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Cation-Radical Cycloaddition and Polymerization Reactions of N-Vinylcarbazole with Electrophilic Ethylenes

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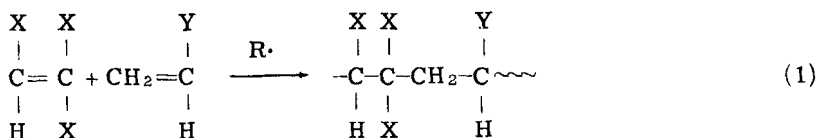
ABSTRACT

The uncatalyzed reactions of N-vinylcarbazole with electrophilic olefins have been studied. The products included both small molecules and polymers. N-Vinylcarbazole reacted with tricarbomethoxyethylene in inert solvents such as benzene at 110°C to form trimethyl 1-carbazol-9-ylbut-1-ene-3,4,4-tricarboxylate. Donor solvents such as acetone or acetonitrile gave trimethyl-1-carbazol-9-ylcyclobutane-2,2,3-tricarboxylate. A variety of additives in the inert solvents also diverted the product from the 3,4,4-tricarboxylate to the 2,2,3-tricarboxylate. These included oxygen, several silver salts, metallic mercury, diphenylpicrylhydrazyl, and tributyltinhydride. Polymers also formed in low yields in many of these reactions. Either homopolyvinylcarbazole or the alternating copolymer of N-vinylcarbazole with tricarbomethoxyethylene formed, depending on the solvent. Pyridine prevented the formation of the former, and tert-butylhydroquinone the latter; thus their formation is ascribed to cationic and free radical processes, respectively. N-Vinylcarbazole reacted with tetracarbomethoxyethylene at 155°C in either inert or donor solvents to produce tetramethyl 1-carbazol-9-ylbut-1-ene-3,3,4,4-tetracarboxylate. In the presence of DPPH,

tetramethyl 1-carbazol-9-ylcyclobutane-2,2,3,3-tetracarboxylate was the product. N-Vinylcarbazole reacted with dimethyl cyanofumarate at 28°C in inert solvents with air present to give dimethyl 4-cyano-1-carbazol-9-ylbut-1-ene-3,4-dicarboxylate, while donor solvents with air present gave dimethyl 2-cyano-1-carbazol-9-ylcyclobutane-2,3-dicarboxylate. N-Vinylcarbazole reacted with 1,2-disubstituted ethylenes at 155°C to give only copolymers. The above results are interpreted as proceeding by electron transfer from N-vinylcarbazole to the electrophilic olefin. In inert solvents the N-vinylcarbazole cation-radical transfers a proton to the anion-radical and couples to form the 1-butene derivative. In donor solvents or in presence of additives which scavenge or stabilize the anion-radical, the N-vinylcarbazole cation-radical reacts instead with the electrophilic ethylene monomer. The resulting butane radical-cation cyclizes and leads to the cyclobutane derivatives. This new cyclobutane synthesis extends the cyclodimerization mechanism of Tada, Shirota, and Mikawa and of Ledwith for electron-rich olefins to the cycloaddition of electron-rich olefins to electron-poor olefins.

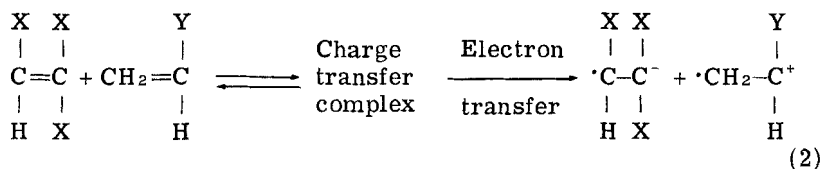
INTRODUCTION

In connection with the synthesis of functional polymers, our work [1-3] has dealt with the synthesis of copolymers, produced in high yields and molecular weights by free-radical copolymerization, of electrophilic trisubstituted ethylenes with electron-rich monosubstituted olefins:



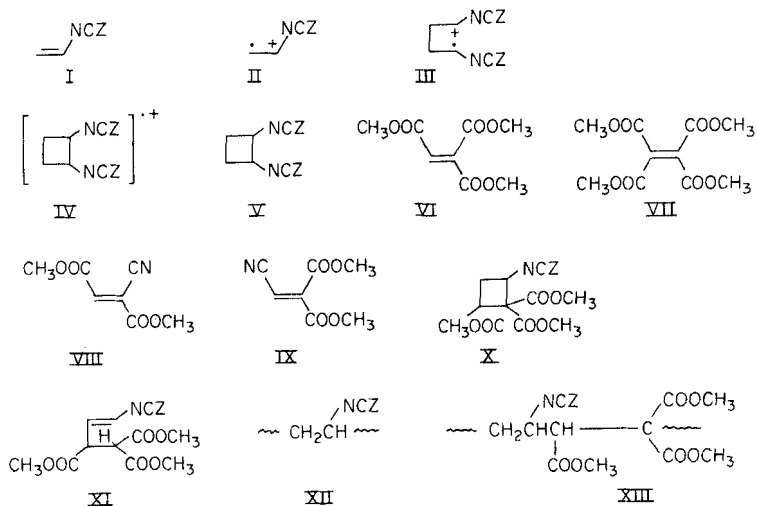
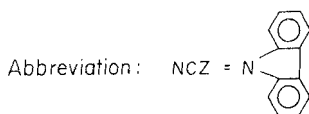
Here X is a strongly electron-attracting group such as cyano or carbomethoxy, and Y is an electron-donor group such as alkoxy or aryl. Conventional radical initiators such as AIBN, benzoyl peroxide, or ultraviolet light were used.

As the substituents X and Y were varied to produce more reactive monomers, spontaneous alternating copolymerizations began to take place [1]. This implied spontaneous radical formation, which presumably occurred by electron transfer from the electron-rich olefin to the electrophilic trisubstituted ethylene [Eq. (2)].

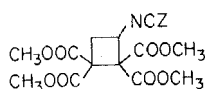


The ion-radicals then initiated free-radical copolymerization. Such copolymerizations have been observed by Stille and co-workers in the reactions of vinylidene cyanide with electron-rich olefins [3].

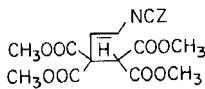
To investigate these phenomena further, we have now studied the reactions of the electron-rich olefin N-vinylcarbazole with electrophilic trisubstituted ethylenes.



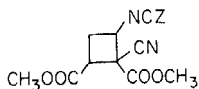
N-Vinylcarbazole (I) readily forms the corresponding cation-radical (II), in the presence of electrophilic trisubstituted ethylenes, and this in turn is capable of initiating either cationic or radical polymerization [4-8]. Moreover, under certain conditions the cation-radical reacts with N-vinylcarbazole to form cyclodimer. The key to this diverse behavior was shown by Tada, Shirota, and Mikawa [5-7] to be the influence of the solvent on the reactivity of the cation-radical



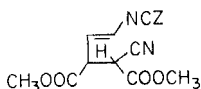
XIV



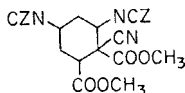
XV



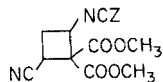
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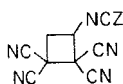
XVII



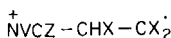
XVIII



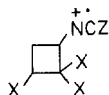
XIX



XX



XXI



XXII

(X = CN, COOCH₃)

(Table 1). In inert solvents cationic polymerization predominates. In strongly basic donor solvents such as DMSO or DMF, cationic reactivity is completely suppressed, and radical polymerization occurs. In solvents of intermediate basicity or donor ability such as acetone or acetonitrile, cationic and radical character coexist. The dimeric cation-radical III undergoes a novel internal cyclization to form the cation-radical IV of the cyclodimer. Transfer of an electron from monomer forms the product cyclodimer V and continues the chain. This cyclodimerization occurs with a variety of electron-rich olefins, although the effect of varying the solvent has not been investigated systematically [9-17].

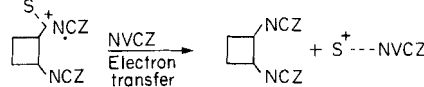
The electrophilic olefins used in the present work were those from our previous investigations, namely tricarbomethoxyethylene (VI), dimethyl cyanofumarate (VIII), and dimethyl 2-cyanoethylene-1,1-dicarboxylate (IX). For comparison, tetracarbomethoxyethylene (VII) and several 1,2-disubstituted electrophilic ethylenes, namely fumaronitrile, dimethyl maleate and N-phenylmaleimide, were also examined.

The electrophilic olefin and N-vinylcarbazole, both at 0.3 M, were allowed to react in various solvents, with or without various additives, at the lowest temperature at which complete reaction occurred. The products, both small molecules and polymers, were separated and identified, and the yields of each were measured.

RESULTS

Generally, the predominant products from the reaction of N-vinylcarbazole with tri- and tetrasubstituted electrophilic ethylenes were

TABLE 1. Tada-Shirota-Mikawa Mechanism for the Effect of Solvents on the Reactions of N-Vinylcarbazole Cation-Radical, ^+NVCZ

Solvent	Reaction	Product
Inert solvent: ^+NVCZ	$^+NVCZ \xrightarrow{\text{Monomer addition}} ^+NVCZ-NVCZ \xrightarrow{\text{Cationic propagation}} \text{Poly-NVCZ}$	
Donor solvent: S^+-NVCZ	$S^+-NVCZ \xrightarrow{\text{Monomer addition}} S^+-NVC-NVC$  $\text{Cyclobutane-NCZ-NCZ-S}^+ \xrightarrow[\text{Electron transfer}]{NVCZ} \text{Cyclobutane-NCZ-NCZ-N}^+ + S^+-NVCZ$	
Strong donor solvent: S^+-NVCZ	$S^+-NVCZ \xrightarrow{\text{Monomer addition}} S^+-NVCZ-NVC \xrightarrow{\text{Free radical propagation}} \text{Poly-NVCZ}$	

small molecules, while only polymers were formed with 1,2-disubstituted ethylenes.

Reaction with Tricarbomethoxyethylene

Tricarbomethoxyethylene (VI) (Table 2) reacted with N-vinylcarbazole at 110°C during 16 hr to form high yields of either 1-butene (XI), cyclobutane (X), or copolymer (XIII), depending on the solvent, along with minor amounts of homopolymer XII (Table 2). Inert solvents formed the 1-butene, donor solvents gave the cyclobutane, and strong donor solvents gave 1:1 copolymer. The cyclobutane X and 1-butene XI were stable under the reaction conditions and did not interconvert except at much higher temperatures. Use of AIBN in either inert or donor solvents led to copolymer. The formation of the small molecules was not initiated by radical initiators or photoinitiated, and was not inhibited by free radical inhibitors.

In benzene, an inert solvent, certain additives (usually at 0.01 M concentration) diverted the product to cyclobutane without accelerating the reaction (Table 3). These included air, several silver and copper compounds, metallic mercury, copper, and Wood's alloy, tributyltin hydride, and diphenylpicrylhydrazyl. Pyridine at this concentration was marginally effective. Several of these additives accomplished

TABLE 2. Product Yields from the Reaction of Tricarbomethoxyethylene VI with N-Vinylcarbazole I in Various Solvents

Additive	Solvent type ^a	Product yield (%)				
		Cyclobutane X	1-Butene XI	Homopolymer XII	Copolymer XIII	
Degassed, no additive	Nondonor					
	Carbon tetrachloride	0	90	2	3	
	Benzene	0	97	0	0	
	Toluene	0	100	0	0	
	Chlorobenzene	0	98	4	2	
	Dichloromethane	0	71	23	6	
Donor	Ethyl ether	98	0	0	0	
	p-Dioxane	99	0	0	0	
	Tetrahydrofuran	98	0	0	0	
	Ethyl acetate	85	0	0	0	
	Acetone	85	0	0	0	
	Acetonitrile	85	0	10	5	
Strongly basic	DMSO	10	0	0	90	
	Nondonor					
Tert-butylhydroquinone	Carbon tetrachloride	0	82	8	10	

Benzene	0	100	0	0	0
Toluene	0	99	1	1	0
Chlorobenzene	0	93	3	3	3
Dichloromethane	0	78	20	2	2
Donor					
p-Dioxane	100	0	0	0	0
Acetone	100	0	0	0	0
Air					
Nondonor					
Carbon tetrachloride	0	79	12	9	9
Dichloromethane	69	0	20	11	11
Benzene	73	0	1	1	1
Toluene	60	0	1	9	9
Chlorobenzene	100	0	0	0	0
Donor					
Tetrahydrofuran	30	0	11	13	13
p-Dioxane	17	0	72	10	10
Ethyl ether	4	0	70	16	16
Ethyl acetate	60	0	0	0	0
Acetone	100	0	0	0	0
Acetonitrile	49	0	7	10	10

(continued)

TABLE 2 (continued)

Additive	Solvent type ^a	Product yield (%)				
		Cyclobutane X	1-Butene XI	Homopolymer XII	Copolymer XIII	
Pyridine	Nondonor	0	100	0	0	
	Carbon tetrachloride	0	100	0	0	
	Benzene	56	16	0	0	
	Chlorobenzene	22	65	0	0	
Donor	Dichloromethane	0	94	4	2	
	Acetonitrile	49	0	3	0	
	Nondonor	69	0	0	0	
	Benzene	88	0	0	0	
Tributyltin hydride	Dichloromethane	66	3	4	2	
	Donor	16	0	0	74	
	p-Dioxane	92	0	6	2	
	Acetonitrile	92	0	6	2	

^a Solvents characterized in Table 6.

^b The reaction between 3 ml of 0.3 M N-vinylcarbazole and 3 ml of 0.3 M tricarboethoxyethylene was carried out in sealed tubes at 110°C for 16 hr. The only exception is the reaction in DMSO, which was carried out at 78°C. Additives were made up to 0.01 M.

TABLE 3. Product Yields from the Reaction of Tricarbomethoxyethylene with N-Vinylcarbazole^a in Presence of Other Additives in Benzene Solution

Additive	Product yield (%)		
	Cyclobutane X	1-Butene XI	Polymer
None	0	100	0
CO ₂	0	100	0
N ₂	0	100	0
Air	97	0	3
Quinones			
2,5-Dimethylbenzoquinone	0	95	5
2,5-Dichlorobenzoquinone	0	100	0
Tetrachlorobenzoquinone	0	100	0
TCNQ ^b	4	96	0
0.1 TCNQ ^b	0	6	91
Silver salts			
Silver hexafluoroantimonate	0	0	100
Silver hexafluorophosphate	0	0	71
Silver fluoride	0	6	94
Silver triflate	2	0	60
Silver carbonate	23	0	77
Silver nitrate	33	8	58
Silver oxide	all	0	e
Silver cyanide	all	0	e
Other salts			
Ferric nitrate	27	0	73
Sodium nitrate	0	68	32
Potassium metaperiodate	0	60	40
Metals			
Copper powder	all	0	e
Copper oxide	all	0	e
Iridium	all	0	e

(continued)

TABLE 3. (continued)

Additive	Product yield (%)		
	Cyclobutane X	1-Butene XI	Polymer
Wood's metal ^c	all	0	e
Mercury ^d	56	26	8
Mercury (0.2 g)	95	5	0
Zinc dust	0	all	e
Selenium	0	all	e
Other compounds			
Tri-n-butyltin hydride	69	0	0
Diphenylpicrylhydrazyl	60	14	10
Pyridine	56	16	0

^aThe reaction between 3 ml of 0.3 M N-vinylcarbazole and 3 ml of 0.3 M tricarbomethoxyethylene in benzene, sealed in degassed tubes was carried out at 110°C for 16 hr. The only exception is the reaction in DMSO, which was carried out at 78°C. Soluble additives were made up to 0.01 M, otherwise 0.01 g of insoluble additive was added to the reaction mixture.

^b7,7,8,8-Tetracyanoquinodimethane.

^c50% Bismuth, 25% lead, 12.5% tin, 12.5% cadmium.

^dReaction mixture shaken with mercury and decanted.

^ePolymer not measured, only ratio of X to XI produced given, not yields.

the same diversion in other inert solvents, except for carbon tetrachloride. Additives with no effect on the cyclobutane:1-butene ratio were tert-butylhydroquinone, quinones, TCNQ, zinc, selenium, and other silver compounds.

A small amount of polyvinylcarbazole formed in several of these reactions, particularly when methylene chloride was the solvent. In benzene, homopolymer formation was initiated by TCNQ, chloranil, and by silver salts. Ether solvents, especially with air present, also gave high amounts of homopolymer. Pyridine or triethylamine inhibited its formation. 1:1 Copolymers also formed in small amounts in the donor solvents and particularly in the strongly basic ones. Tert-butylhydroquinone prevented the formation of copolymer.

Reaction with Tetracarbomethoxyethylene

Tetracarbomethoxyethylene VII (Table 4) reacted with N-vinylcarbazole at 155°C during 16 hr. Either inert or donor solvents yielded the 1-butene XV. Air in benzene or acetonitrile, or DPPH in benzene, caused the cyclobutane XIV to form. Pyridine at this concentration was marginally effective, but tert-butyhydroquinone had no effect on the cyclobutane:1-butene ratio. These results could only be reproduced to $\pm 10\%$ because at this elevated temperature the cyclobutane XIV slowly isomerized to the 1-butene XV.

The yield of homopolyvinylcarbazole was somewhat higher than at 110°C, particularly in methylene chloride and in ether mixtures. Copolymer was not formed.

Reaction with Dimethyl Cyanofumarate

Dimethyl cyanofumarate VIII reacted with N-vinylcarbazole at 28°C during 16 hr (Table 5). In inert solvents in presence of air, mainly the 1-butene (XVII) formed, while in donor solvents in presence of air predominantly the cyclobutane XVI was obtained.

A cyclohexane adduct XVIII, formed with two molecules of N-vinylcarbazole and one of the cyanofumarate, could also be isolated using chloroform, methylene chloride, or 1,2-dichloroethane as solvents.

Reaction with Dimethyl 2-Cyanoethylene-1,1-dicarboxylate

Dimethyl 2-cyanoethylene-1,1-dicarboxylate (IX) gave a cyclobutane adduct XIX from N-vinylcarbazole in presence of air at 28°C.

DISCUSSION

The results of our experiments paralleled to a marked degree those of Tada, Shiota, and Mikawa. In inert solvents we obtained the 1-butene derivatives (rather than cationic homopolymer). Donor solvents led to cycloadduct (rather than cyclodimer), while strongly basic solvents gave free radical copolymer. The parallelism is particularly noteworthy because of the different experimental conditions involved. In their work, the ratio of N-vinylcarbazole to electron acceptor (quinone or oxygen) was 100:1, while in our work the ratio of N-vinylcarbazole to electrophilic olefin was 1:1. Their reactions were

TABLE 4. Product Yields in the Reaction of Tetracarbomethoxyethylene VII with N-Vinylcarbazole I in Various Solvents^a

Additive	Solvent	Cyclobutane XIV	1-Butene XV	Homopolymer XII
Degassed, no additive	Benzene	0	90	5
	p-Dioxane	4	78	8
	Tetrahydropyran	9	81	10
	Tetrahydrofuran	3	66	31
	Acetonitrile	0	85	0
Tert-butylhydroquinone	Benzene	0	92	0
	p-Dioxane	12	63	0
	Tetrahydropyran	0	96	0
	Tetrahydrofuran	35	30	0
	Benzene	85	5	3
Air	p-Dioxane	88	4	8
	Tetrahydropyran	20	80	0
	Acetonitrile	70	30	0
	Benzene	34	39	0
	p-Dioxane	11	68	0
Pyridine	Tetrahydropyran	34	22	4
	Acetonitrile	30	20	0

Diphenylpicrylhydrazyl	Benzene	40	34	0
	Tetrahydrofuran	36	39	0
	Acetonitrile	43	0	0

^aReagents were at 0.3 M, tubes were sealed, heated at 155° C for 16 hr. If air is not cited as being present, samples were degassed. Balance of material not reported was N-Vinylcarbazole.

TABLE 5. Products Yields from the Reaction of Dimethyl Cyanofumarate VIII with N-Vinylcarbazole in Various Solvents in Presence of Air^a

	Product yield (%)			
	Cyclobutane XVI	1-Butene XVII	Homopolymer XII	Copolymer + Cyclohexane ^b XVIII
Carbon tetrachloride	90	10	0	0
Toluene	40	60	0	0
Benzene	70	29	0	1
Chlorobenzene	50	50	0	0
Dichloromethane	82	8	1	9
Ether	80	18	0	0
Tetrahydropyran	90	8	0	2
Tetrahydrofuran	90	10	0	0
Ethyl acetate	90	9	0	1
Acetone	88	9	0	3
Acetonitrile	90	9	0	1

^aThe reaction between 0.3 M N-vinylcarbazole and 0.3 M dimethyl cyanofumarate was carried out in vials at room temperature in the presence of air, 16 hr.

^bCopolymer and cyclohexene adduct was separated from the 1:1 adducts as a mixture; the major portion of the value reported represents cyclohexane adduct.

TABLE 6. Donor Properties of the Solvents Used in this study

Type	Solvent	$\Delta\nu_D$ value ^a	D value ^b
Nondonor	Carbon tetrachloride	-21	0 ^c
	Methylene chloride	-12	0 ^c
	Chlorobenzene	- 2	0 ^c
	Benzene	0	0.1
	Toluene	2	0.1 ^c
	Nitromethane	6	2.7
Donor	Ethyl acetate	39	17.1
	Acetonitrile	49	14.1
	Acetone	64	17.0
	Dioxane	77	14.8
	Ethyl ether	78	19.2
	Tetrahydrofuran	90	20.0
	Tetrahydropyran	93	-
Strong donor	Dimethylformamide	107	26.6
	Dimethyl sulfoxide	141	29.8

^aData of Kagiya, et al. [18].

^bData of Gutmann [19].

^cAssumed.

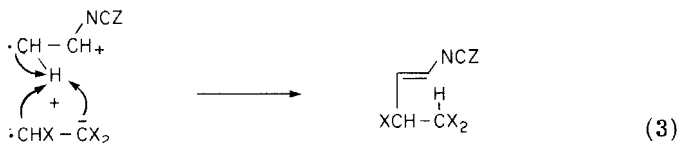
photoinitiated at ambient temperature, while ours were thermally initiated at 28-155°C. Yet the overall results are similar in regard to solvent influence and point toward a common intermediate, namely the cation-radical II of N-vinylcarbazole.

The suggestive similarity of these results leads us to extend the Tada-Shirota-Mikawa mechanism to explain our data (Scheme 1). Our proposal is that N-vinylcarbazole cation-radical reacts with electrophilic ethylene anion-radical to give the 1-butene, but with electrophilic ethylene to give cyclobutane.

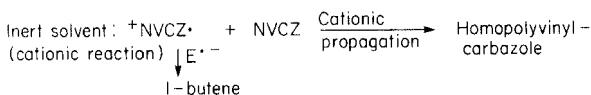
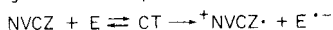
1-Butene Formation in Inert Solvents

Interaction of N-vinylcarbazole with electrophilic ethylene E leads via charge-transfer complexation and thermal excitation, to the

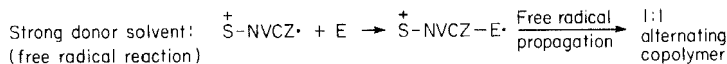
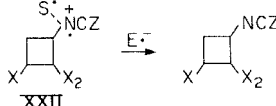
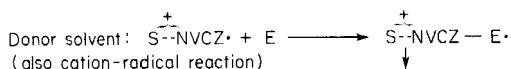
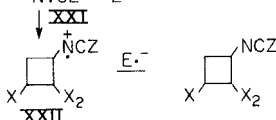
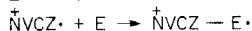
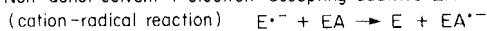
corresponding ion-radicals. These can be regarded as a cationic species and a strong base, respectively. It is reasonable that proton transfer accompanies C-C bond formation to give 1-butene [Eq. (3)].



Charge transfer complex formation and electron transfer:



Non-donor solvent + electron-accepting additive EA:



SCHEME 1. Proposed mechanism for the reaction of N-vinyl-carbazole with electrophilic ethylenes (E).

The fact that more 1-butene formed from tetraester VII than from triester VI may have been caused by the higher reaction temperature (155 vs. 110°C).

Cyclobutane Formation in Donor Solvents

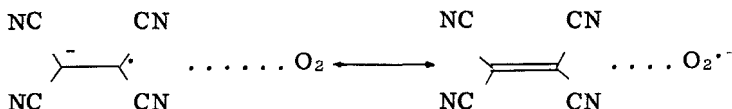
If the solvent possesses donor properties, the cationic nature of the cation-radical is diminished, and with it the propensity to transfer a proton. Accordingly the cation-radical can diffuse away from the

anion-radical and can react with a molecule of electrophilic olefin to form the dimeric cation-radical XXI. Cyclization yields the cation-radical of the cycloadduct XXII, which, being less stabilized than $\text{NVCZ}^{\cdot+}$, can now accept an electron to form product. The electron is supplied by the anion-radical, a stronger electron donor than N-vinylcarbazole, so no chain reaction occurs.

Cyclobutane Formation in Inert Solvents in Presence of Additives

The additives which cause cyclobutane formation are generally 1-electron acceptors. Their function is to scavenge ethylene anion-radicals, so that cation-radical can react with ethylene monomer as in the donor solvents (above).

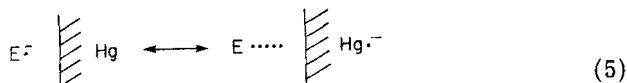
Reversible complexing of oxygen with anion-radicals has been reported for tetracyanoethylene [20], which is structurally similar to our ethylenes [Eq. (4)].



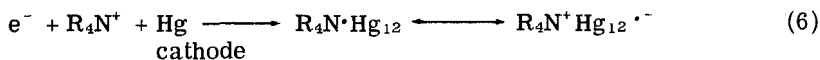
This role for oxygen in our thermal experiments differs from that in the photochemical experiments of Tada, Shiota and Mikawa, where formation of cation-radical occurred by electron transfer from photo-excited N-vinylcarbazole to form $\text{O}_2^{\cdot-}$. However, we observed no acceleration in rates caused by oxygen, and so it appears to alter the product ratio by interacting with reactive intermediates.

Diphenylpicrylhydrazyl DPPH, also a stable radical, is pictured similarly as complexing with anion-radical and removing it from reaction.

Metals are also postulated to scavenge anion-radical in a manner similar to oxygen [Eq. (5)].



The ability of mercury to accept electrons from free radicals is shown by the electrochemical generation of stable, crystalline radical amalgams [21].



Silver ion mainly catalyzed polymerization, but caused cyclobutane formation in the small-molecule fraction, perhaps again by electron acceptance. Tributyltin hydride is very prone to free radical reactions and could again scavenge the anion-radical.

Homopoly-N-vinylcarbazole

This was a very minor product in all but a few experiments and is formed only by cationic polymerization. Runs in methylene chloride gave markedly higher yields of homopolymer, in keeping with the ability of this solvent to promote cationic polymerization.

The rather high and variable yields of polymer obtained with ether solvents, especially in the presence of air, are ascribed to the formation of hydroperoxides which cause both ionic and radical polymerizations of N-vinylcarbazole.

Silver ion and TCNQ also initiated cationic polymerization, probably by generating N-vinylcarbazole cation-radical.

Copolymers

The copolymers formed from trisubstituted ethylenes in the donor and particularly the strong donor, solvents occurred by free radical propagation. They were identical to those formed by AIBN-induced copolymerization, and their formation was prevented by tert-butyl hydroquinone.

No copolymers occurred with tetracarboxymethoxyethylene for steric reasons. Homopolymerization of N-vinylcarbazole did not occur because the tetraester acted as a radical trap.

Copolymers formed from the 1,2-disubstituted ethylenes even in donor solvents, perhaps because the single α -substituent could not stabilize the dimeric cation-radical enough to permit cyclization.

Effects of Olefin Structure on Reactivity

The reactivity sequence among the electrophilic olefins was: (tetracyanoethylene) > dimethyl 2-cyanoethylene-1,1-dicarboxylate > dimethyl cyanofumarate \gg tricarbomethoxyethylene \gg tetracarboxymethoxyethylene > 1,2-disubstituted ethylenes. This reasonable sequence has been observed previously [1, 2, 22] and has been explained in the following terms. At the α position, two groups stabilize carbanions or radicals better than one, and cyano groups perform this function better than carbomethoxy. Groups at the β position offer steric hindrance to bond formation, with carbomethoxy being bulkier than cyano.

EXPERIMENTAL

Methods

Ultraviolet spectra were obtained by using a Cary 14 spectrophotometer. Infrared spectra were obtained by using a Perkin-Elmer grating infrared spectrometer, model 337. Proton NMR spectra were obtained on a Varian T60 spectrometer, and ^{13}C nuclear magnetic resonance spectra were obtained by use of a Bruker WH-90 spectrometer. Chemical shifts are reported on the τ scale using tetramethylsilane as the reference. Melting points were determined in open glass capillary tubes and are uncorrected. All ground glass joints were lubricated by using Lubriseal or Lubriseal High Vac Formula.

Solvents and Reagents

Benzene and toluene were fractionally distilled at atmospheric pressure from and stored over metallic sodium. Chlorobenzene was fractionally distilled at reduced pressure from and stored over metallic sodium. Dichloromethane, 1,2-dichloroethane, carbon tetrachloride, and chloroform were fractionally distilled from soda lime and/or potassium hydroxide and stored over anhydrous potassium carbonate. Pyridine was distilled and stored over potassium hydroxide. p-Dioxane was treated with basic alumina having a Brockmann activity grade of 1 and was fractionally distilled. This was stored over Molecular Sieves and, where indicated, was run through a column of basic alumina just prior to use. Anhydrous ethyl ether was used as obtained from Mallinckrodt (0.05% water). Acetonitrile, obtained from Mallinckrodt as analytical reagent, and anhydrous ethyl acetate from Matheson, Coleman and Bell (MCB) were used without further purification. 1,2-Dimethoxyethane from MCB, acetone from Baker, tetrahydropyran from Aldrich and nitrobenzene, dimethylformamide, dimethyl sulfoxide and 2,2-dimethoxypropane from Eastman Kodak were placed over Molecular Sieves and used without further purification. Tetrahydrofuran from Eastman Kodak was distilled from calcium hydride and placed over molecular sieves. Where indicated, tetrahydrofuran and tetrahydropyran were passed through a column of basic alumina (with a Brockmann activity of 1) just prior to use.

N-Vinylcarbazole was obtained from Pfaltz and Bauer, and from Polyscience. It was recrystallized from methanol (in the dark) and stored in a brown bottle. Tetracyanoethylene was sublimed at 80°C (at atmospheric pressure) and stored under nitrogen, mp $196\text{--}197^\circ\text{C}$. Tetracarbomethoxyethylene, tricarbomethoxyethylene dimethyl 1-cyano-1,2-trans-ethylenedicarboxylate, and dimethyl 2-cyano-1,1-ethylenedicarboxylate, were prepared via the methods reported by Hall and Daly [1] or by Hall and Ykman [2]. N-Phenylmaleimide was sublimed under vacuum and stored under nitrogen.

General Procedure

The procedure followed was dependent upon the reactivity of the electron-deficient olefin. Reactions with tetracyanoethylene and dimethyl 1-cyanoethylene-trans-1,2-dicarboxylate, very reactive olefins, were carried out at room temperature in 4-dram vials equipped with a small magnetic stirrer. Reactions with tricarbomethoxyethylene, tetracarbomethoxy ethylene and most of the other electron deficient olefins were carried out at elevated temperatures in sealed Pyrex tubes.

Those reactions which were degassed were made up as follows. A Pyrex tube containing the reagents was attached to a manifold via a rubber tube. The solution was frozen in liquid nitrogen and placed under vacuum. After closing the stopcock on the manifold the solvent was thawed and refrozen. Vacuum was reapplied. The solution was rethawed and nitrogen was placed in the manifold and tube. The solution was shaken briskly. This was then subjected to two more freeze-thaw cycles. The solution was refrozen and the tube sealed without breaking vacuum. A vacuum of 0.01 Torr was obtained and held for 5 min during each cycle.

The workup of the reactions involved selective precipitation and extraction of the products, recrystallization and/or vacuum distillation if possible and identification by elemental analysis, conventional ^1H and ^{13}C nuclear magnetic resonance spectra, ultraviolet and visible spectroscopy, infrared spectroscopy, mass spectral analysis, and comparison with authentic samples whenever possible. The reproducibility of the experiments was always checked and in most cases 100% material balance of starting material to products was achieved.

The efficiency of the workup procedure was proved by analyzing a known mixture as follows. A solution was made up containing 0.0353 g of tricarbomethoxyethylene, 0.0671 g of N-vinylcarbazole, 0.0431 g of polyvinylcarbazole, 0.011 g of copolymer, and 0.384 g of the cyclobutane adduct of N-vinylcarbazole and tricarbomethoxyethylene in 3 ml of chloroform. This was then poured into 12 ml of methanol, filtered onto a weighted piece of filter paper, dried in the air for 24 hr, weighed, extracted with four 4-ml portions of acetone, dried, and reweighed. The initial methanol precipitate weighed 0.0566 g. The acetone-insoluble polymer weighed 0.0445 g. The methanol-soluble portion weighed 0.1379 g. Based on the NMR spectrum, 61% of the carbazole absorptions in the methanol soluble portion corresponded to N-vinylcarbazole, the remainder being attributed to the cyclobutane carbazole absorptions. On the basis of this value, 55% of the ester absorption was attributed to the cyclobutane and 45% was attributed to tricarbomethoxyethylene. In the starting mixture the N-vinylcarbazole constituted 63.6% of the carbazole absorptions in the NMR and the cyclobutane constituted 52.1% of the ester absorption. A 99% material balance was obtained.

Cationic Polymerization of N-Vinylcarbazole in Various Solvents

The polymerization of a solution containing 0.1 g (0.5 mmole) of N-vinylcarbazole in 1.5 ml each of 22 solvents was initiated with 0.012 g (0.5 mmole) of benzoic acid. The solution was heated at 80°C for 16 hr. This was then precipitated with ethyl ether, filtered, dried and weighed, and the percent conversion to polymer was recorded. The reactions containing p-dioxane, dimethoxyethane and tetrahydropyran as solvent were repeated, except that just prior to making up the samples the solvent was passed through a column of basic alumina having a Brockmann activity of 1.

A sample of polyvinylcarbazole was made and isolated by treating a solution containing 0.4 g of N-vinylcarbazole (2.1 mmole) in 4 ml of dichloromethane with 0.012 g of benzoic acid (1.0 mmole) and warming the solution to 40°C for 12 hr. This was precipitated with 20 ml of methanol, filtered, and leached with acetone. After drying at room temperature for 24 hr the sample was sent for analysis.

ANALYSIS. Calcd for $C_{12}H_{11}N$: C, 87.05%; H, 5.70%; N, 7.25%. Found: C, 86.77%; H, 5.85%; N, 7.25%.

Trans-1,2-Di(carbazol-9-yl)cyclobutane (V)

A modified method reported by McKinley, Crawford and Wang [23] was used. To a solution containing 2 g of N-vinylcarbazole in 88 ml of anhydrous methanol was added 0.2 g of $Fe(NO_3)_3 \cdot 9H_2O$. A deep yellow color formed, and within 30 min a precipitate formed which was immediately filtered to yield 0.76 g of dimer, mp 189-191°C (lit. [23] mp, 189-191°C). Recrystallization from hexane:benzene (20:1) yielded 0.48 g, mp 193-194°C.

ANALYSIS. Calcd for $C_{28}H_{22}N_2$: C, 87.01%; H, 5.74%; N, 7.25%. Found: C, 87.27%; H, 5.92%; N, 7.19%.

NMR($CDCl_3$) indicated aromatic hydrogens, 1.98 and 2.69 (m, 18H); α hydrogens, 3.77 (5, 2H); β hydrogens, 7.25 (m, 4H). The IR spectra revealed a cyclobutane deformation at 1210 and 1230 cm^{-1} and the carbazole absorptions in the region between 700 and 800 cm^{-1} .

Reaction of N-Vinylcarbazole with Tricarbomethoxyethylene

A yellow color was produced when colorless solutions of N-vinylcarbazole and tricarbomethoxyethylene were mixed at room temperature. This color remained indefinitely so long as the solutions were not heated. The major products from the reaction were the cyclobutane,

trimethyl-1-carbazol-9-cyclobutane-2,2,3-tricarboxylate (X) and the open-chain adduct, trimethyl 1-carbazol-9-ylbut-1-ene-3,4,4-tricarboxylate (XI). The product distribution for the reactions between N-vinylcarbazole and tricarbomethoxyethylene in a variety of solvents both with and without additives are given in Table 2.

A typical reaction procedure was as follows. Tricarbomethoxyethylene (0.202 g, 1 mmole) and N-vinylcarbazole (0.193 g; 1 mmole) were placed in 3 ml of solvent in a Pyrex flask, sealed, and heated to 110°C for 16 hr. The workup included a preliminary NMR scan of the reaction solution, precipitation with methanol, filtration, drying and weighing. The weight of the acetone-insoluble precipitate was taken as the amount of polyvinylcarbazole which formed. The weight difference between the precipitate in acetone and the precipitate in methanol was taken as a measure of the amount of copolymer formed. Table 2 lists the percent of each component formed based on initial vinylcarbazole present. The percent of cyclobutane formed is based on the amount of N-vinylcarbazole which has reacted and adjusted for that amount of the remainder which has not reacted as determined by NMR. The acetone was evaporated in each case. The solids were dissolved in deuteriochloroform. If ester groups were not detected and broad aliphatic absorptions existed in the NMR spectra, the weight was added to the insoluble polymeric weight to get the total amount of polyvinylcarbazole formed. The inhibitor used in this series was tert-butylhydroquinone (0.004 g).

Other Additives

To a solution containing 1 mmole of N-vinylcarbazole and 1 mmole of tricarbomethoxyethylene in 3 ml of benzene was added a small amount (0.007 to 0.02 g) of additive. The samples were degassed, sealed, and heated to 110°C. The product distribution was determined by NMR. The polymer reported was precipitated with methanol, filtered, dried, and weighed. A degassed control sample, where no additive was present, was run for each sample. Where material balance in Table 2 does not total 100%, the remainder was found to be recovered N-vinylcarbazole. In those cases where no value is reported for the polymer the percentages of cyclobutane adduct and open chain adduct reflect the ratio observed by NMR and do not represent yields. Samples run with carbon dioxide and nitrogen atmospheres were degassed by the standard procedures and the CO₂ or N₂ was added at atmospheric pressure just prior to sealing. Care had to be taken with the carbon dioxide sample in order to insure that solid CO₂ was not present in the sample when the tube was sealed.

Trimethyl 1-carbazol-9-ylcyclobutane-2,2,3-tricarboxylate (X)

A solution containing 0.202 g (1 mmole) of tricarbomethoxyethylene and 0.193 g (1 mmole) of N-vinylcarbazole in 5 ml of benzene was sealed in a Pyrex tube in the presence of air at atmospheric pressure. This was then heated to 110°C for 16 hr. The solvent was evaporated and extracted with hexane-pentane (1:1) mixture, which was evaporated to yield a thick, clear, colorless oil. This was extracted with hexane and the hexane was evaporated. NMR (CDCl₃) showed aromatic absorptions, 2.05 (m, 2H) and 2.70 (m, 6H); hydrogen α to carbazole, 3.86 (t, 1H); cyclobutane hydrogens 5.65 (q, 1H) and 5.72-7.50 (m, 2H); ester absorptions, 6.24 (several singlets, 6H) and 7.14 (s, 3H); shoulder at 7.15 (indicates presence of cis-trans isomer in sample). The IR spectra exhibits ester absorption at 1740 cm⁻¹, carbazole absorption at 700-800 cm⁻¹, and a broad cyclobutane absorption from 1200 to 1230 cm⁻¹.

ANALYSIS. Calcd for C₂₂H₂₁NO₆: C, 66.83%; H, 5.32%; N, 3.54%. Found: C, 66.87%; H, 5.70%; N, 3.48%.

¹³C NMR (acetone-d₆) showed absorption attributed to the ester methyl carbon at 1180 Hz; the carbazole CH carbons absorb occur at 2510, 2710, and 2840 Hz; the quaternary carbazole carbons absorb at 2790 and 3170 Hz; the ester carbonyl carbons absorb at 2780 and 2870 Hz; the cyclobutane carbons absorb at 2940, 1420, 890, and 590 Hz being, respectively, the carbons in the 1, 2, 3, and 4 positions as indicated by the splitting in the off-resonance spectra.

Attempted vacuum distillation of X gave only XI.

Trimethyl 1-carbazol-9-ylbut-1-ene-3,4,4-tricarboxylate (XI)

A solution containing 0.193 g of N-vinylcarbazole (1 mmole) and 0.202 g of tricarbomethoxyethylene (1 mmole) in 3 ml of benzene was degassed and sealed. This was then heated to 110°C for 16 hr. The solvent was evaporated. The residue was distilled by using a Kugelrohr distillation apparatus. The clear distillate was sent for analysis.

ANALYSIS. Calcd for C₂₂H₂₁NO₆: C, 66.83%; H, 5.32%; N, 3.54%. Found: C, 67.20%; H, 5.52%; N, 3.62%.

NMR (CDCl₃) showed aromatic absorption at 1.98 (m, 2H) and 2.58 (m, 6H), hydrogen α to carbazole at 3.68 (d, J = 8 Hz, 1/2H) and 3.85 (d, J = 8 Hz, 1/2H), a single strong peak at 5.76 (1H), several ester singlets at 6.24 and the remaining absorptions from the butane hydrogens appear as many baseline absorptions from 5.4 to 7.2. The ¹³C NMR revealed the ester methyl carbon absorptions at 1190 Hz. The carbazole CH carbons absorb at 2510, 2720, 2730, 2860, and

2890 Hz, and the quaternary carbons in carbazole absorb at 2800 and 3150 Hz. The ester carbonyl carbons absorb at 3870 and 3780 Hz. The butene carbons absorb at 2900, 2560, 1240, and 1080 Hz, each of the latter absorptions being split into doublets in the off-resonance spectra. The deuterioacetone used as solvent absorbs at 4820 and 670 Hz.

1:1 Copolymer of Vinylcarbazole and Tricarbo-methoxyethylene (XIII)

A solution containing 2.02 g of tricarbo-methoxyethylene and 1.93 g of N-vinylcarbazole (10 mmole of each) in 10 ml of chloroform was irradiated for 24 hr at room temperature. Ethyl ether was added and a polymeric material precipitated. This was extracted three times with 50 ml portions of ether to leave a material which analyzed as a 1:1 copolymer.

ANALYSIS. Calcd for $C_{22}H_{21}NO_6$: C, 66.83%; H, 5.31%; N, 3.54%. Found: C, 65.93%; H, 5.32%; N, 3.55%.

The ether-soluble portion contained the cyclobutane adduct and a trace of unreacted starting material.

Reaction of N-Vinylcarbazole with Tetracarbo-methoxyethylene

When N-vinylcarbazole and tetracarbo-methoxyethylene were mixed together in a solvent, a pale yellow color immediately developed. If the solution was not heated, color remained indefinitely.

Tetracarbo-methoxyethylene was the least reactive of the olefins tested. The reactions were carried out at 155°C for 16 hr. At this temperature many of the solvents were capable of exploding the Pyrex tubes used to carry out the reactions. The major products formed in the reactions were the cyclobutane, tetramethyl 1-carbazol-9-ylcyclobutane-2,2,3,3-tetracarboxylate (XIV), and the open-chain adduct, tetramethyl 1-carbazol-9-ylbut-1-ene-3,3,4,4-tetracarboxylate (XV). The product distribution is reported in Table 4. In a typical reaction, 0.264 g (1 mmole) of tetracarbo-methoxyethylene and 0.193 g (1 mmole) of N-vinylcarbazole were dissolved in 3 ml each of the solvents listed in Table 4. The additives (0.004 g of tert-butylhydroquinone, diphenylpicrylhydrazyl, pyridine, or triethylamine) were added to the N-vinylcarbazole prior to mixing with the tetracarbo-methoxy ethylene. Where indicated the ether solvents were passed through a short column of basic alumina just before use. All the tubes were sealed and heated to 155°C. The runs in nitromethane detonated at this temperature and were not further investigated.

Those samples made up ethyl acetate, dichloroethane, acetonitrile, tetrahydrofuran, and acetone were made up several times but nearly always exploded due to the pressure involved at the elevated temperature. After 16 hr the samples were cooled and the vials broken open. Nuclear magnetic resonance spectra were run on the crude reaction mixture in order to detect the possibility of further reaction(s) occurring during the workup. The formation of polyvinylcarbazole was detected by the presence of a precipitate when the reaction mixture was added to methanol. Any solution in which polymer was detected was added to 10 ml of methanol. The polymer filtered onto weighed filter paper, dried, weighed, leached with four 4-ml portions of acetone, dried, and reweighed. The methanol-soluble portion was evaporated to dryness, dissolved in CDCl_3 , and an NMR spectrum obtained to determine the products and presence of starting material. The results reported in Table 4 are based on the carbazole absorption.

Tetramethyl 1-Carbazol-9-ylcyclobutane-2,2,3,3-tetracarboxylate (XIV)

A solution containing 0.54 g (1.2 mmole) of tetracarboxymethoxyethylene and 0.40 g (1.2 mmole) of N-vinylcarbazole in 10 mmole of benzene was placed in a Pyrex tube and sealed under air atmosphere. This was heated to 155°C for 16 hr. The solvent was evaporated and the residue extracted with a hexane:cyclohexane:benzene mixture (6:2:1). Upon evaporation a solid was obtained which could be recrystallized from a carbon tetrachloride-pentane mixture, mp $172.8\text{--}173.4^\circ\text{C}$; yield 0.76 g (81%).

NMR (CDCl_3) showed aromatic absorptions, at 2.05 (m, 2H) and 2.74 (m, 6H); hydrogen α to carbazole, 3.89 (t, 1H); hydrogens β to carbazole, 5.56 (q, 1H) and 7.18 (q, 1H); ester absorptions, 6.08, 6.12, 6.22, 7.03, (four singlets, 12H).

-ANALYSIS. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_8$: C, 63.53%; H, 5.12%; N, 3.09%. Found: C, 63.38%; H, 5.36%; N, 3.00%.

Attempted vacuum distillation of XIV gave only XV.

Tetramethyl 1-Carbazol-9-ylbut-1-ene-3,3,4,4-tetracarboxylate (XV)

To a solution containing 0.193 g (1 mmole) of vinylcarbazole in 1.5 ml of chlorobenzene was added to 0.264 g (1 mmole) of tetracarboxymethoxyethylene in 1.5 ml of chlorobenzene. This was placed in a Pyrex tube and degassed and sealed. The sample was then heated to 155°C for 16 hr. The tube was broken open and the solvent evaporated. The residue was extracted with pentane and evaporated to

yield a solid which could be recrystallized from a pentane-carbon tetrachloride mixture, mp 96-98°C. NMR (CDCl₃) showed aromatic absorptions at 1.78 (m, 2H) and 2.57 (m, 6H); hydrogen α to carbazole, 3.38 (d, $J = 8$ Hz, 1H) hydrogen β to carbazole, 5.18 (s, 1H) ester absorptions 6.20 (several singlets, 12H).

ANALYSIS. Calcd for C₂₄H₂₃NO: C, 63.53%; H, 5.12%; N, 3.09%. Found: C, 63.42%; H, 5.08%; N, 2.97%.

Reactions between N-Vinylcarbazole and Dimethyl Cyanofumarate

Upon mixing the colorless solutions of N-vinylcarbazole and dimethyl cyanofumarate a deep yellow color formed. As the reaction proceeded the color faded until a colorless solution resulted. A quantitative reaction was obtained within 16 hr at room temperature in the presence of air. The major products were the cyclobutane, 2-cyano-1-carbazol-9-ylcyclobutane-2,3-dicarboxylate (XVI) and the open-chain adduct 4-cyano-1-carbazol-9-ylbutene-3,4-dicarboxylate (XVII). In some of the solvents, i. e., chloroform and dichloromethane, a cyclohexane adduct, 6-cyano-1,3-di-(carbazoyl-9-yl)cyclohexane-5,6-dicarboxylate (XVIII) could be isolated.

In a typical reaction 0.17 g (1 mmole) of dimethyl cyanofumarate and 0.193 g (1 mmole) of N-vinylcarbazole in 3 ml each of 13 solvents were mixed at room temperature in the presence of air. The workup procedure was identical to that reported for the N-vinylcarbazole-tricarboxymethoxyethylene reaction.

The product distributions for the reactions between N-vinylcarbazole and dimethyl cyanofumarate are given in Table 5. With the exception of carbon tetrachloride, the cyclobutane to open-chain ratio increases roughly as the solvent polarity increases. Benzene, chlorobenzene, and toluene exhibited a tendency to produce more open-chain adduct than the other solvents. The chlorinated solvents, which have given similar results to the benzene solvents in other reactions, differed in the reactions between N-vinylcarbazole and dimethyl cyanofumarate by their tendency to produce cyclohexane adduct.

Dimethyl 2-cyano-1-carbazol-9-ylcyclobutane-2,3-dicarboxylate (XVI)

The reaction between 0.17 g (1 mmole) of dimethyl cyanofumarate and 0.19 g (1 mmole) of N-vinylcarbazole was carried out in 3 ml of benzene at room temperature (28°C) in the presence of air. After 16 hr the solvent was evaporated and the residue was extracted with

cyclohexane. The cyclohexane was evaporated and the procedure repeated. NMR (CDCl_3) showed aromatic hydrogens at 1.98 (m, 2H) and 2.65 (m, 6H); hydrogen α to carbazole at 4.42 (t, 1H); ester absorptions, 6.25 (s, 6H); other cyclobutane ring hydrogens, 7.05 (s, 1H), 5.4 to 8.2 (m, 2H). The IR spectrum showed no CN absorptions. The sample could not be satisfactorily purified for analysis.

ANALYSIS. Calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_4$: C, 69.61%; H, 4.97%; N, 7.73%. Found: C, 70.94%; H, 4.98%; N, 6.89%.

Dimethyl 4-cyano-1-carbazol-9-ylbut-1-ene-3,4-dicarboxylate (XVII)

The reaction between 0.17 g (1 mmole) of dimethyl cyanofumarate and 0.19 g (1 mmole) of N-vinylcarbazole was carried out in 3 ml of toluene at room temperature in the presence of air. After 16 hr the solvent was evaporated and the residue chromatographed. The last half of the major zone was found to be enriched with the desired product. This was rechromatographed several times on silica gel, hexane-pentane (1:1) being used to elute. NMR (CDCl_3) indicated the characteristic feature of the open-chain adduct to be four small peaks located at 3.82 (d, $J = 8$ Hz, 1/2H) and 4.04 (d, $J = 8$ Hz, 1/2H). Even after four chromatographings the chain adduct was contaminated with 10 to 20% cyclobutane. The IR spectrum showed CN absorptions at 2220 cm^{-1} (moderate intensity).

Dimethyl 6-cyano-1,3-di(carbazol-9-yl) cyclohexane-5,6-dicarboxylate (XVIII)

A solution containing 0.17 g (1 mmole) of dimethyl cyanofumarate and 0.19 g (1 mmole) of N-vinylcarbazole in 3 ml of dichloromethane was allowed to react at room temperature for 16 hr. The solvent was evaporated and thin layered on silica gel. A substance not corresponding to starting materials or 1:1 adduct was washed off. NMR (CDCl_3) showed absorptions at 1.82 (t, 6H); 2.7 (m, 14H); 6.18 (s, 6H); 6.5-8.7 (m, 4H). The hydrogen α to carbazole exhibited a broad absorption in the region 3.2 to 4.3.

ANALYSIS. Calcd for $\text{C}_{35}\text{H}_{29}\text{N}_3\text{O}_4$: C, 75.68%; H, 5.23%. Found: C, 75.36%; H, 5.19%.

Reaction of N-Vinylcarbazole with 2-Cyanoethylene-1,1-dicarboxylate

The reaction between N-vinylcarbazole and 2-cyano-1,1-dicarboxymethoxyethylene was carried out in benzene and produced an initial

TABLE 7. Spectral Data

Compound	α Hydrogen		β Hydrogen, NMR	$^{13}\text{C-NMR}$ (off-resonance splitting)	
	NMR	IR, cm^{-1}		C_x	Hz
XX	3.75 (t, 1H)	1210-1230 ^a	3.82 (d, J = 8 Hz, 1/2H)		
XVII			4.04 (d, J = 8 Hz, 1/2H)		
XVI	4.42 (t, 1H)		3.38 (d, J = 8 Hz, 1H)		
XV					
XIV	3.89 (t, 1H)		3.68 (d, H = 8 Hz, 1/2H)	C ₁	2900 (d)
XI			3.85 (d, J = 8 Hz, 1/2H)	C ₂	2560 (d)
				C ₃	1240 (d)
				C ₄	1080 (d)
X	3.86 (t, 1H)	1210-1230		C ₁	2940 (d)
				C ₂	1420 (s)
				C ₃	890 (d)
V	3.77 (m, 2H)	1210-1230		C ₄	590 (q)

^aData of Bawn et al. [26].

deep yellow color. The reaction was only a third as fast as the cyanofumarate reaction. The polymer which formed (6%) was precipitated in methanol, filtered off, and the methanol evaporated. This was then dissolved in chloroform. Solids precipitated, were filtered off, and were recrystallized from chloroform, mp 161-163°C.

ANALYSIS. Calcd for $C_{21}H_{18}N_2O_4$: C, 69.61%; H, 4.97%; N, 7.73%. Found: C, 70.99%; H, 5.24%; N, 7.82%.

When the sample was subsequently dissolved in carbon tetrachloride, carbazole was found to be present, being insoluble in carbon tetrachloride.

ANALYSIS. Calculated for 8.4% carbazole present: C, 70.99%; H, 5.04%; N, 7.79%.

Spectral Assignments

Assignments of the NMR absorptions of 1,2-transdicarbazol-9-ylcyclobutane (V), the dimer of N-vinylcarbazole, have been made by Ellinger [24]. A comparison of the absorptions of the dimer with the cyclobutane adducts obtained revealed similar features (see Table 7). The absorptions for the hydrogen α to carbazole in the cyclobutanes appeared in the region between 3.0 and 4.5 τ . All of the cyclobutane adducts exhibited a triplet absorption for the α hydrogen having a 1:2:1 ratio. The β hydrogens of the open-chain adducts exhibited a multiplet (usually four small peaks in nearly a 1:1:1:1 pattern) which was shifted downfield by 0.2 to 0.3 τ from the position of the α hydrogens on the corresponding cyclobutane adduct. A ^{13}C nuclear magnetic resonance and off-resonance spectra confirmed the above structural assignments.

A comparison of the infrared absorptions of the cyclobutane with those of V revealed both had absorptions in the region from 1200 to 1230 cm^{-1} which were similar in nature (for IR assignment see Crellin and Ledwith [25]). The open-chain adduct XI did not exhibit this characteristic absorption.

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