

butyronitrile at 50° gives pertinent information. The rate of decomposition of this azo compound at 80° is $\sim 1.7 \times 10^{-4} \text{ mol}^{-1} \text{ sec}^{-1}$ and E_A is $\sim 30 \text{ kcal/mol}$.⁷ At 50° the rate constant is estimated to be $\sim 3.5 \times 10^{-6} \text{ mol}^{-1} \text{ sec}^{-1}$. Thus the initial highest concentration of isobutyronitrile radical or the isobutyronitrile-peroxy radical in the presence of oxygen in these experiments is about $4 \times 10^{-8} \text{ mol/l}$. 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 Section⁸

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 ($1 \times 10^{-2} \text{ mol}$) of N-vinylcarbazole and 0.02 g ($1 \times 10^{-4} \text{ mol}$) of 2,6-di-*t*-butylphenol and 0.05 g ($\sim 3 \times 10^{-4} \text{ mol}$) 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 azobisisobutyronitrile produced no polymer while the one without 2,6-di-*t*-butylphenol afforded $\sim 0.2 \text{ g}$ 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 ($2 \times 10^{-4} \text{ mol}$) and 0.2 g ($1 \times 10^{-3} \text{ mol}$). 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

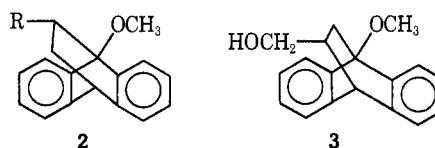
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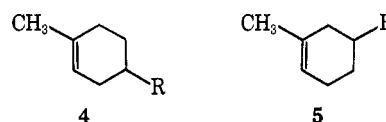
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N-Vinylphthalimide (1) has been available commercially for over a decade and numerous accounts of its use as a monomer have been published, but its potential as a dienophile in the Diels–Alder reaction seems to be limited to the report of adduct formation with anthracene and hexachlorocyclopentadiene.³ So far no unsymmetrically substituted diene has been condensed with it in order to study its regioselectivity 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



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



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°. 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.

(2) Supported by the Office of Naval Research.

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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).

acrylate moiety. This increases that carbon's attraction for the more electron rich carbon atom (C-1) in the isoprene molecule and leads to the higher ratio of the "para" adduct.

In N-vinylphthalimide delocalization of the unshared electron pair on the nitrogen atom should make the β -carbon atom of the vinyl group negative, but this effect would be counteracted by delocalization involving the carbonyl groups as well as by the inductive effects of the oxygen atoms. These effects do not lead to a clear cut prediction of the major adduct to be expected with 9-methoxyanthracene, although with isoprene one would expect an adduct corresponding to **4** as the major product since no dienophile has yet given a major adduct corresponding to **5**.

The Diels-Alder reaction of 1- and 9-methoxyanthracene went readily at 200° and only one adduct was isolated. Its pmr spectrum revealed a doublet for the bridgehead proton which showed it was the nonvicinal adduct corresponding to **3**.

Isoprene and **1** gave a crystalline adduct which was dehydrogenated to N-*p*-tolylphthalimide. The adduct was also synthesized from the known methyl acrylate-isoprene adduct.

It appears that 9-substituted anthracenes are more sensitive to steric and electronic effects governing orientation than are 2-substituted butadienes and that **1** behaves like an unconjugated dienophile in its condensation with 9-methoxyanthracene.

Experimental Section

N-(9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11-yl)phthalimide.— **1** (1 g) and 1.3 g of 9-methoxyanthracene⁵ were fused at 200° for 50 hr. The mixture was then dissolved in ethanol, filtered, and then concentration gave 0.43 g of colorless solid, mp 200–203°. The pmr spectrum (CDCl₃) showed a doublet at 4.4 ppm ($J = 2.5$ Hz) for the bridgehead proton.

Anal. Calcd for C₂₅H₁₉NO₃: C, 78.72; H, 5.02. Found: C, 78.57; H, 4.92.

When anthracene and **1** were condensed in a similar fashion a 60% yield of N-(9,10-dihydro-9,10-ethanoanthracen-11-yl)phthalimide, mp 183–185°, was obtained. Recrystallizations from benzene-petroleum ether gave an analytically pure sample, mp 196–197° (lit.⁵ 180–181°).

N-(1-Methyl-4-cyclohexenyl)phthalimide.— **1** (10 g), 4 g of isoprene and 0.1 g of hydroquinone dissolved in 15 ml of acetone were heated in a rocking autoclave at 175–185° for 28 hr. Extraction of the product with 250 ml of hot ethanol left 3.7 g of apparently polymeric material, mp 175–230° dec. From the extract 1.77 g (13%) of white crystals were obtained. Recrystallization gave the analytical sample, mp 141–143°.

Anal. Calcd for C₁₅H₁₇NO₂: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.99; H, 6.21; N, 5.68.

The methyl acrylate adduct of isoprene⁷ on treatment with hydrazine gave a product which by means of a Curtius reaction was converted into an amine which gave a phthalimide, mp 139–140°, that was identical with the adduct of **1** and isoprene.

When 1.2 g of the N-vinylphthalimide-isoprene adduct was heated for 80 min at 297–358° with 0.1 g of 10% palladium on charcoal, hydrogen was evolved. Fractional crystallization from ethanol then gave 0.19 g of white crystals, mp 201–203°. A mixture of this product and N-*p*-tolylphthalimide,¹⁰ mp 202–203°, melted at 202–203° while a mixture of this product and N-*m*-tolylphthalimide,¹⁰ mp 171–173°, melted at 160–185°.

Registry No.— **2** (R = phthalimido), 25577-21-3; **4** (R = phthalimido), 25577-22-4; N-vinylphthalimide, 3485-84-5; isoprene, 78-79-5; 9-methoxyanthracene, 2395-96-2.

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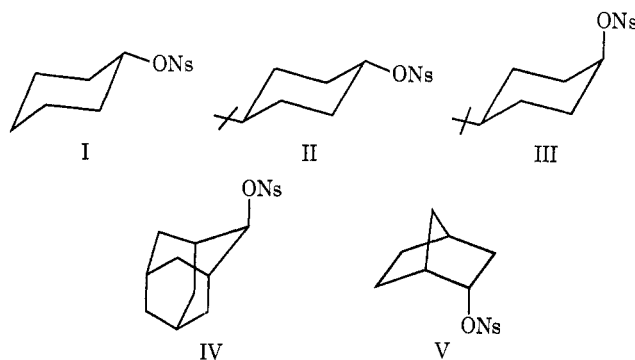
The Effect of Pressure on Some Sterically Hindered Solvolysis Reactions¹

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In several earlier publications^{2–4} we have shown that the activation volume of a solvolysis reaction may depend somewhat on the occurrence of participation. In at least some of the reactions for which participation has been claimed, steric hindrance has been proposed⁵ as an alternative explanation of the rate ratio of epimeric substrates, and since steric hindrance evidently also has small effects on the activation volume, at least in the Menshutkin reaction,^{6,7} we considered it desirable to study the pressure-promoted hydrolysis of the following closely related nosylates.



In these reactions the formation of an ion pair should be unhindered for I and II and hindered for IV and V. In I, the leaving group is expected to depart from an equatorial position. In II, the 4-*tert*-butyl group forces it to leave from that position. In IV, the rigid adamantyl ring system forces it to leave from the axial position; hindrance is then provided by the axial 3- and 5-hydrogen atoms. In V, hindrance has been considered to be exerted by the 6-*endo*-hydrogen atom.⁵ We hoped that a large difference between the pressure coefficients of II and III would furthermore enable us to calculate the effect of pressure on A, a measure of the size of the nosyloxy group.⁸ The results are shown in Table I.

The absolute ΔV^* values are somewhat larger than those observed in earlier studies; the reason for this is that the more precise conductance method employed here allows its determination from observations over a smaller range (1 kbar) and with smaller pressure intervals (see ref 6 for a full discussion of this point).

The observations clearly do not show a correlation between ΔV^* and steric hindrance. While the ΔV^* values for I and II do seem to be slightly less negative

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- (5) See, e.g., H. C. Brown, *Chem. Brit.*, 199 (1966).
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