous studies which indicated no association of betaine dipolar ions in benzene solution.[20]

The predominant resonance structure of the dipolar ions, III, is stabilized by charge separation and conjugation. A possible resonance structure for these compounds could be an uncharged structure derived from 1,1-dinitroethene; however, this unstable ethene always reacts further.[23] Zeldin and Shechter[15] showed that a stable product related to the unstable ethene may be obtained if the double bond of the ethene shifts and a zwitterion containing a nitronate anion, IV,

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[18] A chloroform solution 0.005 *M* with respect to tetramethyl-2-tetrazene and tetranitromethane was prepared and the reaction was followed spectrophotometrically. As absorption due to tetrazene decreased (282 mμ), absorption at 325 mμ appeared and then decreased as the absorption due to the dipolar ion species (390 mμ) began to predominate.

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is produced. Even in some cases where this may happen subsequent decomposition takes place, but, if conjugation between the nitronate portion and another group is effected, additional stability is imparted to the species and decomposition does not occur.[28] The dianion 4,4-dinitrobutenoate, $^{-}C(NO_2)_2$—CH=CH-COO^{-},[28] and the dipolar ions are examples where charge separation and conjugation are both operative.[29]

It has been observed that free radicals are formed in reactions of tetranitromethane with other unsaturated organic compounds.[11] A photoinduced transfer of one or two nitro groups from the tetranitromethane to the unsaturated compound inside an electron donor-acceptor complex was suggested to explain the observed products of this reaction. In the present work a similar complex might exist as an intermediate and indeed epr spectral data confirm that the tetramethyl-2-tetrazene radical cation is formed when tetranitromethane reacts with this tetrazene in polar solvents.[30]

Experimental Section[31]

1,1,4-Trimethyl-4-(β,β-dinitrovinyl)-2-tetrazene.—A solution of 1.16 g of tetramethyl-2-tetrazene (0.01 mole), prepared by the oxidation of 1,1-dimethylhydrazine[32] and estimated to be 97% pure (ultraviolet spectrum), in 30 ml of *n*-hexane was introduced into a three-necked flask fitted with a dropping funnel and stirrer. The flask was cooled in ice and flushed with dry nitrogen. A solution of 1.96 g of tetranitromethane (0.01 mole), used as received from Trojan Powder, Allentown, Pa., in 30 ml of *n*-hexane was added slowly to the stirred tetrazene solution over a period of about 1 hr. The resulting brown species was allowed to warm to room temperature. Nitrous oxide, nitric oxide, and carbon dioxide gases were evolved[33] during this warming period and a yellow solid precipitated. At room temperature the light yellow hexane solution was decanted from the solid, which was subsequently washed with small amounts of hexane. The solid was dried in a vacuum desiccator and 0.72 g of yellow solid, mp 124° (33% yield), was isolated. This was recrystallized from ether and dried to give 0.66 g of solid, mp 129° (30% yield).

Anal. Calcd for $C_5H_{10}N_6O_4$: C, 27.53; H, 4.62; N, 38.52; mol wt, 218. Found: C, 27.44; H, 4.62; N, 38.82; mol wt, 214 (freezing point depression in benzene).

In a similar preparation cooled to $-78°$ instead of 0°, reaction of the starting materials gave a dark reddish violet species. After warming to room temperature, 2.025 g of yellow-brown solid, mp 106° (94% yield), was recovered. Recrystallization from ether yielded 1.30 g of yellow solid, mp 129° (60% yield). A second recrystallization gave a light yellow solid, mp 131–132°.

The ultraviolet absorption spectrum of a freshly prepared ethanol solution of the twice-recrystallized solid had λ_{max} 389 mμ (log ϵ 4.36) and 249 mμ (log 3.84), λ_{min}^{EtOH} 308 mμ (log ϵ 3.14). The infrared spectrum of the solid in a potassium bromide disk was obtained: 2980 (w), 1640 (vs), 1535 (s), 1495 (m), 1460 (m), 1390 (m), 1365 (m), 1325 (s), 1310 (s), 1280 (vs), 1180 (s), 1120 (w), 1105 (m), 1070 (w), 1055 (w), 925 (w), 837 (w), 804 (w), 748 (w), and 729 (m) cm^{-1}; $\nu_{max}^{CHCl_3}$ 1650 cm^{-1} (log ϵ 2.74) and 1285 cm^{-1} (log ϵ 3.11).

1,4-Diisopropyl-1-methyl-4-(β,β-dinitrovinyl)-2-tetrazene.—A yellow solid, mp 80–81°, was obtained when 1,4-diisopropyl-1,4-dimethyl-2-tetrazene and tetranitromethane were mixed as described previously.

Anal. Calcd for $C_9H_{18}N_6O_4$: C, 39.41; H, 6.61; N, 30.64. Found: C, 39.55; H, 6.65; N, 30.49.

The infrared spectrum of the material in a potassium bromide disk was obtained: 2940 (w), 1630 (vs), 1525 (s), 1465 (s), 1430 (w), 1410 (w), 1375 (s), 1360 (s), 1315 (s), 1280 (s), 1260 (vs), 1175 (s), 1140 (m), 1120 (m), 1105 (s), 1045 (m), 1020 (w), 913 (m), 878 (w), 874 (w), 853 (w), 777 (m), 744 (m), and 721 (m) cm^{-1}. The ultraviolet absorption spectrum had λ_{max}^{EtOH} 391 mμ (log ϵ 4.36) and 252 mμ (log ϵ 3.84), λ_{min}^{EtOH} 310 mμ (log ϵ 3.20).

1,4-Dicyclohexyl-1-methyl-4-(β,β-dinitrovinyl)-2-tetrazene.—The orange solid, mp 140°, was prepared in an analogous manner.

Anal. Calcd for $C_{15}H_{26}N_6O_4$: C, 50.85; H, 7.34; N, 23.73. Found: C, 51.37; H, 7.60; N, 23.46.

This compound had λ_{max}^{EtOH} 393 mμ (log ϵ 4.37) and 255 mμ (log ϵ 3.84), λ_{min}^{EtOH} 313 mμ (log ϵ 3.18). Infrared spectrum of the solid in a potassium bromide disk was obtained: 3030 (w), 2900 (m), 2820 (vs), 1620 (vs), 1525 (s), 1475 (m), 1455 (m), 1415 (m), 1385 (m), 1365 (m), 1340 (m), 1325 (s), 1280 (vs), 1265 (vs), 1250 (vs), 1230 (vs), 1180 (s), 1160 (m), 1080 (w), 1060 (w), 1045 (w), 1005 (w), 744 (w), 733 (w), and 698 (w) cm^{-1}.

1,1-Dinitro-2,3-diaza-3-methyl-1-butene.—This compound was prepared by mixing 0.01 mole of tetranitromethane in 50 ml of ether with 0.01 mole of 1,1-dimethylhydrazine in 50 ml of ether at room temperature. A red oil was formed and the ether solution was decanted from the oil. Evaporation of the ether solution gave an oil which crystallized upon standing. A yellow solid, mp 72°, was obtained on recrystallization from ether.

Anal. Calcd for $C_3H_6N_4O_4$: C, 22.23, H, 3.73; N, 34.56. Found: C, 22.31; H, 4.01; N, 34.19.

The ultraviolet spectrum exhibited λ_{max}^{EtOH} 326 mμ (log ϵ 4.06), λ_{min}^{EtOH} 267 mμ (log ϵ 3.44). An infrared spectrum in a potassium bromide disk was obtained: 1600 (s), 1530 (s), 1450 (m), 1420 (w), 1400 (w), 1375 (w), 1290 (s), 1260 (m), 1170 (m), 1090 (w), 1035 (w), 878 (m), 824 (m), 804 (m), 732 (w), and 711 (w) cm^{-1}.

Reaction of III ($R = CH_3$) with Acid and Base.—Concentrated aqueous solutions of hydrogen chloride or potassium hydroxide were added to the evacuated dipolar ion, III ($R = CH_3$), and the gaseous products were identified.[33] In each case methyl azide and dimethylamine or its hydrochloride salt were identified. Reaction with potassium hydroxide yielded potassium nitromethanenitronate which was identified by its ultraviolet spectrum in dilute potassium hydroxide.[17] Reaction of III ($R = CH_3$) with dilute potassium hydroxide (pH 12) also formed the nitronate salt, but a slurry of the starting material could be recovered unchanged after 24-hr stirring with a dilute hydrochloric acid solution (pH 2).

Acknowledgment.—We wish to thank Dr. Arnold T. Nielsen and Dr. W. H. Urry for helpful discussions.

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(29) The importance of conjugation is also shown by the reaction of 4,4,4-trinitrobutyramide with ammonia.[21] Spectroscopic evidence for a zwitterionic intermediate related to IV was obtained, but this species spontaneously eliminated an ammonium ion to produce the conjugated system of the eventual product, 4,4-dinitro-2-butenamide.

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(33) Gaseous products were qualitatively identified by comparison with known infrared spectra: R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.*, **28**, 1218 (1956).