Regioselectivity in the Diels-Alder Reaction of 9-Substituted Anthracenes

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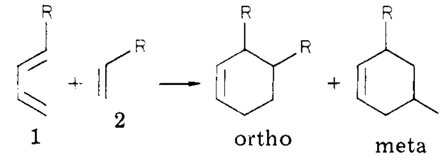
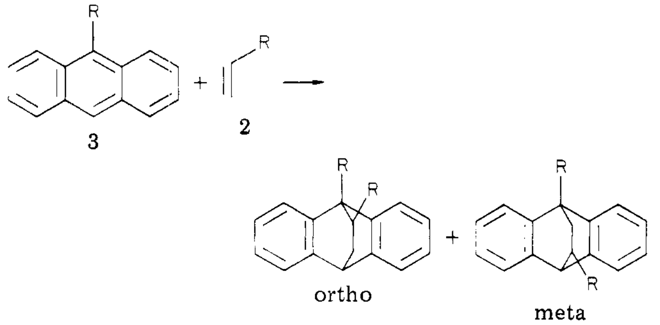
The regioselectivity in the cycloaddition reactions of some 9-substituted anthracenes with acrylic acid, acrylonitrile, and allyl alcohol has been determined by ^{1}H NMR analysis. The ortho regioisomer was preferred in all but two of the cases, the reactions of 9-nitro- and 9-carboxyanthracene with acrylic acid. The regioisomer ratios were found to remain constant over the course of the reactions; consequently, they are almost certainly of kinetic origin. The regioselectivity that was observed was predicted in ten out of the eleven reactions using CNDO/2 frontier molecular orbital energies and coefficients. The neglect of the first-order charge interactions or hydrogen-bonding effects could be the origin of the incorrect prediction. The regioselectivity could not be rationalized by a diradical mechanism nor by a localized charge mechanism.

The Diels-Alder reaction between 1-substituted 1,3-butadienes (1) and monosubstituted dienophiles (2) can yield



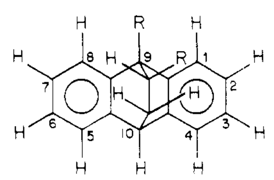
two regioisomers, ortho and meta. The ortho regioisomer is preferred in all of the experimental cases that are known.[1-12] The 9-substituted anthracenes (3) are analogous to the 1-substituted 1,3-butadienes, yet in their reactions with monosubstituted dienophiles the preferred regioisomer is found to be dependent on the substituent combination that is used.[2,13,14] In fact, completely different regioisomer ratios are obtained with substituent combinations which have very similar electronic and steric characteristics. Thus, the difference in regioselectivity between the 9-substituted anthracenes and the analogous 1-substituted 1,3-butadienes is not anticipated nor is it apparent why this difference should exist.



Most of the investigations of the Diels-Alder reaction of the 9-substituted anthracenes were carried out before the availability of modern separation techniques.[2,13,14] The regioisomers were separated by a manual procedure which relied on the contrasting geometric crystalline forms of the regioisomers, and no analysis of the crude reaction products was made before purification.[13a] Consequently, the regioisomer ratios currently available in the literature may not be reliable. In this investigation, the Diels-Alder reaction of 9-substituted anthracenes is reexamined experimentally to obtain more accurate regioisomer ratios and theoretically to determine the origin of its regioselectivity.

Results and Discussion

Regioselectivity of 9-Substituted Anthracenes. The 9-substituted anthracenes were reacted with acrylic acid, acrylonitrile, and allyl alcohol. The regioisomer ratios of the reaction products were determined by ^{1}H NMR analysis by the electronic integration of the areas of the bridgehead protons before separation. The bridgehead protons (H-10 in 4) of the two regioisomers differed in chemical shift by δ ~0.3. The regioisomer ratios were determined over the course of the reactions and in all cases were found to be within experimental error of the ratios of the final products. Therefore, the adducts are stable to the reaction conditions and are almost certainly the kinetic products. Also, the Diels-Alder adducts were isolated and characterized in several of the reactions (Table I). The melting points of these adducts were in excellent agreement with those reported in the literature,[13a] and their NMR spectra were consistent with the assigned structures.



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In the reactions that we investigated, the ortho regioisomer was preferred in all but two of the cases (Table II). Furthermore, the regioselectivity that we observed was different in some cases from that observed in the earlier investigations. The origin of these differences was prob-

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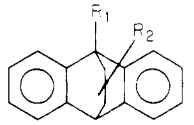
Table I. Characterization of Diels-Alder Adducts of 9-Substituted Anthracenes



			melting point, C		¹H NMR spectrum[c]	
R_1	R_2	regioisomer	this work[a]	lit.[b]	solvent	chemical shift, δ
NO_2	COOH	meta	227-227.5	225	Me_2SO-d_6	7.8-7.0 (m, 8 H), 4.9 (d, J = 2 Hz, 1 H), 3.3-2.4 (m, 3 H)
NO_2	COOH	ortho	255-262	267-268	Me_2SO-d_6	7.8-6.8 (m, 8 H), 4.57 (t, J = 2.5 Hz, 1 H), 3.67 and 3.47 (dd, J = 5 Hz, 1 H), 2.6-1.6 (m, 2 H)
CN	COOH	ortho	211-211.5	212-214	Me_2SO-d_6	7.8-7.0 (m, 8 H), 4.57 (t, J = 2.5 Hz, 1 H), 3.3-3.0 (m, 1 H), 2.6-1.9 (m, 2 H)
CN	COOH	meta	190-191		Me_2SO-d_6	7.8-7.1 (m, 8 H), 4.9 (d, J = 2 Hz, 1 H), 3.3-2.9 (m, 1 H), 2.6-2.3 (m, 2 H)
CHO	CN	ortho	179-180	181.5-182	$CDCl_3$	10.95 (s, 1 H), 7.7-7.1 (m, 8 H), 4.45 (t, J = 2.5 Hz, 1 H), 3.4-3.0 (m, 1 H), 2.6-2.0 (m, 2 H)
CN	CN	ortho	165-166	166.5-167.5	$CDCl_3$	8.0-7.2 (m, 8 H), 4.5 (t, J = 2.5 Hz, 1 H), 3.45-3.1 (m, 1 H), 2.6-2.0 (m, 2 H)

[a] Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. [b] Reference 13a. [c] Chemical shifts (δ) are relative to Me_4Si (δ = 0). Signals are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The NMR spectra were recorded on a Varian T-60 spectrometer.

Table II. Regioselectivity in the Diels-Alder Reactions of 9-Substituted Anthracenes

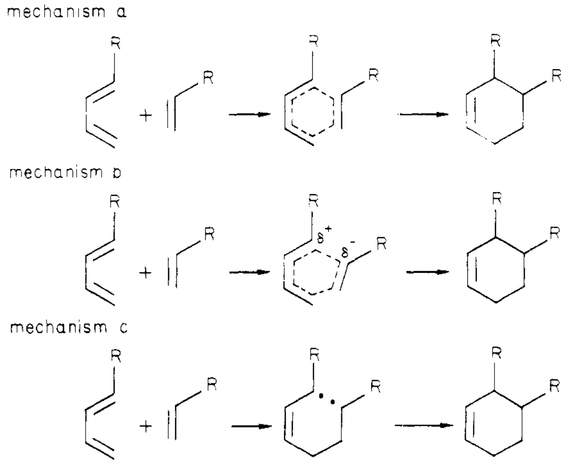
		experimental ortho:meta	
substituent	dienophile	this work	lit. values[a]
OCH_3	acrylic acid		100:0
OCH_3	acrylonitrile		100:0
OCH_3	allyl alcohol		0:100
CN	acrylic acid	65:35	100:0
CN	acrylonitrile	100:0	34:66
CN	allyl alcohol	65:35	68:32
COOH	acrylic acid	44:56	0:100
COOH	acrylonitrile	63:37	
COOH	allyl alcohol	no adduct observed	
CHO	acrylic acid	100:0	100:0
CHO	acrylonitrile	100:0	100:0
NO_2	acrylic acid	19:81	meta predominates
NO_2	acrylonitrile	63:37	56:44
NO_2	allyl alcohol	no adduct observed	0:100

[a] References 13a and 14.

ably our better analytical technique and milder reaction conditions.

Theoretical Considerations. Though the Diels-Alder reaction was discovered in 1928,[15] its mechanism is still the source of much controversy. Depending on one's point of view, there are three possible mechanisms which can account for most of the experimental data that have been accumulated for the Diels-Alder reaction.[1,16-18] Currently the most favored mechanism is a concerted one in which there is a six-centered transition state with simultaneous formation of the two σ bonds. However, there are two variations in the concerted mechanism (Scheme I): (1) mechanism a has a symmetrical transition state with σ bond formation to the same extent, and (2) mechanism b has an unsymmetrical transition state with σ bond formation to different extents resulting in localized partial charges on the diene and dienophile. The other possible mechanism has a stepwise diradical transition state in which the diradical would be spin paired (mechanism c).

Scheme I



For cycloaddition reactions involving a concerted mechanism, the regioselectivity should be explainable by considering the molecular orbital interactions between the diene and the dienophile in the transition state.[19] A

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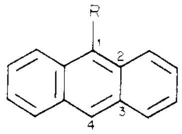
Table III. CNDO/2 Frontier Molecular Orbitals of 9-Substituted Anthracenes

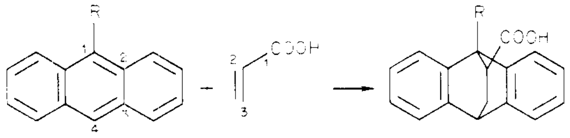


R	conformation[b]	HOMO coefficients[a] C-1	C-2	C-3	C-4	energy of HOMO, eV	LUMO coefficients[a] C-1	C-2	C-3	C-4	energy of LUMO, eV
COOH	perpendicular	0.437	0.100	0.097	0.431	−9.69	0.432	0.120	0.101	0.443	0.299
COOH	planar	0.441	0.078	0.097	0.403	−9.74	0.386	0.168	0.089	0.470	−0.027
NO_2	perpendicular	0.443	0.086	0.096	0.420	−10.15	0.437	0.134	0.101	0.452	−0.136
NO_2	planar	0.452	0.051	0.096	0.382	−10.29	0.354	0.193	0.083	0.479	−0.653
CHO	perpendicular	0.433	0.110	0.095	0.439	−9.58	0.435	0.112	0.101	0.435	0.381
CHO	planar	0.438	0.091	0.098	0.411	−9.66	0.384	0.163	0.087	0.463	−0.027
OCH_3	perpendicular	0.383	0.179	0.081	0.489	−8.84	0.459	0.064	0.103	0.382	0.843
OCH_3	planar	0.374	0.158	0.084	0.476	−8.92	0.451	0.065	0.106	0.391	0.898
CN	planar	0.429	0.104	0.095	0.427	−9.61	0.422	0.142	0.097	0.449	0.136

[a] These are absolute values. [b] The perpendicular conformation has the plane of the substituent perpendicular to the plane of the anthracene moiety, while in the planar conformation the substituent is in the plane of the anthracene moiety.

simplification of this approach which has been used successfully to explain the Diels–Alder regioselectivity of 1-substituted 1,3-butadienes is the Frontier Molecular Orbital Theory, which considers only the interactions between the frontier molecular orbitals (FMO) of the diene and the dienophile.[20-24] Consequently, we have applied this approach to the Diels–Alder reactions of the 9-substituted anthracenes.

Some of the reactions of the 9-substituted anthracenes are of the normal electron demand type:[25] that is, the energy separation between the HOMO of the diene and the LUMO of the dienophile is much smaller than the energy separation between the LUMO of the diene and the HOMO of the dienophile. Usually the latter MO interaction is neglected in such reactions. However, the energy separation between the interacting MO's is similar in most of the cases. In these latter cases both MO interactions will significantly affect the regioselectivity; consequently, we have included both FMO interactions in our theoretical approach.



The frontier molecular orbital approach is derived from the second-order perturbation expression for the energy change which accompanies the orbital interactions of the two molecules that are involved in a cycloaddition reaction.[19] In the FMO approach the perturbation expression simplifies into eq 1. In this expression, the E's are the

$$\Delta E = \frac{2[c^{A}{}_{1}c^{D}{}_{2}\gamma_{cc} + c^{A}{}_{4}c^{D}{}_{3}\gamma_{cc} + c^{A}{}_{2}c^{D}{}_{1}\gamma'_{cc}]^2}{E^{A}{}_{HOMO} - E^{D}{}_{LUMO}} + \frac{2[c^{A}{}_{1}c^{D}{}_{2}\gamma_{cc} + c^{A}{}_{4}c^{D}{}_{3}\gamma_{cc} + c^{A}{}_{2}c^{D}{}_{1}\gamma'_{cc}]^2}{E^{D}{}_{HOMO} - E^{A}{}_{LUMO}} \quad (1)$$

FMO energies, the c^{A}'s are the atomic orbital coefficients of the 9-substituted anthracene, the c^{D}'s are the atomic orbital coefficients of the dienophile, and the γ_{cc}'s are the transition state resonance integrals for carbon p orbitals.

The stabilization energy from the FMO interactions was calculated from eq 1, using the CNDO/2 FMO energies and coefficients (Table III).[26,27] Resonance integrals of 7.0 eV for the primary orbital interactions and 2.8 eV for the secondary orbital interactions were used in the calculations.[33] The FMO calculations were carried out on the nine reactions that we studied plus two reactions in the literature. In these latter two cases, only one regioisomer was isolated in high yield (80%);[13a] consequently, the observed regioisomer must be the preferred product. However, it must be pointed out that kinetic control was not established in these two cases.

From the FMO calculations, the preferred regioisomer was predicted in every case but one, the reaction of 9-carboxyanthracene and acrylic acid (Tables II and IV). These calculations also correctly predicted that acrylic acid would yield less ortho isomer than acrylonitrile in the cyano, carboxyl, and nitro cases, and that both of the dienophiles would give approximately the same isomer ratio with 9-formylanthracene. Furthermore, the large energy difference between the regioisomers in the reactions of 9-methoxyanthracene agreed with the experimental observation of 100% ortho isomer. However, there was considerable variation in the relationship between the FMO energy differences and the observed isomer ratios

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(24) (a) P. V. Alston, R. M. Ottenbrite, and T. Cohen, *J. Org. Chem.*, **43**, 1864 (1978), and references cited therein; (b) T. Cohen, R. J. Ruffner, D. W. Shull, W. M. Daniewski, R. M. Ottenbrite, and P. V. Alston, *J. Org. Chem.*, **43**, 4052 (1978).

(25) R. Sustmann, *Pure Appl. Chem.*, **40**, 569 (1974).

(26) CNDO/2 method: J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

(27) Standard bond lengths[26] were used in the CNDO/2 calculations except for the nitro group[28] for which a N–C bond distance of 1.41 Å and a N–O bond distance of 1.25 Å were used. The bond angles in the anthracene moiety were assigned the standard value of 120°, while the crucial bond angles in the substituent were optimized. The effects of conformational changes on the frontier molecular orbitals were determined for the 9-substituted anthracenes (3, R = NO_2, CHO, COOH, OCH_3). In these cases, the conformation in which the plane of the substituent was perpendicular to the plane of the anthracene moiety was found to be more stable than the planar conformation. This theoretical observation is in agreement with the experimental data that are available for the 9-substituted anthracenes.[29-32]

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(29) J. Trotter, *Acta Crystallogr.*, **12**, 922 (1959).

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(31) J. Trotter, *Acta Crystallogr.*, **12**, 237 (1959).

(32) J. C. J. Bart and G. M. J. Schmidt, *Isr. J. Chem.*, **9**, 429 (1971).

(33) These values have been used successfully to predict the regioselectivity in the Diels–Alder reaction of substituted 1,3-butadienes.[24]

Table IV. FMO Energy Differences between the Regioisomers of 9-Substituted Anthracenes

		ΔΔenergy($\Delta E_{\text{ortho}} - \Delta E_{\text{meta}}$), kcal/mol[a]		
9-substituent	dienophile	HOMO diene/ LUMO dienophile	HOMO dienophile/ LUMO diene	total
CN	acrylic acid	−0.214	−0.848	−1.062
CN	acrylonitrile	−0.150	−1.551	−1.701
CN	allyl alcohol[b]	0.009	−0.423	−0.414
COOH	acrylic acid	0.066	−0.310	−0.244
COOH	acrylonitrile	0.037	−0.573	−0.536
CHO	acrylic acid	−0.700	−0.141	−0.841
CHO	acrylonitrile	−0.472	−0.231	−0.703
NO_2	acrylic acid	1.031	−0.616	0.415
NO_2	acrylonitrile	0.685	−1.152	−0.467
OCH_3	acrylic acid	−7.209	1.150	−6.059
OCH_3	acrylonitrile	−4.769	1.918	−2.851

[a] A negative energy difference favors the ortho regioisomer, and a positive energy difference favors the meta regioisomer. FMO's of perpendicular conformation were used in the calculations for the nitro, carboxyl, methoxyl, and formyl cases.
[b] No secondary orbital interactions with this dienophile.

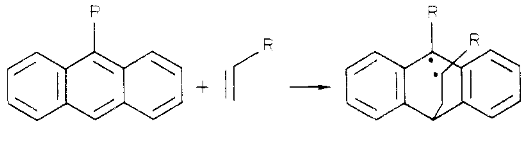
when all of the reactions were considered as a whole. The main source of this variation was the reactions of 9-formylanthracene, whose FMO energy differences were somewhat lower than expected for a 100:0 isomer ratio. However, when one considers the approximations that were made in order to carry out these calculations, the observed agreement between theory and experimental becomes gratifying.

The incorrect prediction by the theory in the reaction of 9-carboxyanthracene with acrylic acid could have been caused by the neglect of the first-order charge interactions. The first-order charge interactions which favor the meta regioisomer are expected to have some effect on the regioselectivity in this case because of the presence of the highly polar carboxyl group on both the diene and the dienophile.[34] However, these electrostatic interactions are usually not predominant in the Diels–Alder transition state and can only determine the regioselectivity when the selectivity of the FMO's is small, as in this case.

In all of the reactions except the addition of 9-nitroanthracene with acrylic acid, the same regioisomer is preferred by the FMO's of the planar and perpendicular conformations of the diene. In this latter case, the meta regioisomer is preferred by the perpendicular conformation, while the ortho regioisomer is preferred by the planar conformation. Experimental and theoretical results indicate that perpendicular conformation is preferred.[27,30,31]

Within the concerted mechanism, localized charge accumulation can take place due to nonsynchronous bond formation in the transition state (mechanism b). If this charge formation is determining the regioselectivity, one would expect reactions involving dienes and dienophiles which contain substituents of the same electronic character to prefer the same regioisomer. However, two incidences were observed where the above generalization did not hold. The reactions of 9-nitroanthracene with acrylic acid and acrylonitrile preferred different regioisomers, as did the reactions of 9-carboxyanthracene with acrylic acid and acrylonitrile.

Firestone[16] has indicated that the available data on the Diels–Alder reaction can be explained by a diradical mechanism. If the reactions of the 9-substituted anthracenes involved a diradical transition state, one would expect the addition of the dienophile to the diene to take place initially at the unsubstituted carbon. Maximum stabilization of the diradical transition state will occur in this orientation because of the delocalizing effect of the substituents. Thus, a diradical mechanism would favor the formation of the ortho regioisomer in every case. However, the meta regioisomer was found to be preferred in two cases, thereby disfavoring the diradical mechanism.



In the reactions of the 9-substituted anthracenes with acrylic acid, there is the possibility of the reactions taking place through a hydrogen bonding complex[36] since carboxylic acids are known to form dimers in aprotic solvents. If the dimer of acrylic acid is reacting instead of the acrylic acid monomer, then one would expect the HOMO diene–LUMO dienophile interaction to determine the regioselectivity in the concerted mechanism.[37] Such an approach allows the prediction of the preferred regioisomer in every case (Tables II and IV). For the diradical and localized charge accumulation mechanisms, the reaction of the dimer

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(34) The repulsion or attraction energy from the first-order charge interactions[35] has been calculated for the reactions of the 9-substituted anthracenes (**3**, R = NO_2, COOH, CHO, CN) with acrylic acid and acrylonitrile. In the nitro, carboxyl, and cyano cases, these interactions favored the meta regioisomer. Furthermore, the repulsion between the reactants was greater with acrylic acid than with acrylonitrile and greater in the perpendicular conformation of the diene than in its planar conformation. In the 9-formylanthracene case, little repulsion or attraction was predicted when the dienophile approached the diene from the aldehyde proton side. The model that was used in these calculations had the reacting molecules in parallel planes (3 Å apart), with the terminal atoms of the diene moiety symmetrically below the carbon–carbon double bond of the dienophile. This distance of separation was chosen because molecular orbital calculations have shown that little change in the geometry of the reactants has taken place at this stage of the reaction. Thus, it must be assumed that the energy differences that are observed in this model will be retained in the transition state whose geometry is not known. The theoretical justification for this type of model has been presented by Hudson;[19b] however, Firestone[16] has expressed doubt about the validity of this type of approach for predicting regioselectivity.

(35) A. Devaquet and L. Salem, *J. Am. Chem. Soc.*, **91**, 3793 (1969).

(36) We thank a referee for bringing this to our attention. Also, this referee has indicated that hydrogen bonding between the 9-substituent and acrylic acid or relief from the steric crowding (9-substituent and peri hydrogens) could be the origin of the preferred meta orientation in the carboxyl and nitro cases. However, we feel that the data do not support such explanations because (1) if relief from steric crowding was causing the initial attack of the unsubstituted dienophile carbon at the 9 position of the diene, then this phenomenon should also have been observed in the formyl and methoxyl cases which also have steric crowding and (2) if a hydrogen bonding complex between the 9-substituent and acrylic acid leads to the preferred meta orientation, such preference should have also been seen in the formyl case as well as with 1-carboxyl-1,3-butadiene.[4c]

(37) Molecular orbital calculations by ourselves [unpublished] and Houk and Strozier [*J. Am. Chem. Soc.*, **95**, 4094 (1973)] have shown that hydrogen bonding of carbonyl-containing dienophiles causes a decrease in the FMO molecular orbital energies without reversing the relative magnitudes of the LUMO coefficients of the double bond moiety.

instead of the monomer does not account for the reversals in regioselectivity in some of the cases.

Comparison of the Regioselectivity of the 9-Substituted Anthracenes and 1-Substituted 1,3-Butadienes. Of the 9-substituted anthracenes used in this study, only their cyano, methoxy, and carboxyl counterparts are reported for the 1-substituted 1,3-butadienes. In the cyano and methoxy cases the same regioisomer is preferred;[2,12] however, opposite regioisomers are preferred in the carboxyl case when acrylic acid is used as the dienophile.[1,4c] The major difference between 9-carboxyanthracene and 1-carboxy-1,3-butadiene is that the former prefers to be nonplanar while the latter prefers to be planar. This nonplanarity in the 9-carboxyanthracene will decrease the resonance between the substituent and the anthracene moiety as well as increase the repulsion (electrostatic and steric) between the carboxyl substituents in the Diels–Alder transition state.[34]

Conclusion

Unlike their 1-substituted butadiene counterparts, the 9-substituted anthracenes were found to prefer either the ortho or meta regioisomer depending on the substituent combination. The preferred regioisomers were predicted from FMO theory in ten out of the eleven reactions that were investigated using a concerted transition state model. This same model has been used previously to explain the regioselectivity in the Diels–Alder reaction of the 1-substituted 1,3-butadienes.[24a] The neglect of the first-order charge interactions or hydrogen bonding effects could be the origin of the incorrect prediction. Furthermore, the regioselectivity that was observed could not be rationalized by a diradical mechanism nor by a localized charge mechanism.

Experimental Section[38]

Adducts of 9-Cyanoanthracene and Acrylic Acid. The 9-cyanoanthracene (2.0 g, 9.8 mmol) was added to 20 mL of a 50:50 mixture of acrylic acid and benzene, containing a trace of hydroquinone. Then the solution was refluxed for 9 days. Upon cooling, the mixture was extracted with four 25-mL portions of 10% sodium hydroxide solution. The sodium hydroxide solution was acidified with 6 N hydrochloric acid, resulting in the precipitation of the desired adducts. The adducts were recovered by filtration and washed with 50 mL of water. The crude yield was 85%. The isomer ratio was determined by NMR analysis of this crude product.

The crude material was dissolved in hot benzene, and by slow evaporation of the solvent at room temperature two distinct crystalline forms were observed. The crystals were separated manually after decantation of the supernatant liquid. The ortho and meta adducts had melting points of 211–211.5 and 190–191, respectively. Recrystallization in benzene did not change the melting points.

The regioisomer ratio was also determined at various times as the reaction proceeded to completion. The reaction solution was evaporated to dryness under reduced pressure, and the resulting residue was recrystallized in benzene to remove most of the unreacted 9-cyanoanthracene. Neither adduct was detected in the recovered 9-cyanoanthracene by NMR analysis. The adduct mixture was then analyzed by ^{1}H NMR to determine the regioisomer ratio. The regioisomer ratio was found to be constant over the course of the reaction and agreed within experimental error with the ratio that was determined after the reaction was completed. The regioisomer ratios were as follows: (1) 67:33 at 2 days of reaction, (2) 63:37 at 4 days of reaction, and (3) 65:35 for the completed reaction.

Adducts of 9-Nitroanthracene and Acrylic Acid. The procedure was the same as the one for 9-cyanoanthracene. The crude yield was 94%.

Adducts of 9-Carboxyanthracene and Acrylic Acid. The procedure was the same as the one for 9-cyanoanthracene. The crude yield was 81%.

Adducts of 9-Formylanthracene and Acrylic Acid. The procedure was the same as the one for 9-cyanoanthracene. The crude yield was 95%.

Adducts of 9-Formylanthracene and Acrylonitrile. The 9-formylanthracene (2.06 g, 10 mmol) was dissolved in 30 mL of acrylonitrile containing a trace of hydroquinone. The solution was refluxed for 6 days, after which the acrylonitrile was removed under reduced pressure. The residue was analyzed by NMR to determine the isomer ratio (only the ortho regioisomer was observed). The crude residue was then recrystallized in benzene to give 2.2 g (85%) of the ortho regioisomer. Further recrystallization gave white crystals which melted at 179–180 °C. The isomer ratio was also determined at shorter reaction times, and in every case the observed ratio agreed within experimental error with the ratio that was determined after the reaction was completed.

Adducts of 9-Carboxyanthracene and Acrylonitrile. The procedure was the same as the one for 9-formylanthracene. The yield was 91%.

Adducts of 9-Nitroanthracene and Acrylonitrile. The 9-nitroanthracene (2.23 g, 10 mmol) was dissolved in 30 mL of acrylonitrile containing a trace of hydroquinone. The solution was refluxed for 8 days, after which the acrylonitrile was removed under reduced pressure. The residue was recrystallized in benzene to remove most of the unreacted 9-nitroanthracene. Neither adduct was observed in the recovered 9-nitroanthracene by NMR analysis. The adduct mixture was then analyzed by NMR to determine the regioisomer ratio. NMR analysis indicated that ~20% of the 9-nitroanthracene had reacted. The regioisomer ratio was determined at shorter reaction times, and in every case the observed ratios agreed within experimental error with the ratio that was determined after 8 days of reaction.

Adducts of 9-Cyanoanthracene and Acrylonitrile. The procedure was the same as that for 9-nitroanthracene.

Adducts of 9-Cyanoanthracene and Allyl Alcohol. The 9-cyanoanthracene (2.0 g, 9.8 mmol) was dissolved in 25 mL of allyl alcohol containing a trace of hydroquinone. The solution was refluxed for 10 days, and the allyl alcohol was removed under reduced pressure. The residue was recrystallized in benzene to remove unreacted 9-cyanoanthracene. Neither adduct was observed in the recovered 9-cyanoanthracene by NMR analysis. The adduct mixture was then analyzed by NMR to determine the regioisomer ratio. The regioisomer ratio was also determined at shorter reaction times, and in every case the ratio agreed within experimental error with the ratio that was determined after 10 days of reaction.

Adducts of 9-Nitroanthracene and Allyl Alcohol. The procedure was the same as that for 9-cyanoanthracene. No adduct was observed by NMR.

Adducts of 9-Carboxyanthracene and Allyl Alcohol. The procedure was the same as that for 9-cyanoanthracene. No adduct was observed by NMR.

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Registry No. 2 (R = COOH), 79-10-7; **2** (R = CN), 107-13-1; **2** (R = CH_2OH), 107-18-6; **3** (R = CN), 1210-12-4; **3** (R = COOH), 723-62-6; **3** (R = CHO), 642-31-9; **3** (R = NO_2), 602-60-8; *m*-**4** (R^1 = NO_2; R^2 = COOH), 71974-89-5; *o*-**4** (R^1 = NO_2; R^2 = COOH), 71974-90-8; *o*-**4** (R^1 = CN; R^2 = COOH), 71948-83-9; *m*-**4** (R^1 = CN; R^2 = COOH), 71948-84-0; *o*-**4** (R^1 = CHO; R^2 = CN), 66296-78-4; *o*-**4** (R^1 = CN; R^2 = CN), 71948-85-1; *o*-**4** (R^1 = CN; R^2 = CH_2OH), 71948-86-2; *m*-**4** (R^1 = CN; R^2 = CH_2OH), 71948-87-3; *o*-**4** (R^1 = COOH; R^2 = COOH), 71974-91-9; *m*-**4** (R^1 = COOH; R^2 = COOH), 71974-92-0; *o*-**4** (R^1 = COOH; R^2 = CN), 71948-88-4; M-**4** (R^1 = COOH; R^2 = CN), 71948-89-5; *o*-**4** (R^1 = CHO; R^2 = COOH), 66296-68-2; *o*-**4** (R^1 = NO_2; R^2 = CN), 71948-90-8; *m*-**4** (R^1 = NO_2; R^2 = CN), 71948-91-9.

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[38] The 9-substituted anthracenes and dienophiles were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis. The NMR analyses were carried out on a Varian T-60 spectrometer. The melting points were carried out on a Thomas-Hoover melting point apparatus and are uncorrected.