## An Inhibitor-Initiated Polymerization of N-Vinylcarbazole

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In the course of our study of organic redox reactions as a means of generating free radicals in solution, we have noticed N-vinylcarbazole to be one of the most effective reductants among the amines, and this can be attributed at least in part to the formation of the cation radical which can be resonance stabilized.[1]
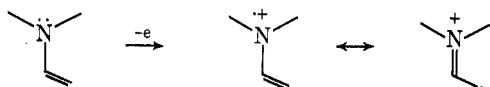

There have been a number of reports in the literature about the atypical nature of this particular cation-radical intermediate. For example, both ionic and free-radical inhibitors usually exert little or no effect on the polymerization of N-vinylcarbazole when electron acceptors such as tetracyanoethylene and p-chloranil are used as initiators.[2,3] It is believed that the formation of the cation radical was involved in the initial step of the process. Also, it was reported more recently that when ferric ion is used as the oxidant in the presence of oxygen, it led to the formation of a dimer of N-vinylcarbazole, *trans*-1,2-dicarbazylcyclobutane.[4]

In this note we wish to report our more recent findings that highly hindered phenols such as 2,6-di-*t*-butylphenol and 2,4-di-*t*-butylphenol, usually inhibitors of free-radical chain process, do not retard but rather accelerate the polymerization of N-vinylcarbazole in methanol to result in the formation of lower molecular weight poly-*n*-vinylcarbazole when azobisisobutyronitrile was used as initiator.

When a solution containing 2 g (1×10^{-2} mol) of N-vinylcarbazole and 0.02–0.2 g (1×10^{-4}–1×10^{-3} mol) of 2,6-di-*t*-butylphenol and 0.05 g ($\sim 3 \times 10^{-4}$ mol) of azobisisobutyronitrile in 50 ml of methanol was heated under nitrogen atmosphere at 50° for 5 hr, it produced a gummy precipitate, weighing from 1.2 to 1.5 g. Trituration of the gummy solid in benzene afforded white solid melting at a wide range from 150–250°. Infrared spectrum of the solid resembles that of poly-N-vinylcarbazole. There is no unsaturation as bromination in carbon tetrachloride and permanganate oxidation tests were negative. Exploratory molecular weight determination by Rast method gave a value of ~ 510, indicating this is probably a mixture of low molecular weight polymers. This may also explain the appreciable solubility of this solid in benzene, whereas high molecular weight poly-N-vinylcarbazole obtained commercially dissolves only slightly in benzene and toluene at room temperature.

In accompaning experiments under identical conditions, the one without the phenol afforded only a small amount, ~ 0.2 g, of polymer at the end of 5 hr; the one with the phenol (1×10^{-4} mol) but without azo compound produced no trace of polymer after 5 hr. In another run, the reaction with azo compound, 2,6-di-*t*-butylphenol and N-vinylcarbazole, each of the same amount as in the previous experiment, in methanol was carried out in open air with vigorous stirring at 50°, it yielded about the same amount of polymers at the end of 5 hr, whereas the blank run without phenol produced no polymeric substance.

The effect of hindered phenols in free-radical polymerization of N-vinylcarbazole is indeed unusual and hard to explain. One conjecture, based on the aforementioned information, will be that there is an interaction between the isobutyronitrile radical and/or the isobutyronitrile–peroxy radical and the phenol to result in the formation of the phenoxy radical which in turn undergoes a redox process with N-vinylcarbazole as indicated in the following equations.
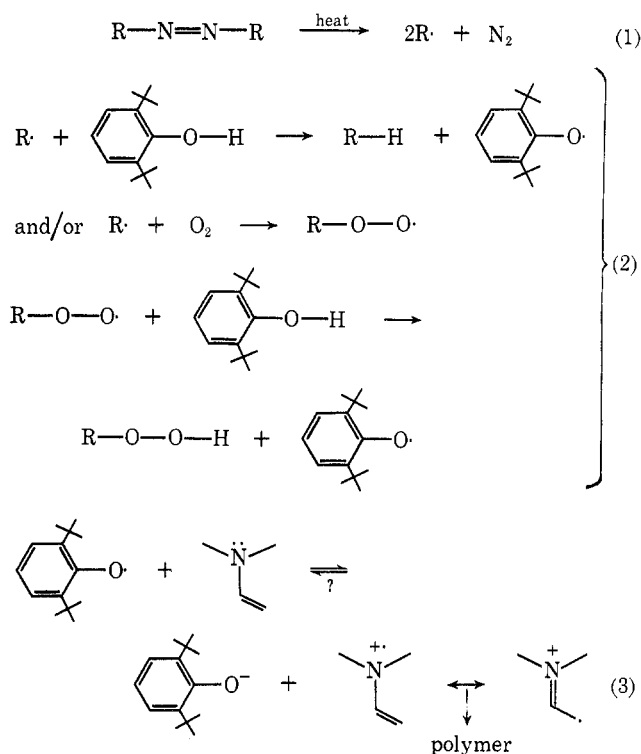
The interaction between alkylperoxy radical and phenols to afford the alkyl hydroperoxide and the phenoxy radicals is well documented.[5] The direct hydrogen abstraction from the phenol by isobutyronitrile radical may parallel the reaction between benzhydryl radical and thiophenol.[6] The constancy in the yield of polymer in various runs containing 2,6-di-*t*-butylphenol from 1×10^{-4} to 1×10^{-3} mol might suggest that reaction 2 is the principal path for the consumption of the isobutyronitrile radical and also that in the polymerization process, the atypical cation radical intermediate, insensitive toward various scavengers, is involved. Consideration of the rate of decomposition of azobiso-

(1) C.-H. Wang, *Chem. Ind. (London)*, 751 (1964).
(2) L. P. Ellinger, *ibid.*, 1982 (1963).
(3) H. Scott, T. P. Konen, and M. M. Labes, *Polym. Lett.*, **2**, 689 (1964).
(4) C.-H. Wang, C. C. Sizman, and K. Stevenson, *J. Org. Chem.*, **35**, 2045 (1970).

(5) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956).
(6) C.-H. Wang and S. G. Cohen, *J. Amer. Chem. Soc.*, **79**, 1924 (1957).

butyronitrile at 50° gives pertinent information. The rate of decomposition of this azo compound at 80° is ~1.7 × 10⁻⁴ mol⁻¹ sec⁻¹ and E_A is ~30 kcal/mol.[7] At 50° the rate constant is estimated to be ~3.5 × 10⁻⁶ mol⁻¹ sec⁻¹. Thus the initial highest concentration of isobutyronitrile radical or the isobutyronitrile–peroxy radical in the presence of oxygen in these experiments is about 4 × 10⁻⁸ mol/l. which is negligibly small compared to the concentration of phenols in any of the experiments.

Simple phenols are less effective as initiators in this process than the hindered ones, indicating probably that the hindered phenoxy radicals are more stable and capable of existing long enough to undergo the redox reaction with N-vinylcarbazole. The nature of the redox initiated polymerization of N-vinylcarbazole *via* a cation radical is poorly understood at the present time, except it differs from ordinary radical initiated polymerization process *via* a carbon radical whereas the former process is insensitive toward oxygen and phenoxy radicals as well as other inhibitors mentioned earlier.

Experimental Section[8]

Chemicals.—N-Vinylcarbazole, mp 65–67°, was obtained from Matheson Coleman and Bell; 2,6-di-*t*-butylphenol, mp 35–37°, 2,4-di-*t*-butylphenol, mp 24–26°, phenol, mp 40–41°, and azobisisobutyronitrile, mp 103° dec, were obtained from Eastman. Methanol anhydrous AR was obtained from Mallinckrodt.

Polymerization of N-Vinylcarbazole.—(a) A solution of 2 g (1 × 10⁻² mol) of N-vinylcarbazole and 0.02 g (1 × 10⁻⁴ mol) of 2,6-di-*t*-butylphenol and 0.05 g (~3 × 10⁻⁴ mol) of azobisisobutyronitrile in 50 ml of methanol was heated under nitrogen atmosphere at 50° for 5 hr. The reaction mixture produced a yellowish gummy mass. Upon drying the solid weighed 1.2 g. The solid was triturated with benzene and turned into a yellowish white solid, melting at a wide range from 150 to 250°. The infrared spectrum in KBr possesses the following bands at 3030, 1650, 1600, 1560, 1500, 1450, 1240, 750, 720 cm⁻¹, resembling that of poly-*n*-vinylcarbazole.[9] This solid did not decolorize either bromine in carbon tetrachloride or permanganate solution in acetone–water medium.

In the blank runs, the one without azoisobutyronitrile produced no polymer while the one without 2,6-di-*t*-butylphenol afforded ~0.2 g of polymeric material of comparable property with that from experiment a.

(b) In two parallel experiments, the conditions and reagents were maintained the same as in (a) except that the amount of 2,6-di-*t*-butylphenol was increased to 0.04 g (2 × 10⁻⁴ mol) and 0.2 g (1 × 10⁻³ mol). The reaction proceeded as in (a) and the products were worked up in the same manner as in (a). The yields of the polymeric products in these two runs were 1.2 g and 1.5 g, respectively.

(c) When 2,4-di-*t*-butylphenol was used instead of 2,6-di-*t*-butylphenol as in (a), the reaction produced a polymeric substance resembling that from (a) weighing 1.1 g. With phenol, on the other hand, no polymer was obtained. However, when the reaction with phenol was heated at 50° for a longer time (20 hr), a trace amount of polymeric substance was obtained. Identification of this trace amount of substance was not attempted.

(d) Reaction a was repeated by carrying out the procedure in open air with vigorous stirring instead of under nitrogen atmosphere. It yielded a polymeric substance weighing 1.1 g. However, with azobisisobutyronitrile but no 2,6-di-*t*-butylphenol in open air, the yield of a polymeric substance was practically nil at the end of 5 hr.

Registry No.—N-Vinylcarbazole, 1484-13-5.

(7) F. W. Lewis and M. S. Matheson, *J. Amer. Chem. Soc.*, **71**, 747 (1949).
(8) Melting points are not corrected. Spectral analysis was performed in the analytical laboratories of Arthur D. Little, Inc., Cambridge, Mass.
(9) Reference polymer from General Aniline and Film Corp., Union, N. J.

The Diels–Alder Reaction of N-Vinylphthalimide with Isoprene and 9-Methoxyanthracene

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N-Vinylphthalimide (1) has been available commercially for over a decade and numerous accounts of its use as a monomer have been published, but its potential as a dienophile in the Diels–Alder reaction seems to be limited to the report of adduct formation with anthracene and hexachlorocyclopentadiene.[3] So far no unsymmetrically substituted diene has been condensed with it in order to study its regiospecificity in this reaction. Since vinylamine, like vinyl alcohol, is unavailable for use in a Diels–Alder reaction, the use of 1 potentially offers two step syntheses of various amines such as 11-amino-9,10-dihydro-9,10-ethanoanthracene. This pharmacologically interesting amine has so far been prepared only by a four-step synthesis from anthracene.[4]

9-Methoxyanthracene when condensed with acrylic acid, methyl acrylate, acrylonitrile, and acrylamide gives an adduct corresponding to 2, but allyl alcohol, having no conjugated system, gives rise to 3.[5]

2   **3**
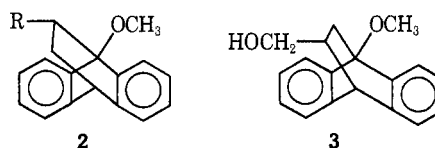
Isoprene, like other 2-substituted butadienes, gives rise to mainly the "para" adduct 4 rather than the isomeric adduct corresponding to 5 when condensed

4   **5**
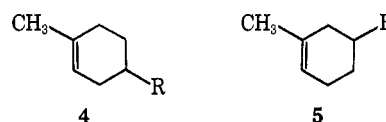
with acrylic acid, acrolein,[6] methyl acrylate, acrylyl chloride, acrylamide,[7] styrene, 2-vinylpyridine,[8] etc.

Recently, the reaction of methyl acrylate with isoprene was reported to give a 7:1 ratio of the two adducts corresponding to 4 and 5, respectively, when the reaction was run at either room temperature or at 120°.[9] When the reaction occurred in benzene at 7–12° and was catalyzed by aluminum chloride, a 19:1 ratio was obtained with the "para" adduct again predominating.[9]

Supposedly the aluminum chloride complexes with the carbonyl oxygen of the methyl acrylate and intensifies the positive charge on the β-carbon atom of the

(1) National Institutes of Health, Predoctoral Fellow, 1966–1967.
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(6) E. Lehman and W. Paasche, *Ber.*, **66B**, 1068 (1935).
(7) D. R. Wilgus, Ph.D. Thesis, University of Colorado, 1951.
(8) J. S. Meek, R. T. Merrow, and S. J. Cristol, *J. Amer. Chem. Soc.*, **74**, 2667 (1952).
(9) T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121 (1966).