greater than ±0.2 e Å^{-3}. The numerical data associated with this determination are supplied as supplementary material.

Hydrolysis–Oxidation of (−)-19. A 102-mg (1.19 mmol) sample of (−)-19, $[\alpha]^{20}_D$ −38.5°, dissolved in 20 mL of isopropyl alcohol was heated to reflux with sodium hydroxide (425 mg) under a nitrogen atmosphere for 24 h. The cooled reaction mixture was made acidic by addition of 3 N hydrochloric acid and then made basic with 3 N ammonium hydroxide solution. The product was extracted into ether (3 × 50 mL), and the combined ether layers were washed with water and brine prior to drying. The filtered solution was treated with activated manganese dioxide (500 mg) under nitrogen and the mixture was stirred at room temperature for 40 min. The excess MnO_2 was filtered off and the filtrate was concentrated in the absence of heat to leave a brown oil. This material was purified by low temperature (−35 to −40 °C) chromatography on Florisil (elution with petroleum ether) to give 20.5 mg (38%) of (−)-5 as a colorless oil: $[\alpha]^{20}_D$ −24.3° (c 10, ether).

Analogous treatment of (+)-18 (367 mg, 0.68 mmol), $[\alpha]^{20}_D$ + 23.2° (c 5.5, C_2H_5OH), afforded 99 mg of (+)-5, $[\alpha]^{20}_D$ +11.5° (c 49.5, ether).

Procedure for the Determination of the Rates of Racemization. Levorotatory 5 (79 mg) was dissolved in 3 mL of purified diglyme (freshly distilled from Na-K alloy) and the diglyme solution was divided into 23 glass tubes (sample volume 0.12–0.13 mL). Each tube was sealed under high vacuum after three freeze–thaw cycles. Analogously, a 99-mg sample of (+)-5, $[\alpha]^{20}_D$ +11.5° (c 49.5, ether), dissolved in 3 mL of purified diglyme was distributed among 26 tubes.

After the addition of a group of tubes to a constant temperature bath, a short equilibration period (ca. 5 min) was allowed to pass and a tube was removed as an accurate timer was started and quenched at −78 °C. Tubes were then removed and quenched at appropriate times. Each tube was opened, the solution was placed in a 0.1-dm polarimeter cell, and the rotation was recorded at 436 nm. Each rotation was plotted, using the previously described rate law, and the method of least squares was applied to evaluate the rate constants.

Procedure for the Determination of the Rates of Bond Shifting in 5 and 6. A small amount of 5 or 6 (ca. 30 mg) and dioxane (2–3 μL) were dissolved in diglyme-d_{14} in an NMR tube. Solutions were degassed by repeated freeze–thaw cycles (liquid nitrogen, three cycles) and sealed under high vacuum. The samples were heated in a constant temperature bath and a short equilibration period (about 2 min) was allowed for each measurement. As each tube was removed, it was cooled to −78 °C and its ^{1}H NMR spectrum (90 MHz) was recorded. The total amount of $C_{22}H_{20}$ isomers relative to dioxane did not change at 128.2 °C over a period of 32.5 h. The expanded scale methyl region was integrated, using a planimeter relative to the dioxane singlet. The data were plotted, using the previously described rate law, and the method of least squares was applied to evaluate the rate constants.

Acknowledgment. This investigation was supported by the National Science Foundation by means of Grant CHE-7900333. We are particularly indebted to Dr. Charles Cottrell for his help with the recording of spectra involved in our DNMR studies and for assistance with the allied computer program.

Registry No. 5, 31462-32-5; (−)-**5**, 79980-69-1; (+)-**5**, 79980-70-4; **6**, 79980-71-5; **10**, 30450-25-0; **11**, 64363-61-7; **12**, 79918-56-2; **13**, 79918-57-3; **14**, 79918-58-4; **15**, 31462-33-6; **16**, 31462-35-8; (−)-**17**, 73462-83-6; (+)-**18**, 79918-59-5; (−)-**19**, 79980-72-6.

Supplementary Material Available: Tables of atomic coordinates with standard deviations, bond lengths, and bond angles together with their associated standard deviations (6 pages). Ordering information is given on any current masthead page.

Electronic Control of Stereoselectivity. 11. Long-Range Modulation of Stereoselection in Diels–Alder Cycloadditions of *N*-Methyltriazolinedione to Aryl-Substituted 9-Butadienylidenebenzonorbornenes[1]

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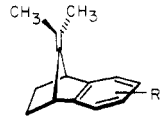
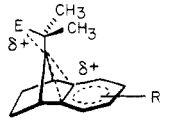
Received July 28, 1981

Three 9-butadienylidenebenzonorbornenes (**4a–c**) have been synthesized and their ability to enter into Diels–Alder reaction examined. Although these substances are unreactive to a host of dienophiles, tetracyanoethylene enters into [2 + 2] addition with **4b** and **4c**. However, these reactions do not allow for examination of the stereoselectivity question. When recourse was made to the more reactive *N*-methyltriazolinedione reagent, [4 + 2] adducts **9** and **10** were produced in the following syn/anti ratios: **4a**, 49:51; **4b**, 24:76; **4c**, 24:76. The chemical shifts of the *N*-methyl groups in the urazole segments of these adducts proved quite divergent and conducive to reliable structural assignment. The results are interpreted in terms of zwitterion intervention, with charge delocalization into the aromatic ring where this is feasible (the tetrafluoro example excluded). Because of this long-range homoaromatic stabilization, closure of the second C–N bond from the anti direction is kinetically favored.

The syn/anti stereoselection which operates when aryl-substituted 9-isopropylidenebenzonorbornenes (**1**) and



1



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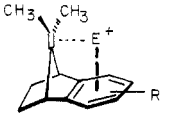

3

related molecules engage in reaction with electrophiles has proven to be a convenient tool with which to assess relative electrophilicity.[3-7] For those weaker reagents which depend upon π-bond-induced polarization for their reactivity and which consequently engage in bridged ion formation

(1) Part 10: Paquette, L. A.; Klinger, F.; Hertel, L. W. *J. Org. Chem.* **1981**, *46*, 4403.
(2) NATO Postdoctoral Fellow.

(3) (a) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. *J. Am. Chem. Soc.* **1978**, *100*, 6510. (b) Hertel, L. W.; Paquette, L. A. *Ibid.* **1979**, *101*, 7620. (c) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. C.; Beno, M. A.; Christoph, G. G., *Ibid.*, in press.
(4) (a) Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 6509. (b) Okada, K.; Mukai, T. *Tetrahedron Lett.* **1979**, 3429.
(5) (a) Hoffmann, R. W.; Becherer, J. *Tetrahedron* **1978**, *34*, 1187. (b) Becherer, J.; Hoffmann, R. W. *Ibid.* **1978**, *34*, 1193. (c) Hoffmann, R. W.; Hauel, N. *Tetrahedron Lett.* **1979**, 4959.
(6) Malpass, J. R.; Walker, M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 585.
(7) Paquette, L. A.; Bellamy, F.; Wells, G. J.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1981**, *103*, 7122.

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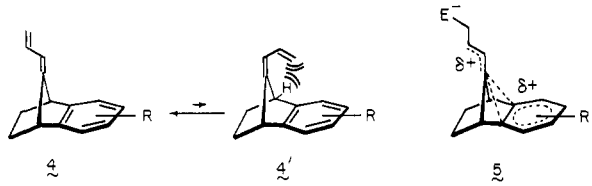
(see 2), anti addition is favored because of the development of energetically favorable long-range delocalization into the benzene ring. For this class of reactions, an increase in the electron-withdrawing capability of R leads to a reduction in the level of homoaromatic interaction and to isolation of progressively larger amounts of syn products. When powerful electrophiles are involved, charge delocalization to the aromatic ring is unimportant. In these cases, the kinetically dominant influence is thought to be transient π-complex formation (see 3), a phenomenon which leads to exclusive syn attack,[3] irrespective of the electronic nature of R (guided electrophile capture).

The special structural features of benzonorbornenyl systems have provoked additional fundamental studies of stereocontrol by electronic means. In this paper, we report the synthesis of the first 9-butadienylidenebenzonorbornenes (4) and describe their behavior toward reactive dienophiles. 1,1-Disubstituted butadienes are known to be reluctant to enter into [4 + 2] cycloaddition because their cisoid conformations are difficult to attain.[8] The title compounds are no exception, molecular models suggesting that 4′ experiences serious nonbonded steric interactions which are absent in 4. Experimental results, derived



4 4′ 5

chiefly from studies involving tetracyanoethylene (TCNE), suggest that the customarily disadvantaged two-step zwitterionic mechanism is able to compete energetically in such circumstances. To the extent that the anti conformation dominates, proper pπ orbital alignment for concerted [$\pi 4_s + \pi 2_s$] bond formation cannot materialize. The recent investigation by Nishida and co-workers[8d] has provided convincing evidence that TCNE enters into kinetically controlled formation of a zwitterionic intermediate which collapses to a thermodynamically unstable four-membered-ring adduct. In certain instances, this first-formed product experiences subsequent ring opening and intramolecular recyclization to more stable cyclohexene derivatives. Zwitterionic behavior has also been encountered with dienes of fixed transoid geometry.[8d,9]

The aims of the present study were to determine if dienes of type 4 could be made to enter into Diels–Alder cycloaddition and to establish the stereochemical course of these reactions. If concerted bond formation to dienophiles is indeed conformationally impeded as discussed above, an unsymmetrical transition state is mandated. Should diradicaloid intermediates intervene on the energy hypersurface as suggested by certain MO calculations,[10,11] the flanking aromatic ring will have little opportunity to control stereoselectivity. On the other hand, if zwitterionic intermediates are generated, the aryl moiety should function to favor anti stereoselection through homoaromatic delocalization of the positive charge (cf 5).

(8) (a) Stewart, C. A., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 117; *J. Org. Chem.* **1963**, *28*, 3320. (b) Fisch, J. J.; Husk, G. R. *Ibid.* **1966**, *31*, 589. (c) Bartlett, P. D. *Q. Rev., Chem. Soc.* **1973**, *24*, 473. (d) Kataoka, F.; Shimizu, N.; Nishida, S. *Ibid.* **1980**, *102*, 711.

(9) Huisgen, R.; Ortega, J. P. *Tetrahedron Lett.* **1978**, 3975.

(10) (a) Jug, K.; Krüger, H.-W. *Theor. Chim. Acta* **1979**, *52*, 19. (b) Dewar, M. J. S.; Griffin, A. C.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 6225. (c) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *Ibid.* **1978**, *100*, 5650.

(11) For a recent critical survey of the mechanistic aspects of the Diels–Adler reaction, consult Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

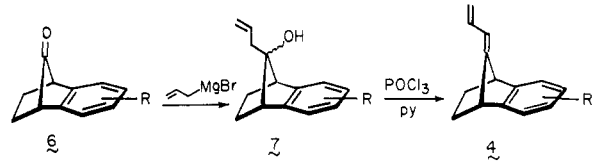
Table I. Summary of Urazole Cycloadduct Results

diene	urazole adduct distribution (9/10),[a] % ¹H NMR integration of reaction mixture	urazole adduct distribution (9/10),[a] % isolated yields	Δδ of N-methyl peaks, ppm
4a	49:51	48:46	0.20
4b	24:76	25:54	0.26
4c	24:76	25:68	0.20

[a] The values cited represent the average percentages derived from duplicate experiments.

Results

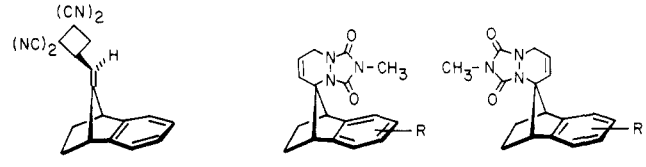
The preparation of 4a–c was achieved by condensation of the respective benzonorbornenones (6) with the Grignard reagent obtained from allyl bromide and Rieke's magnesium.[12] From among the several reagent combinations examined for the purpose of dehydrating the resulting tertiary alcohols 7, phosphorus oxychloride in pyridine was found to produce the desired 1,3-dienes most cleanly and efficiently.



6 7 4

a, R = $(F)_4$; b, R = H; c, R = 1,4-$(OCH_3)_2$

Initial experiments involving 4 and maleic anhydride, N-phenylmaleimide, dimethyl acetylenedicarboxylate, hexafluoro-2-butyne, or singlet oxygen provided little, if any, indication that Diels–Alder chemistry was occurring, even under forcing conditions in certain cases. On a more positive note, heating of 4b with an excess of TCNE in benzene solution for 5–6 h gave a darkly colored solution from which 8 could be isolated in 49% yield as the principal product. The structural assignment, which is based upon detailed analysis of the ^1H and ^{13}C NMR spectra, conforms to mechanistic expectation.[8] A qualitative microscale experiment with 4c revealed this substance to behave analogously. However, tetrafluoro derivative 4a proved totally unreactive toward TCNE, even with prolonged heating.



8 9 10

a, R = $(F)_4$; b, R = H; c, R = 1,4-$(OCH_3)_2$

Clearly, the proclivity of TCNE for [2 + 2] cycloaddition did not provide us the possibility of examining the question of stereoselection. A still more reactive diene, one that would ultimately deliver [4 + 2] product, was required. N-Methyltriazolinedione (NMTD) fulfilled this role nicely. In dichloromethane solution at room temperature, NMTD reacted efficiently with 4a–c to give mixtures of syn (9) and anti adducts (10). Since the singlet N-methyl chemical shifts of the adduct pairs are widely separated, it proved possible to perform direct ^1H NMR integration of unpurified product mixtures (Table I). The isomers were subsequently separated chromatographically and individually characterized (see Experimental Section). The

(12) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

stereochemistry of these urazoles was assigned on the basis of the following: (a) the higher field position of the methyl signals in **9** (δ 2.88–2.77) relative to **10** (δ 3.08–3.03), a circumstance attributable to shielding by the underlying aromatic ring;[2,13] (b) upfield shifting of the olefinic protons in **10** as a consequence of similar through-space effects; and (c) deshielding of the exo protons on the ethano bridge in **10** as a result of the anisotropy of the proximate urazole moiety.

The data of Table I indicate that the benzo and 1,4-dimethoxybenzo systems give rise to a product distribution which favors the anti urazole by a factor of 3:1. When the aryl ring is made electron deficient by fourfold fluorine substitution, the **9**/**10** ratio is seen to fall to unity.

It is important at this juncture to recognize that urazoles **9** and **10** are not subject to equilibration either under the conditions of the cycloaddition reaction or at somewhat more elevated temperatures. Thus, recrystallization of the individual products from a variety of solvents with heating did in no instance lead to the formation of their epimers as gauged by ^{1}H NMR spectroscopy. Accordingly, the product distributions cited in Table I reflect kinetic control during ring closure. We have no experimental facts dealing with the question of diazetidine intervention prior to formation of the six-membered heterocyclic products. However, this issue is not linked to the stereoselection phenomenon.

The predominant anti addition seen with **4b** and **4c**, but not **4a**, is highly reminiscent of the stereoselectivities observed in the capture of weak electrophiles by 9-isopropylidenebenzonorbornenes.[3] The observed *variation* in product ratios cannot be rationalized in terms of steric effects which remain essentially constant throughout the series, nor do π-orbital distortion or frontier orbital control appear to play any consequential role within such dienes. Rather, the polarization component,[14] an expression of latent homoaromatic delocalization which reaches a maximum in the benzo and dimethoxybenzo derivatives, is deemed to be the overwhelming energetic factor. Further, there is, of course, a causal connection between such long-range electronic stabilization and stereoselection. Attention is called to the apparently limiting 24:76 ratio which we believe reflects in part the benzeno/ethano size differential (compare **1**).[3,4]

The [4 + 2] cycloaddition of **4** with NMTD is therefore considered to be a prototype Diels–Alder reaction which proceeds via a two-step *dipolar* mechanism. The intervention of zwitterionic intermediates, while not proven directly, is herein inferred from the unreactive nature of several usually reactive (in concerted processes) dienophiles, the observed stereoelectronic control (and suitable parallelisms), as well as the known predilection of triazolinediones to enter into ionic reactions having the negative charge on the heterocyclic moiety.[15] Although the present examples may represent one extreme in the spectrum of nonconcerted Diels–Alder reactions, it now appears unquestioned that dipolar transition-state characteristics are entirely feasible.[11]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrometer. The ^{1}H NMR spectra were determined with a Varian EM-390 spectrometer and apparent splittings are given in all cases. The ^{13}C NMR spectra were obtained with a Bruker WP-80 instrument. Mass spectra were measured with an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalytical determinations were made at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

9-Butadienylidene-5,6,7,8-tetrafluorobenzonorbornene (4a). An allylmagnesium bromide stock solution was prepared as follows. A 100-mL three-necked flask equipped with a magnetic stirrer, condenser, and nitrogen inlet tube was blanketed with nitrogen. A mixture of freshly cut potassium metal (1.49 g, 38.2 mmol), anhydrous magnesium chloride (2.04 g, 21.4 mmol), and dry tetrahydrofuran (50 mL) was placed therein, heated at the reflux temperature for 2 h, and stirred at room temperature for 30 min. This mixture was cooled to −25 °C and treated very slowly during 30 min with allyl bromide (1.85 g, 15.3 mmol). Upon completion of the addition, stirring was maintained for 30 min at −25 °C and needed amounts of the reagent were withdrawn by syringe technique.

A cold (−25 °C) solution of 5,6,7,8-tetrafluorobenzonorbornen-9-one[3c,17] (464 mg, 2.02 mmol) in anhydrous tetrahydrofuran (12 mL) was treated dropwise during 30 min with 9 mL of the above Grignard solution. The reaction mixture was stirred at −20 °C for 1 h and hydrolyzed by addition of saturated ammonium chloride solution (55 mL). The product was extracted into ether (5 × 20 mL), and the combined organic layers were washed with brine, dried, and evaporated. There was obtained 521 mg (95%) of **7a** as a colorless solid: mp 67–68 °C (from cyclohexane); IR (KBr) 3510, 3440, 2980, 2945, 1500, 1480 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.03–5.5 (m, 1 H), 5.27–4.90 (m, 2 H), 3.27 (br s, 2 H), 2935 (m, 2 H), 2.10 (t, J = 3 Hz, 3 H), 1.22 (dd, J = 11, 3 Hz, 2 H); mass spectrum, m/e calcd (M^+) 272.0824, obsd 272.0833.

A solution of **7a** (167 mg, 0.614 mmol) was dissolved in dry pyridine (2 mL) and treated with phosphorus oxychloride (104 mg, 0.678 mmol) at room temperature. This mixture was heated to reflux for 15 min, cooled to 20 °C, and poured onto ice containing a little hydrochloric acid. The product was extracted into ether (4 × 15 mL), and the combined organic layers were washed with 1 N hydrochloric acid (3 × 15 mL), saturated sodium bicarbonate solution, and brine prior to drying. After solvent removal and silica gel chromatography (hexane elution), there was isolated 138 mg (88%) of **4a** as a colorless solid: mp 64.5–65.5 °C (from 95% ethanol); ^{1}H NMR ($CDCl_3$) δ 6.40 (dt, J = 16.5, 10.5 Hz, 1 H), 5.63 (d, J = 10.5 Hz, 1 H), 5.10 (dd, J = 16.5, 1.5 Hz, 1 H), 5.06 (dd, J = 10.5, 1.5 Hz, 1 H), 4.27 (br s, 1 H), 3.83 (br s, 1 H), 2.00 (m, 2 H), 1.33 (m, 2 H); mass spectrum, m/e calcd (M^+) 254.0718, obsd 254.0726.

Anal. Calcd for $C_{14}H_{10}F_4$: C, 66.14; H, 3.96. Found: C, 66.08; H, 4.05.

9-Butadienylidenebenzonorbornene (4b). Treatment of 9-benzonorbornenone[3c,18] (329 mg, 2.08 mmol) with 9 mL (2.3 mmol) of the allyl Grignard reagent as above, followed by medium-pressure liquid chromatography on silica gel (elution with petroleum ether–ethyl acetate, 3:1), afforded 378 mg (91%) of **7b** as a colorless oil: IR (neat) 3560, 3450, 2960, 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.10 (m, 4 H), 6.03–5.43 (m, 1 H), 5.2–4.8 (m, 2 H), 2.95 (m, 2 H), 2.27 (m, 2 H), 2.03 (m, 3 H), 1.17 (m, 2 H); mass spectrum, m/e calcd (M^+) 200.1201, obsd 200.1196.

Dehydration of **7b** (61 mg, 0.30 mmol) with phosphorus oxychloride (167 mg, 1.09 mmol) in pyridine (1 mL) in the predescribed manner gave after preparative TLC isolation (silica gel, elution with 3% dichloromethane in hexane) 24 mg (43%) of **4b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.10 (m, 4 H), 6.43 (dt, J = 16.5, 10.5 Hz, 1 H), 5.57 (d, J = 10.5 Hz, 1 H), 5.03 (dd, J = 16.5, 2 Hz, 1 H), 4.93 (dd, J = 10.5, 2 Hz, 1 H), 3.93 (br s, 1 H), 3.50 (br s, 1 H), 1.93 (m, 2 H), 1.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) 158.0 (s), 146.8 (s), 146.4 (s), 133.6 (d), 125.8 (d), 120.2 (d), 120.1 (d), 114.9 (t), 111.2 (d), 47.5 (d), 43.1 (d), 26.8 (t), 26.7 ppm (t);

(13) Feiner, N. F.; Abrams, G. D.; Yates, P. *Can. J. Chem.* **1976**, *54*, 3955.
(14) Fijimoto, H.; Inagaki, S. *J. Am. Chem. Soc.* **1977**, *99*, 7424.
(15) (a) Horn, K. A.; Browne, A. R.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 5381. (b) Browne, A. R.; Paquette, L. A. *Ibid.* **1978**, *43*, 4522. (c) Paquette, L. A.; James, D. R.; Birnberg, G. H. *J. Am. Chem. Soc.* **1974**, *96*, 7454.
(16) (a) Huisgen, R.; Konz, W. E.; Gream, G. E. *J. Am. Chem. Soc.* **1970**, *92*, 4105. (b) Evnin, A. B.; Miller, R. D.; Evanega, G. R. *Tetrahedron Lett.* **1968**, 5863.
(17) Hankinson, B.; Heaney, H.; Price, A. P.; Sharma, R. P. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 2569.
(18) Muneyuki, R.; tanida, H. *J. Org. Chem.* **1966**, *31*, 1988.

mass spectrum, m/e calcd (M^+) 182.1095, obsd 182.1091.

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.57; H, 7.73.

9-Butadienylidene-5,8-dimethoxybenzonorbornene (4c). Treatment of 5,8-dimethoxybenzonorbornen-9-one[3c] (3.12 g, 14.3 mmol) with 54 mL (18 mmol) of the allyl Grignard reagent as above gave, after workup and recrystallization from cyclohexane, 3.20 g (86%) of **7c** as a white solid: mp 92.5–93.5 °C; IR (KBr) 3520, 3080, 2945, 2835, 1645, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.60 (s, 2 H), 6.1–5.53 (m, 1 H), 5.2–4.87 (m, 2 H), 3.77 (s, 6 H), 3.20 (m, 2 H), 2.4–1.93 (m, 4 H), 1.17 (dd, J = 11, 3 Hz, 2 H); mass spectrum, m/e calcd (M^+) 260.1412, obsd 260.1420.

Dehydration of **7c** (151 mg, 0.58 mmol) with phosphorus oxychloride (197 mg, 0.58 mmol) in pyridine as before and chromatography of the product on silica gel (elution with petroleum ether–ethyl acetate, 4:1) afforded 61 mg (43%) of **4c** as a white solid: mp 88–89 °C (from isopropyl alcohol); IR (CH_2Cl_2) 2960, 2900, 2825, 1495, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.53 (s, 2 H), 6.66–6.0 (m, 1 H), 5.50 (d, J = 10.5 Hz, 1 H), 4.98 (dd, J = 16.5, 2 Hz, 1 H), 4.90 (dd, J = 10.5, 2 Hz, 1 H), 4.15 (br s, 1 H), 3.77 (s, 7 H), 1.90 (m, 2 H), 1.30 (m, 2 H); mass spectrum, m/e calcd (M^+) 242.1307, obsd 242.1313.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.74; H, 7.11.

Cycloaddition of 4b and Tetracyanoethylene. A solution of **4b** (90 mg, 0.40 mmol) and freshly sublimed TCNE (77 mg, 0.60 mmol) in benzene (1.5 mL) was heated at the reflux temperature for 6 h. The solvent was evaporated and the residue was purified by silica gel chromatography (elution with petroleum ether–ethyl acetate, 4:1) to give 75 mg (49%) of **8** as a colorless crystalline solid: mp 173–174 °C dec (from chloroform–ether); IR ($CHCl_3$) 3020, 2980, 2945, 2240, 1700, 1565 cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 7.10 (m, 4 H), 5.20 (d, J = 9 Hz, 1 H), 4.47 (m, 1 H), 4.07 (br s, 1 H), 3.67 (br s, 1 H), 3.6–3.0 (m, 2 H), 2.03 (m, 2 H), 1.33 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 165.9 (s), 144.8 (s), 144.6 (s), 126.8 (d), 126.7 (d), 120.6 (d), 110.0 (s), 102.0 (d), 47.6 (d), 44.0 (d), 43.6 (s), 43.0 (d), 38.5 (t), 33.1 (s), 26.9 (m), 26.3 (m) (the CN singlets were not recorded); mass spectrum, m/e calcd (M^+) 310.1218, obsd 310.1225.

Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55. Found: C, 77.47; H, 4.52.

Cycloaddition of 4a with *N*-Methyltriazolinedione. A solution of NMTD (24.5 mg, 0.216 mmol) in dichloromethane (2 mL) was added dropwise during 1 H to a solution of **4a** (50 mg, 0.197 mmol) in the same solvent (2 mL). After being stirred for 2 h, the reaction mixture was evaporated in vacuo. Analysis of the residual pink oil by ^1H NMR indicated **9a** and **10a** to be present in a 49:51 ratio. Two additional similar experiments gave the same result. The pair of adducts were separated by preparative TLC on silica gel (elution with hexane–ethyl acetate, 1:1).

For **9a**: 33 mg (46%) was isolated; white solid, mp 222–224 °C (from isopropyl alcohol); ^1H NMR ($CDCl_3$) δ 6.06–5.6 (m, 2 H), 4.27 (m, 2 H), 4.12 (m, 2 H), 3.08 (s, 3 H), 2.53 (m, 2 H), 1.38 (dd, J = 12, 4.5 Hz, 2 H); mass spectrum, m/e calcd (M^+) 367.0943, obsd 367.0949.

For **10a**: 35 mg (48%) was isolated; colorless solid, mp 232–233 °C (from isopropyl alcohol); ^1H NMR ($CDCl_3$) δ 6.27–5.9 (m, 2 H), 4.16 (m, 2 H), 3.97 (m, 2 H), 2.88 (s, 3 H), 2.13 (m, 2 H), 1.40 (m, 2 H); mass spectrum, m/e calcd (M^+) 367.0943, obsd 367.0951.

Anal. Calcd for $C_{17}H_{13}N_3O_2F_4$: C, 55.59; H, 3.57. Found: C, 55.60; H, 3.63.

Cycloadditon of 4b with *N*-Methyltriazolinedione. Treatment of **4b** (82 mg, 1.45 mmol) with NMTD (61 mg, 0.54 mmol) in dichloromethane solution (5 mL) as described above afforded a 24:76 mixture of **9b** and **10b**. For isolation purposes, this mixture was combined with a second produced from 108 mg (0.59 mmol) of **4b** (ratio also 24:76). Chromatographic separation was achieved on silica gel (elution with ethyl acetate–hexane, 1:1).

For **9b**: 77 mg (25%) was isolated; white solid, mp 132–133 °C; IR (CH_2Cl_2) 3020, 2960, 2875, 1770, 1705, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (m, 4 H), 6.28 (dt, J = 10.5, 1.0 Hz, 1 H), 5.97 (dt, J = 10.5, 3.0 Hz, 1 H), 4.20 (dd, J = 3.0, 1.0 Hz, 2 H), 3.73 (m, 2 H), 2.77 (s, 3 H), 2.06 (m, 2 H), 1.30 (m, 2 H); mass spectrum, m/e calcd (M^+) 295.1320, obsd 295.1328.

For **10b**: 166 mg (54%) was isolated; colorless solid, mp 145–145.5 °C (from chloroform–hexane); IR (CH_2Cl_2) 3060, 2940, 2870, 1765, 1710, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (m, 4 H), 5.68 (m, 2 H), 4.22 (m, 2 H), 3.77 (m, 2 H), 3.03 (s, 3 H), 2.43 (m, 2 H), 1.30 (dd, J = 12, 4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 156.8 (s), 150.0 (s), 144.2 (s), 132.6 (d), 126.8 (d), 123.3 (d), 121.8 (d), 75.9 (s), 51.0 (d), 45.4 (t), 26.0 (m), 25.4 ppm (m); mass spctrum, m/e calcd (M^+) 295.1320, obsd 295.1328.

Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.14; H, 5.88. Found: C, 68.90; H, 5.93.

Cycloaddition of 4c with *N*-Methyltriazolinedione. Reaction of **4c** (50 mg, 0.207 mmol) with NMTD (26 mg, 0.23 mmol) in dichloromethane (5 mL) afforded a 24:76 mixture of **9c** and **10c**. For isolation purposes, this mixture was combined with a second produced from 45 mg (0.186 mmol) of **4c** (ratio also 24:76). The adducts were separated by preparative TLC on silica gel (elution with petroleum ether–ethyl acetate, 1:1).

For **9c**: 35 mg (25%) was isoalted as a colorless oil; ^1H NMR ($CDCl_3$) δ 6.63 (s, 2 H), 6.2 (br d, J = 10 Hz, 1 H), 5.93 (dt, J = 10, 3 Hz, 1 H), 4.17 (m, 2 H), 3.90 (m, 2 H), 3.82 (s, 6 H), 2.83 (s, 3 H), 2.03 (m, 2 H), 1.30 (m, 2 H); mass spectrum, m/e calcd (M^+) 355.1532, obsd 355.1537.

For **10c**: 96 mg (68%) was isolated; white solid, mp 164–165 °C (from chloroform/hexane); IR (KBr) 3060, 3000, 2990, 2945, 2865, 1765, 1705, 1455 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.63 (s, 2 H), 5.73 (m, 2 H), 4.27 (m, 2 H), 3.97 (m, 2 H), 3.73 (s, 6 H), 3.03 (s, 3 H), 2.40 (m, 2 H), 1.30 (m, 2 H); mass spectrum, m/e calcd (M^+) 355.1532, obsd 355.1537.

Anal. Calcd for $C_{19}H_{21}N_3O_4$: C, 64.21; H, 5.96. Found: C, 63.85; H, 5.99.

Acknowledgment. This investigation was made possible by the generous financial support of the National Cancer Institute (CA-12115).

Registry No. 4a, 79917-57-0; **4b**, 79917-58-1; **4c**, 79917-59-2; **6a**, 51716-08-6; **6b**, 6165-88-4; **6c**, 79917-60-5; **7a**, 79917-61-6; **7b**, 79917-62-7; **7c**, 79917-63-8; **8**, 79933-07-6; **9a**, 79917-64-9; **9b**, 79917-65-0; **9c**, 79917-66-1; **10a**, 79981-52-5; **10b**, 79981-53-6; **10c**, 79980-57-7; TCNE, 670-54-2; NMTD, 13274-43-6.