of material isolated in this way, the yield was 51% of a mixture of cis- and trans-dideuterated olefins in a 7:3 ratio.

Thermolyses: Apparatus and Methods. A 15-cm-diameter stainless-steel beaker mounted with three asbestos-cement plates and firebrick halves in a cubical plywood container was surrounded by a commercial insulative diatomacious filler ("Celatom" diatomite, Eagle-Picker Industries, Inc.) and fitted with stainless-steel immersion heaters and a stirrer. The bath held approximately 7 kg of molten $NaNO_2$ and KNO_3,[36] maintained at temperature with a Model 253 precision temperature controller (0-500 °C, Bailey Instrument Co.). The temperature was measured by a frequently calibrated Hewlett-Packard 2802A thermometer accurate to ±0.05 °C.

Thermolysis tubes for initial kinetic work were constructed from 1-mm wall thickness, 5-mm o.d. borosilicate glass tubing; they were detergent washed, acid washed, base washed, and dried at 200 °C prior to use. Later work employed Pyrex ampules made from 6-mm tubing (11-13 cm long, 1.4-1.6 mL volume). Large-scale pyrolyses were carried out in "20 mL" (volume 29 mL) and "50 mL" (volume 65 mL) ampules (Kontes) with 6-mm tubing butted on for sealing under vacuum. All ampules were subjected to the following washing procedure: 12 h of soaking in concentrated HCl(aq); rinsing with water; soaking in concentrated NH_3(aq)/EDTA solution for 24-72 h; copious rinsing with water; drying in an oven for at least 24 h at ~250-275 °C and pumping under high vacuum ($<10^{-4}$ mm).

Olefins to be pyrolyzed were freshly purified by preparative GLC and then introduced into the ampules by (conditioned) capillary tubing or by syringe; each ampule was subjected to freeze-pump-thaw cycles and sealed under high vacuum. Samples in ampules were suspended in the salt bath in a wire cage, removed after a determined period of time, and then cooled in water or under a stream of air. The pyrolysate was condensed in the small end of the ampule with liquid N_2, and the ampule was opened. The contents were diluted, after weighing, with 3-4 volumes of isooctane. Recovery of material ranged from 83% to 100%; no polymer was observed. A few microliters were utilized for GLC analyses, and the rest of the solution was subjected to preparative GLC to isolate the various isomers for NMR analyses. Kinetic data were obtained by analyzing the condensed, diluted pyrolysate at least three times by GLC.

Conditioned ampules were made by pyrolyzing *cis*-cyclooctene in the ampules (pressure ~250-830 mm) at 291.6-350 °C for periods of 2-9 days. The ampules were then broken open, emptied, and pumped under high vacuum. When these ampules were used, care was taken to seal them so that all the surface had been conditioned.

Treatment of kinetic data to obtain rate constants was carried out by using a standard least-squares program on the University of Oregon PDP-10 computer.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work and for funds to add a deuterium Fourier transform NMR capability to the Oregon XL-100 spectrometer, to Professor A. H. Andrist for obtaining some ^2H NMR spectra during a period in which the University of Oregon deuterium NMR capability was inoperative, to Professor F. W. Dahlquist for assistance in securing FT ^2H NMR spectra, and to Professor G. M. Whitesides for helpful correspondence.

Registry No. 1, 931-89-5; **4**, 4103-11-1; **5**, 79839-59-1; **6**, 79839-60-4; **8**, 3008-37-5; *cis*-**9**, 79839-61-5; *trans*-**9**, 79839-62-6; **10**, 79839-63-7; **11**, 79839-64-8; **12**, 79839-65-9; benzaldehyde, 100-52-7.

---

[36] Cason, J.; Rapoport, H. "Laboratory Text in Organic Chemistry"; Prentice-Hall: Englewood Cliffs, NJ, 1962; p 279.

Cycloaddition and Polymerization Reactions of *N*-Ethyl-3-vinylcarbazole with Electron-Poor Olefins

M. Abdelkader and H. K. Hall, Jr.*

The Chemistry Department, University of Arizona, Tucson, Arizona 85721

Received April 7, 1981

Reaction of *N*-ethyl-3-vinylcarbazole (1) and trimethyl ethylenetricarboxylate (2) yielded the cyclobutane adduct trimethyl 1-(*N*-ethyl-3-carbazyl)-2,2,3-cyclobutanetricarboxylate (3) and homopoly(*N*-ethyl-3-vinylcarbazole) (4). The formation of **3** was favored by polar solvents and high temperatures. Formation of homopolymer **4** was suppressed by dimethyl sulfoxide but unaffected by the addition of radical inhibitors. With AIBN as initiator, the alternating copolymer **5** was obtained (as well as some cycloadduct **3**). Dimethyl cyanofumarate (**6**), more reactive than **2**, reacted with **1** at room temperature to yield cyclobutane adduct dimethyl 1-(*N*-ethyl-3-carbazyl)-2-cyano-2,3-cyclobutanedicarboxylate (**7**) and homopolymer **4**. Reaction of **1** with tetramethyl ethylenetetracarboxylate (**8**) at high temperature resulted in cyclobutane adduct tetramethyl 1-(*N*-ethyl-3-carbazyl)-2,2,3,3-cyclobutanetetracarboxylate (**9**). These reactions were interpreted as proceeding via predominantly zwitterionic tetramethylene intermediates.

Introduction

Functionally substituted olefins react thermally with themselves or with other olefins to produce a variety of products, both small molecules and polymers. Small molecules include cyclobutanes, 1-butenes and cyclohexanes; polymers include homopolymers of either or both olefins and alternating 1:1 copolymers.[1-4] Various mechanisms have been suggested for these reactions. We have been using the concept of a tetramethylene intermediate,[2,5,6] produced by bond formation between the β-carbons of the two olefin molecules, which is a resonance hybrid of zwitterion and spin-paired biradical forms. The various small molecules derived from collapse of various conformations of the intermediate tetramethylene T, and do not diagnose the relative contributions of the two resonance forms. The polymer products are more diagnostic. Homopolymers of one or the other monomer can form by cationic or anionic initiation at either end of a predominantly zwitterionic tetramethylene, whereas alternating copolymers will form from a predominantly biradical

---

[1] Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.

[2] Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.

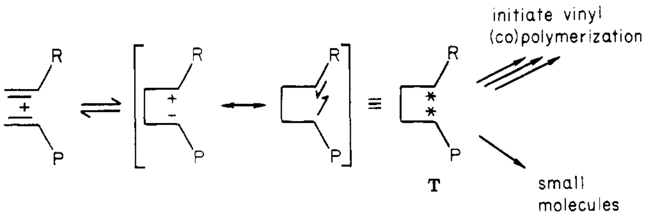
[3] Stille, J. K.; Oguni, N.; Chung, D. C.; Tarvin, R. F.; Aoki, S.; Kamachi, M. *J. Macromol. Sci. Chem.* **1975**, *A9(5)*, 745.

[4] Hall, H. K., Jr.; Ykman, P. *J. Am. Chem. Soc.* **1975**, *97*, 800.

[5] Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

[6] Chmurny, A. B.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 4237.

0022-3263/82/1947-0292$01.25/0



R = electron-rich substituent
P = electron-poor substituent

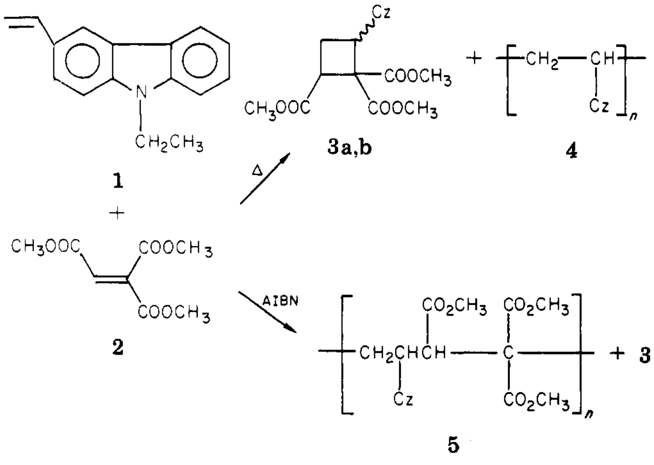
tetramethylene. Increased solvent polarity favors the former but not the latter.

In our previous work on reactions of electron-rich styrenes with electrophilic tri- and tetrasubstituted ethylenes,[8] *p*-(dimethylamino)styrene, by these criteria, was found to react via a zwitterionic tetramethylene, and cyclobutane adducts were obtained. Increasing solvent polarity accelerated the cyclobutane formation. On the other hand, *p*-methoxystyrene reacted with electrophilic ethylenes to form a biradical tetramethylene,[7] leading to spontaneous copolymerization of the reactants, along with formation of a dihydropyran derivative or a 1-butene. Solvent polarity had only a small influence on these reactions.

N-Ethyl-3-vinylcarbazole (**1**) is a readily available olefin,[9] whose double bond displays intermediate electron richness between *p*-(dimethylamino)styrene and *p*-methoxystyrene. This study was undertaken to more sharply delineate the point of mechanism change from zwitterionic to biradical tetramethylene intermediates.

Results

Trimethyl Ethylenetricarboxylate (2). *N*-Ethyl-3-vinylcarbazole (**1**) with trimethyl ethylenetricarboxylate (**2**) gave a transient yellow color and yielded trimethyl 1-(*N*-ethyl-3-carbazyl)-2,2,3-cyclobutanetricarboxylate (**3**) and homopoly(*N*-ethyl-3-vinylcarbazole) (**4**). The results are summarized in Table I. At 50 °C the reaction was not complete after 16 h. An additional experiment run neat at 116 °C resulted in more than 98% yield of **3**. Cyclobutane formation is favored in polar solvents. Homopolymer **4**, generally a minor product, was slightly favored in 1,2-dichloroethane and acetonitrile but was completely suppressed in the basic solvent dimethyl sulfoxide.



Cz = *N*-ethyl-3-carbazyl-

Table I. Reaction of *N*-Ethyl-3-vinylcarbazole (1) with Trimethyl Ethylenetricarboxylate (2)

solvent[a]	rctn time, h	cyclobutane adduct 3, %	homopolymer 4,[b] %
benzene	16	20.5	1.4
dimethyl sulfoxide	16	36.7	0
acetonitrile	16	37.5	4.3
1,2-dichloroethane	16	38.9	4.7
1,2-dichloroethane[f]	22	49.9	6.8
1,2-dichloroethane[g]	21	24.3	0
phenyl isocyanate	92.5	0	18.0[c]
propionaldehyde	92.5	33.7	6.0[d]
benzaldehyde	26	59.7	8.2[e]

[a] Conditions: 2 mmol of **1** and 2 mmol of **2** in 4 mL of solvent at 50 °C under vacuum. [b] Anal. Calcd C, 86.8; H, 6.8; N, 6.3. Found: C, 85.6; H, 6.8; N, 6.0. [c] Polymer analysis: C, 82.6; H, 6.6; N, 6.1; O, 4.5. [d] Reaction temperature: 58 °C. Polymer analysis: C, 70.4; H, 6.1; N, 4.0; O, 19.5. This material was not examined further. [e] Reaction temperature: 68 °C. Polymer analysis: C, 82.6; H, 6.8; N, 5.4; O, 5.2. This material was not investigated further. [f] DPS inhibitor (20 mg) was added. [g] Triethylamine (1 mL) was added.

Table II. Reactions of *N*-Ethyl-3-vinylcarbazole with Dimethyl Cyanofumarate[a]

solvent	time, h	homopolymer 4, %	cyclobutane 7, %	ratio of isomers of 7
acetonitrile	16.5	8.1	91.8	2.9
1,2-dichloroethane[c]	45.5	60.1	39	1.8

[a] Conditions: reactions were run at room temperature under vacuum. [b] 1 mmol of **1** and 1 mmol of **6** in 4 mL of acetonitrile. [c] 1.4 mmol of **1** and 1.4 mmol of **6** in 4 mL of 1,2-dichloroethane.

The free-radical inhibitor bis(4-hydroxy-3-*tert*-butyl-5-methylphenyl) sulfide (DPS) did not affect the formation of **3** or **4**. Trimethylamine, an inhibitor of cationic polymerizations, stopped the formation of homopolymer **4** and diminished the yield of **3**. Heating **1** and **2** with AIBN in benzene at 72 °C for 45 h gave the 1:1 alternating copolymer **5** in 77% yield along with 15% of cyclobutane adduct **3**.

Several reagents which are potential traps for a zwitterion intermediate[10] were used as solvents. These included phenyl isocyanate, acetonitrile, propionaldehyde, and benzaldehyde. Acetonitrile did not affect the reaction. Phenyl isocyanate suppressed the formation of cyclobutane **3**. The aldehydes did not affect the reaction significantly, but the composition of the polymer is anomalous.

Cyclobutane adduct **3** was composed of cis and trans isomers in 1:1 ratio. The isomers, separated by chromatography, were obtained as oils which resisted crystallization. Infrared and NMR spectra, as well as elemental analyses, confirmed the overall structures but did not permit an assignment of cis or trans isomers. The homopolymer **4**, a white powder, was characterized by elemental analysis and by NMR spectra.

Dimethyl Cyanofumarate (6). The more reactive olefin dimethyl cyanofumarate (**6**) was allowed to react with **1** (Table II). In solution the reagents formed an orange-red solution which became colorless overnight. The reaction was complete and formed dimethyl 1-(*N*-ethyl-3-carbazyl)-2-cyano-2,3-cyclobutanedicarboxylate (**7**) and homopolymer **4**. Again, the stereochemistry of the electron-poor olefin was preserved in the cycloaddition, only the 1,3 cis and 1,3 trans isomers of **7** being obtained. Here the assignment to isomers **7a** and **7b** respectively can be achieved satisfactorily from the NMR and IR spectra.

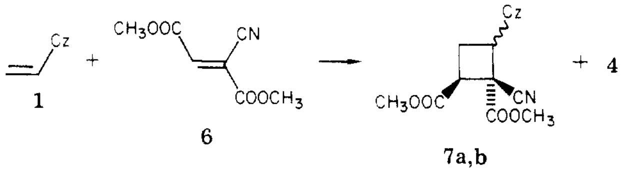
---

(7) Hall, H. K., Jr.; Abdelkader M. *J. Org. Chem.* **1981**, *46*, 2948.

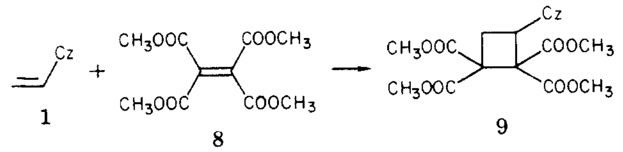
(8) Hall, H. K., Jr.; Dunn, L. C.; Padias, A. B. *J. Org. Chem.* **1980**, *45*, 835.

(9) Limburg, W. W.; Williams, D. J. *Macromolecules* **1973**, *6*, 787.

(10) Huisgen, R.; Schug, R. *J. Chem. Soc., Chem. Commun.* **1975**, 60.



Tetramethyl Ethylenetetracarboxylate (8). The more sterically hindered olefin tetramethyl ethylenetetracarboxylate (8) was less reactive. It did not react at 28 °C or even at 85 °C, but it reacted at 130 °C with 1 to give cyclobutane adduct 9 in 64.8% yield.



Photochemical and One-Electron Reactions of 1. Irradiating a 0.5 M solution of 1 in benzene or acetonitrile with UV light yielded only homopolymer 4 (20% after 140 h in benzene and 66% after 68 h in acetonitrile). Addition of sensitizer, 1,4-dicyanobenzene[11] in acetonitrile or 4,4′-dimethoxybenzophenone in benzene, did not influence the reaction. Photochemical irradiation of a mixture of 1 and 2 yielded mostly homopolymer 4 and some cyclobutane adduct 3.

Finally, by treating 1 with electron-acceptor ferric perchlorate[12] without light at 28 °C, only homopolymer 4 was obtained. In the presence of 2, this reaction also yielded only homopolymer 4.

Discussion

The results of our investigation can be interpreted very simply. The reactions of *N*-ethyl-3-vinylcarbazole (1) with electrophilic olefins 2, 6, and 8 proceed via tetramethylene intermediates T exhibiting predominantly zwitterionic character.

The only small molecule formed in these reactions was the cyclobutane adduct. Cyclobutanes in principle might form from either a highly zwitterionic tetramethylene (for example, propenyl ether and tetracyanoethylene[2]) or from a biradical tetramethylene intermediate (for example, butadiene and trifluoroethylene[13]), so no conclusion as to the nature of T can be reached on this basis.

The only polymer formed in the reactins of *N*-ethyl-3-vinylcarbazole (1) with electron-poor olefins was polymer 4, involving cationic homopolymerization[14] and implying initiation by a zwitterionic T. That 1 could undergo free-radical copolymerizations with these olefins was verified by deliberate AIBN initiation. Nevertheless no copolymers spontaneously formed in the thermal reactions.

The increased reactions rates for cyclobutane formation in polar solvents also support a zwitterion intepretation. Trapping experiments with various reagents did not succeed, but trapping is generally successful only for highly stabilized zwitterions.[2]

The ability to stabilize a positive charge, due to the decreasing basicity of the para substituent, decreases in the series *p*-(dimethylamino)styrene > *N*-ethyl-3-vinylcarbazole > *p*-methoxystyrene. The lower basicity of the nitrogen of 1 is ascribed to its involvement with the second aromatic ring. However the ability to resonance stabilize a radical remains approximately constant in this series. Therefore the change from a zwitterionic to a biradical mechanism occurs as the electron-donating character of the aromatic group decreases. The reactivities of the three electrophilic olefins, 6 > 2 > 8, is in accord with previous results and interpretations.[7]

To exclude a cation-radical cycloaddition mechanism (proposed for reactions of *N*-vinylcarbazole with electrophilic ethylenes[15]), we deliberately formed the cation radical of 1 by irradiation under UV light with or without sensitizer present. The product was homopolymer 4 formed by cationic polymerization. In the presence of 2, some cycloadduct 3 was formed. When we used ferric perchlorate as electron acceptor in the dark, only homopolymer 4 was formed, even in the presence of trimethyl ethylenetricarboxylate (2). Cation-radical formation is much more efficient when using ferric perchlorate. Exclusive cationic polymerization prevails, inasmuch as no cyclobutane 3 was detected. This proves that no tetramethylene intermediate was formed. It is interesting to note that in methanol solution Ledwith and co-workers obtained the cyclo dimer of 1 from the cation radical.[16] No cyclo dimer was observed in our reaction conditions.

Experimental Section

Instrumentation. NMR spectra were recorded with Varian EM 360L nuclear magnetic resonance spectrometer. The infrared spetral data were obtained from Perkin-Elmer infrared spectrophotometers (Model 710A and 398) standardized with polystyrene. Melting points were obtained from a Thomas-Hoover capillary melting apparatus. Photochemical reactions were run with ultraviolet lamps (2535 Å) in Rayonet Srinavasan-Griffin photochemical reactor at 42–45 °C. Chemical analyses were performed by the University of Arizona Analytical Center in Tucson, AZ.

Reactants. ***N*-Ethyl-3-vinylcarbazole (1)** was synthesized following the procedure of Limburg and Williams.[9]

Trimethyl ethylenetricarboxylate (2) was synthesized according to Daly's procedure,[17] except that in the preparation of trimethyl 1,1,2-ethanetricarboxylate, before the slurry was poured in ice and water, most of the methanol was removed on a rotary evaporator. Triester 2 was obtained pure after distillation and recrystallization from ether in 53.8% yield.

Dimethyl cyanofumarate (6) was synthesized according to Daly's procedure,[17] except that the reaction temperature was kept below 0 °C and a cold solution of hydrochloric acid was added to neutralize the excess triethylamine. Dimethyl cyanofumarate (6) was obtained in a yield of 33.7% from dimethyl 1-bromo-1-cyanosuccinate.

Tetramethyl ethylenetetracarboxylate (8) was also prepared according to Daly's procedure.[17]

Typical Experimental Procedure. In general the reactions were run in a 10-mL Pyrex tube equipped with a vacuum-line Teflon valve (Chemvac Associates, POR-10). The reaction vessel containing the reaction mixture, composed of equimolar amounts of each reactant, was placed in a dry ice–acetone bath, degassed under full vacuum (less than 0.2 mm of Hg), and then sealed. It was then placed in an oil bath at the desired temperature, ±1 °C, with magnetic stirring (in the case of dimethyl cyanofumarate the reaction vessel was left at room temperature). Finally the reaction was quenched with an excess of methanol; the polymer precipitated and was isolated by filtration, washed, dried, and finally weighed. The methanol was evaporated from the filtrate; the residue was weighed and examined by NMR spectroscopy to determine the yield of cyclobutane adduct.

Trimethyl 1-(*N*-Ethyl-3-carbazyl)-2,2,3-cyclobutanetricarboxylate (3). Reaction of *N*-ethyl-3-vinylcarbazole (1; 0.443

---

(11) (a) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 53. (b) Asanuma, T.; Yamamoto, M.; Nishijima, Y. *Ibid.* **1975**, 56.

(12) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

(13) Bartlett, P. D. *Q. Rev. Chem. Soc.* **1970**, *24*, 473.

(14) DeMola, A. H.; Ledwith, A.; Yanus, J. F.; Limburg, W. W.; Pearson, J. M. *J. Polym. Sci. Chem. Ed.* **1978**, *16*, 761.

(15) Glogowski, M.; Hall, H. K., Jr. *J. Macromol. Sci. Chem.* **1979**, *A13*, 369.

(16) Bell, A.; Crellin, R. A.; Fujii, H.; Ledwith, A. *J. Chem. Soc., Chem. Commun.* **1969**, 251.

(17) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22.

g, 2 mmol) and trimethyl ethylenetricarboxylate (**2**; 0.404 g, 2 mmol) in 1,2-dichloroethane (4 mL) yielded homopolymer **4** (4.7%) and a mixture of the 1,3 cis and trans isomers of the cyclobutane adduct **3** (38.9%), which precipitated out of hexane at −78 °C as an oil. Anal. Calcd for $C_{24}H_{25}O_6N$: C, 6.81; H, 6.0; N, 3.3. Found: C, 67.8; H, 6.1; N, 2.9.

The two isomers were isolated by column chromatography, using silica gel and hexane as eluent: IR ($CDCl_3$) 2940 (m, CH), 1730 (s, C=O), 1600 cm^{-1} (m, C=C); for isomer **3a**, ^{1}H NMR ($CDCl_3$) δ 1.4 (t, 3 H, CH_3), 2.87 (m, J = 10 Hz, 2 H, CH_2), 3.1, 3.77 (3 s, 9 H, OCH_3), 4.32 (m, 3 H, NCH_2 and $CHCO_2CH_3$), 4.8 (t, J = 10 Hz, 1 H, HCAr), 7.2–8.2 (m, 7 H, aromatic); for isomer **3b**, ^{1}H NMR ($CDCl_3$) δ 1.5 (t, 3 H, CH_3), 2.65–3 (m, J = 14 Hz, 2 H, CH_2), 3.23, 3.83, 3.97 (3 s, 9 H, OCH_3), 3.33–3.8 (m, J = 14 Hz, 2 H, CHAr and $CHCO_2CH_3$), 4.3 (q, 2 H, NCH_2) 7.2–8.2 (m, 7 H aromatic).

Poly(*N*-ethyl-3-vinylcarbazole) (4). In a quartz tube, a mixture of 0.433 g (2 mmol) of *N*-ethyl-3-vinylcarbazole (**1**) and 0.01 g of the 1,4-dicyanobenzene was dissolved in 4 mL of acetonitrile. The reaction vessel was irradiated by UV light in a reactor for 69 h. Formation of a precipitate occurred. The mixture was dripped into 90 mL of anhydrous ether. The mixture was filtered to yield 0.248 g (56.0%) of homopolymer **4**[11,16] (the filtrate contained only starting material). The homopolymer was insoluble in acetone, acetonitrile, ether, and methanol: IR (KBr) 2900 (m, CH), 1600 cm^{-1} (m, C=C); ^{1}H NMR ($CDCl_3$) δ 0.3–2.6 (m, 6 H, CH_3, CH_2, CH), 3.3–4.4 (m, 2 H, NCH_2), 5.5–8.3 (m, 7 H, aromatic). Anal. Calcd for $C_{16}H_{15}N$: C, 86.8; H, 6.8; N, 6.3. Found: C, 85.6; H, 6.8; N, 6.0.

Poly(*N*-ethyl-3-vinylcarbazole-*alt*-trimethyl ethylenetricarboxylate) (5). A mixture composed of 0.404 g (2 mmol) of triester, 0.443 g (2 mmol) of *N*-ethyl-3-vinylcarbazole, and 0.01 g of azobis(isobutyronitrile) (AIBN) was dissolved in 4 mL of benzene, cooled in a dry ice–acetone bath, and degassed under full vacuum. The reaction vessel was placed in an oil bath at 72 °C for 45 h. The reaction was quenched with 100 mL of methanol; the precipitate was separated by filtration, washed, and dried to yield 0.652 g (77.0%) of copolymer **5**. The filtrate after workup contained 0.128 g (15.1%) of cyclobutane adduct **3** and starting material: IR (KBr) 2940 (m, CH), 1720 (s, C=O), 1600 cm^{-1} (m, C=C); ^{1}H NMR ($CDCl_3$) δ 1–1.6 (m, 3 H, CH_3), 2–4.7 (m, 15 H), 6.5–8.5 (m, 7 H, aromatic). Anal. Calcd for $C_{24}H_{25}O_6N$: C, 68.1; H, 6.0; N, 3.3. Found C, 68.4; H, 5.97; N, 3.52.

Dimethyl 1-(*N*-Ethyl-3-carbazyl)-2-cyano-2,3-cyclobutanedicarboxylate (7). A mixture of 0.222 g (1 mmol) of **1** and 0.169 g (1 mmol) of dimethyl cyanofumarate (**8**) was reacted neat for 16.5 h at room temperature. After workup, a mixture of only two isomers (1,3 cis and 1,3 trans) of the cyclobutane adduct **7** was obtained in 91.8% yield: IR (KBr) 2960 and 2945 (m, CH), 2240 (w, CN), 1740 (s, C=O), 1620, 1590 cm^{-1} (s, C=C). Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.8; H, 5.7; N, 7.2. Found: C, 70.9; H, 5.6; N, 7.1.

One isomer crystallized in hexane at room temperature, and the solution contained both isomers. Isomer **7a** was recrystallized from hexane: mp 144.5–145.5 °C; ^{1}H NMR ($CDCl_3$) 1.4 (t, 3 H, CH_3), 2.75–3.1 (m, 2 H, CH_2), 3.2, 3.8 (2 s, 6 H, OCH_3), 4.2–4.5 (7, 4 H, CH_2N, $CHCOOCH_3$, and CHAr), 7.2–8.25 (m, 7 H, aromatic) (1,3-cis isomer).

At −78 °C in hexane, a mixture of both isomers precipitated, while the solution contained pure isomer **7b**, which was an oil: ^{1}H NMR ($CDCl_3$) δ 1.4 (t, 3 H, CH_3), 2.45–3.35 (2 t, J = 10 Hz, 2 H, CH_2), 3.85, 3.9 (2 s, 6 H, OCH_3), 4.3 (m, 4 H, CH_2N, CHAr, $CHCO_2CH_3$), 7.1–8.25 (m, 7 H, aromatic) (1,3-cis isomer).

Tetramethyl 1-(*N*-Ethyl-3-carbazyl)-2,2,3,3-cyclobutanetetracarboxylate (9). A mixture of **1** (0.222 g, 1 mmol) tetramethyl ethylenetetracarboxylate (**8**; 0.260 g, 1 mmol) in 1,2-dichloroethane (2 mL) was reacted under vacuum at 130 °C for 21.5 h. After removal of the solvent, 30 mL of methanol was added and at −78 °C unreacted tetraester crystallized out. After filtration and evaporation of methanol, the residue was dissolved in 40 mL of hexane and placed at −78 °C to yield the cyclobutane adduct **9** as an oil. Under vacuum crystals are obtained (0.312 g, 64.8%): mp 68–70 °C; IR ($CDCl_3$) 2925 (w, CH), 1720 (s, C=O), 1600 cm^{-1} (w, C=C); ^{1}H NMR ($CDCl_3$) δ 1.42 (t, 3 H, CH_3), 2.68 (m, 2 H, CH_2), 3.15, 3.85, 3.15, 3.85, 3.9 (3 s, 12 H, OCH_3), 4.35 (q, 2 H, NCH_2), 4.82 (q, 1 H, J = 12 Hz, CH), 7.22–8.2 (m, 7 H, aromatic). Anal. Calcd for $C_{26}H_{27}O_8N$: C, 64.85; H, 5.65; N, 2.91. Found: C, 64.61; H, 5.82; N 2.86.

Acknowledgment. We are deeply indebted to Sonatrach Corporation (Algeria) and to the Materials Research Division, National Science Foundation, Grant DMR 78-09290 for support, and to Dr. A. B. Padias, Dr. P. Nogues, Dr. H. A. A. Rasoul, and Mr. Robert Sentman for helpful suggestions.

Registry No. 1, 1486-07-3; **2**, 51175-48-5; *cis*-**3**, 79917-22-9; *trans*-**3**, 79917-23-0; **4**, 25569-45-3; **5**, 79917-26-3; **6**, 54797-29-4; **7** (isomer 1), 79917-24-1; **7** (isomer 2), 79980-56-6; **8**, 1733-15-9; **9**, 79917-25-2.

Studies on Paraionic Compounds. Anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxides. Formation and Stability of a Novel Series of $4n\pi$ Heterocyclic Betaines

Gury Zvilichovsky* and Mordechai David

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received May 18, 1981

Different substituted anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium hydroxides were prepared by the reaction of 1,3-dicarbonyl compounds with derivatives of 4-phenyl-3,5-dihydroxypyrazole. These diazapentalene derivatives belong to a new series of $4n\pi$ cyclic betaines which are named "paraionic" heterocycles. The effects of substituents on the stability of both the anionic and the cationic rings were kinetically studied. Selective cleavage of either the anionic or the cationic ring was achieved by varying the conditions of the reaction with morpholine. Electron releasing groups on the cationic ring and electron attracting groups on the anionic ring enhance the stability of the bicyclic system. They also cause a hypsochromic shift of the visible light absorption.

The term paraionic is derived from the observation that both the anion and the cation coexist parallel to one another with the absence of conjugation between them. There is, however, some interaction which is responsible for the extra stability as well as the color and deserves further study. The first group of this series was reported[1]

0022-3263/82/1947-0295$01.25/0