

bromo-4,4-dinitrobutyrate, respectively. The crude esters were hydrolyzed to the corresponding acids by refluxing with constant-boiling hydrochloric acid for 8 hr. Recrystallization of the crude acids from water gave 4-chloro-4,4-dinitrobutyric acid as a granular, white solid, mp 95.4–96.2°.

Anal. Calcd for $C_4H_6ClN_2O_6$: C, 22.6; H, 2.4; N, 13.2; Cl, 16.7. Found: C, 22.8, 22.9; H, 2.5, 2.4; N, 12.6, 12.5; Cl, 17.1, 16.8.

The 4-bromo acid, mp 90–91° (lit.³ mp 88–89°), was obtained as glistening white plates.

Kinetic Procedure.—Measurements of the rates of reaction of these acids with diphenyldiazomethane were carried out as described previously.⁴ The data summary in Table I results from at least five kinetic runs for each substrate.

Registry No.—4-Chloro-4,4-dinitrobutyric acid, 24057-18-9; 4-fluoro-4,4-dinitrobutyric acid, 15895-15-5; 4-bromo-4,4-dinitrobutyric acid, 5029-14-1; diphenyldiazomethane, 883-40-9.

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(3) K. Klager, *J. Org. Chem.*, **16**, 161 (1951).

(4) H. E. Ruskie and L. A. Kaplan, *ibid.*, **30**, 319 (1965).

An Unusual Aspect of the Dimerization of N-Vinylcarbazole by Redox Reactions. The Participation of Molecular Oxygen

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The remarkable atypical features of polymerization on N-vinylcarbazole by either an ionic or a free-radical process have been recorded in a number of recent investigations. For example, it is difficult to present an adequate mechanism for the commercial preparation of poly-N-vinylcarbazole employing sodium chromate in hot aqueous dispersion or to account for the following observations when π -complex electron acceptors such as *p*-chloranil, tetracyanoethylene, and trinitrobenzene were used as initiators:^{2,3} water (which normally inhibits ionic polymerization), thiophene (a potent retarder of conventional cationic propagation), and acrylonitrile (a material readily polymerized by radical or anionic species) each have qualitatively no effect on the polymerization of N-vinylcarbazole.

(1) (a) To whom correspondence should be addressed; (b) Senior Honors Thesis, Wellesley College, 1968.

(2) L. P. Ellinger, *Chem. Ind.* (London), 1982 (1963).

(3) H. Scott, G. A. Miller, and M. M. Labes, *Tetrahedron Lett.*, No. 17, 1073 (1963).

Also, it has been noted that conventional free-radical polymerization of this monomer initiated by azobisisobutyronitrile is sensitive to oxygen but unaffected by the presence of oxygen when π -complex electron acceptors are used as initiators.⁴ Further, highly hindered phenols such as 2,6-di-*t*-butylphenol and 2,4-di-*t*-butylphenol, powerful inhibitors of free-radical chain reactions, do not retard but rather accelerate the azobisisobutyronitrile-initiated polymerization of N-vinylcarbazole in methanol.⁵

In an earlier study we have reported that ferric nitrate initiated polymerization of N-vinylcarbazole and 4-vinylpyridine proceeding by a one-electron transfer process⁶ and that a dimer of N-vinylcarbazole, *trans*-1,2-dicarbazylcyclobutane, was among the products.⁷ In extension of this study we have examined the reaction between N-vinylcarbazole and hydrogen peroxide, a redox couple analogous to the interaction between dimethylaniline and benzoyl peroxide,⁸ which also afforded the dimeric product, *trans*-1,2-dicarbazylcyclobutane.

During the course of this investigation, we have found evidence of molecular oxygen participation in the formation of this dimer when either ferric nitrate or hydrogen peroxide is employed as an oxidant. In this note we wish to report our recent findings and suggest a role for molecular oxygen in the reaction sequence.

When reaction mixtures containing 5.0 mmol of N-vinylcarbazole and 0.05–0.5 mmol of ferric nitrate (hydrate) in methanol–water medium (9:1 v/v) were stirred at room temperature under nitrogen atmosphere over a period of 4 hr, they furnished some poly-N-vinylcarbazole of rather low molecular weight and a trace amount of dimer. The hydrolysis products of the monomer, carbazole, and acetaldehyde isolated as its 2,4-dinitrophenylhydrazone derivative were found to be the major products. In open air, for the same period of time, it afforded the same dimer in 15–20% of the theoretical yield in addition to the hydrolysis products. Under a stream of oxygen with 0.05–0.5 mmol of ferric nitrate the yield of the dimer was raised to 37–40%. Parallel observations were obtained when hydrogen peroxide was used as oxidant under comparable conditions. Under a nitrogen atmosphere, the yield of the dimer was practically nil with concentrations of hydrogen peroxide varying from 0.057 to 0.57 mmol. The bulk of the yield was found to be the hydrolysis products. In the presence of oxygen the dimer was obtained in 15–17% yield. The concentration of hydrogen peroxide in these reactions has no effect on the yield of the dimer. It is apparent that oxygen is not used in the regeneration of the oxidants but nevertheless essential in the formation of the dimer. It seems necessary for us to reexamine the mechanism of the dimer formation which we proposed in one of our earlier reports.

The interaction of molecular oxygen with free radicals is well known. The formation of the peroxy radical by oxygen with the intermediary radicals in this sequence of transformations should result in the forma-

(4) H. Scott, T. P. Konen, and M. M. Labes, *Polym. Lett.*, **2**, 689 (1964).

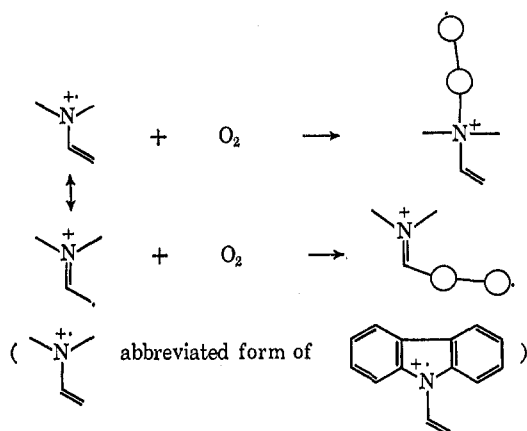
(5) C. H. Wang, unpublished results.

(6) C. H. Wang, *Chem. Ind.* (London), 751 (1964).

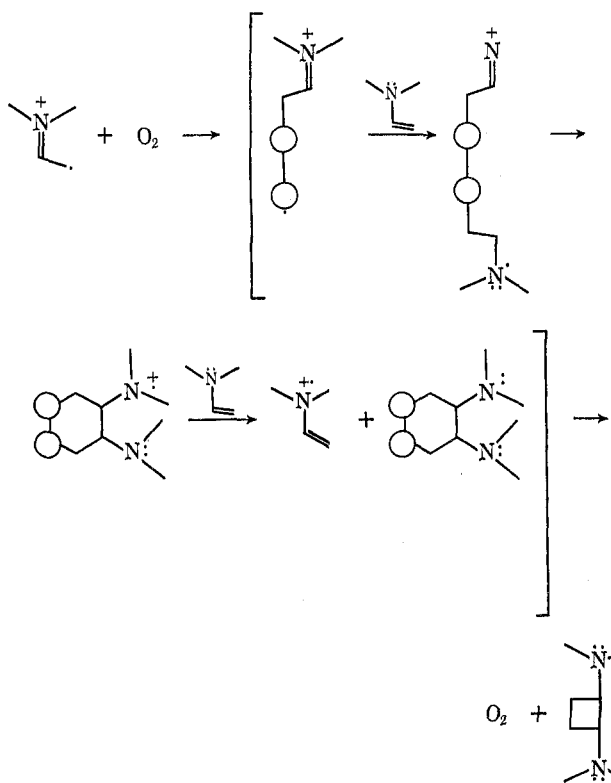
(7) S. McKinley, J. V. Crawford, and C. H. Wang, *J. Org. Chem.*, **31**, 1963 (1966).

(8) L. Horner and W. Kirmse, *Justus Liebigs Ann. Chem.*, **567**, 48 (1955).

tion of either a nitrogen peroxy radical, which is practically unknown, or the carbon peroxy radical.



The formation of carbon peroxy radical will eventually suppress the competitive reactions, namely, the hydrolysis of the N-vinyl group and the chain reaction of N-vinylcarbazole polymerization. It is also plausible that the carbon peroxy radical will add to the carbon-carbon unsaturation, which will lead to the formation of the six-membered ring peroxide intermediate and eventually to the final product.



The mechanism proposed is purely conjectural, since the isolation of the cyclic oxygen-containing intermediate was not fruitful and the detection of singlet oxygen was not carried out. However, the fact that no dimer formed when oxygen was excluded lends credence to the direct participation of molecular oxygen in the dimer formation.

Experimental Section⁹

Formation and Identification of the Dimer.—To a solution of 1 g (5.0×10^{-3} mol) of N-vinylcarbazole (Matheson Coleman

and Bell), mp 67° , in 100 ml of 9:1 methanol-water, 0.02 g (5×10^{-5} mol) of ferric nitrate (Mallinckrodt), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, was added. The mixture was stirred at room temperature in open air and a white precipitate gradually appeared. At the end of 4 hr the solid was collected. The yield was 0.25 g (ca. 25%): mp $189\text{--}192^\circ$ (recrystallization from 1:1 ethanol-acetone raised the melting point to $191\text{--}193^\circ$); nmr δ_{TMS} 7-8.2 (16 H, aromatic), 6.26 (2 H, NCH), and 2.4-3.2 (4 H, methylene).

Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2$: C, 87.01; H, 5.74; N, 7.25; mol wt, 386.5. Found: C, 86.74; H, 5.80; N, 7.31; mol wt, 373 (Rast method, Nagy), 386 (mass spectrum).

All data correspond to the reported dimer, *trans*-1,2-dicarbazylicyclobutane.¹⁰ Concentration of the filtrate by evaporation afforded 0.2 g of another white solid, which was identified as carbazole by melting point and by comparison of their infrared spectra. The mother liquid furnished acetaldehyde in ca. 20% yield based on the isolation of acetaldehyde 2,4-dinitrophenylhydrazone, mp $146\text{--}147^\circ$ (lit.¹¹ mp 148°).

In other runs under identical conditions except with a gentle stream of oxygen, the yield of the dimer was 37-40% of the theoretical; the yield was not altered when the reaction was carried out at -10° instead of at room temperature. Efforts to detect the presence of peroxide intermediate in both cases failed. Under a stream of nitrogen only a trace amount of the dimer was obtained. The rest of the products were qualitatively identified as carbazole, acetaldehyde, and perhaps some low molecular weight poly-N-vinylcarbazole.

Increasing the amount of ferric nitrate up to tenfold in other runs did not substantially affect the corresponding yield of the dimer in the presence of either an oxygen or a nitrogen atmosphere.

Parallel experiments were carried out between N-vinylcarbazole and hydrogen peroxide. In a typical run, 2.25 ml (5.7×10^{-3} mol) of 0.06% hydrogen peroxide (Baker Analyzed reagent, 3% diluted to 0.06% with water) was added to a solution of 1 g (5.0×10^{-3} mol) of N-vinylcarbazole in 100 ml of 9:1 methanol-water solution. The solution was stirred at room temperature for 4 hr under a stream of (a) oxygen and (b) nitrogen and (c) in open air.

The experiments were worked up essentially in the same manner as in the previous ones. The yield of the dimer was ca. 10% in a, 0% in b, and ca. 3% in c. Change of the amount of hydrogen peroxide in each case did not alter the yield of the dimer to an appreciable degree.

Registry No.—*trans*-1,2-Dicarbazylicyclobutane, 1484-96-4.

(9) Elementary analysis was performed by M. S. Nagy, Massachusetts Institute of Technology. Melting points are not corrected. The nmr spectrum was recorded by using a Varian A-60 spectrometer from A. D. Little Analytical Laboratories. The mass spectrum was done by using a A.E.I. MS9 mass spectrometer with the generous help from Dr. G. Dudek, Harvard University.

(10) L. P. Ellinger, J. Fenney, and A. Ledwith, *Monatsh. Chem.*, **96**, 131 (1965).

(11) G. R. Cleo and W. H. Perkin, Jr., *J. Chem. Soc.*, **125**, 1804 (1924).

Sodium Arylsulfonates from Phenols

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Direct sulfonation of aromatic compounds often yields mixtures of isomeric sulfonic acids which are difficult to separate; however, sulfur-containing compounds of other types can be prepared free of isomers. Many can be oxidized to sulfonic acids.¹ The recently

(1) E. E. Gilbert, "Sulfonation and Related Reactions," Interscience Publishers, New York, N. Y., 1965, p 201.