

head. Distillates were fractionated again using an 8-in. Vigreux column to obtain the fractions given in Table II.

TABLE II

Fraction	Boiling range, °C	Amount, g	n_D^{25} , deg
8	69–70 (27–28 mm)	7	1.4248
9	99–101 (0.1 mm)	73	1.4503
10	115–130 (0.07 mm)	16	
11	Residue	45	1.4470

Fraction 9, d^{25}_D 0.968, revealed no hydroxyl or carbonyl group in its infrared spectrum. Its nmr was consistent with a cyclic structure, and its molecular weight by differential vapor phase

thermistor was 271. A mass spectrum revealed an intense m/e peak at 288 (4×72 , the molecular weight of butylene oxide).

Ethylene Oxide.—Ethylene oxide was treated in a manner similar to that described for propylene oxide above. Both $(C_2H_5)_2OBF_4$ and BF_3 were tested. Only dioxane and non-distillable semicrystalline poly(ethylene oxide) were obtained.⁵

Registry No.—*cis*-2-Ethyl-4-methyl-1,3-dioxolane, 1568-99-6; *trans*-2-ethyl-4-methyl-1,3-dioxolane, 1860-13-5; 2,5,8,11-tetramethyl-1,4,7,10-tetraoxacyclodecane, 15129-24-5; triethyloxonium tetrafluoroborate, 14323-65-0; dioxane, 123-91-1.

Diels–Alder Reactions Involving Azonia Polycyclic Aromatic Compounds and Nucleophilic Dienophiles

D. L. FIELDS, T. H. REGAN, AND JEAN C. DIGNAN

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received July 11, 1967

A study of Diels–Alder additions involving the 4a-azoniaanthracene ion, **1**, and a series of dienophiles shows that **1** is more reactive toward nucleophilic than toward electrophilic dienophiles. Furthermore, nmr analyses of adducts derived from **1** and unsymmetrical dienophiles indicate that the cycloadditions occur stereoselectively, giving one of the two possible positional isomers as a mixture, where possible, of two geometrically isomeric forms. Other azonia polycyclic aromatic compounds obeying the principle of “inverse” electron demand in Diels–Alder additions are shown to include azonianaphthacene, -benz[a]anthracene, and -dibenz[a,c]anthracene salts, a diazoniapentaphene salt, and an azonianaphthalene salt bearing electron-withdrawing substituents.

The concept of an “inverse” electron demand in Diels–Alder reactions was first proposed by Bachmann and Deno,^{1a} and an experimental example of such a system involving 1,2,4,5-tetrazines was studied qualitatively by Carboni and Lindsey.^{1b} The first kinetic study related to this phenomenon was recently provided by Sauer and Wiest^{1c} through an investigation of the reaction of hexachlorocyclopentadiene with a series of dienophiles. Acting contrary to the “Alder rule,”² the electron-deficient hexachlorocyclopentadiene was shown to be much more reactive with electron-rich dienophiles, such as cyclopentadiene, styrene, and 2,3-dihydrofuran, than with typical electrophilic dienophiles, such as maleic anhydride and tetracyanoethylene. The 4a-azoniaanthracene ion, **1**,³ is known to add maleic anhydride, esters of fumaric and maleic acids, and acrylonitrile across its 9,10 positions.⁴ We report here a part of our study of the Diels–Alder reactions involving azonia polycyclic aromatic com-

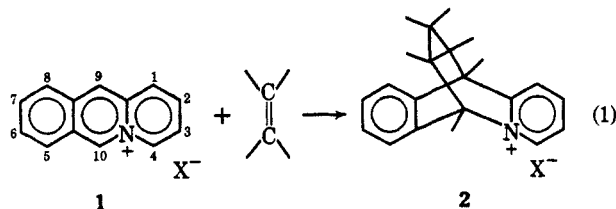
pounds, and **1** (eq 1) in particular, in which these compounds represent another general class of reactant which obeys the principle of Diels–Alder reaction with “inverse” electron demand.

Results and Discussion

Adduct Synthesis.—The dienophiles employed in condensations with **1** ($X^- = Br^-$), the reaction conditions, and the physical characterization of the products are tabulated in Table I. Adducts **2a**, **2b**, and **2c** were prepared by allowing a mixture of **1** and excess olefin in methanol to react in an autoclave at 70° for the periods indicated. The remaining adducts, which were derived from higher boiling dienophiles, were produced by allowing a mixture of **1** and a 5 *M* excess of dienophile in a suitable solvent to react either at room temperature or at reflux temperature until **1** was completely consumed as shown by the absence of 399- μ absorbance in the ultraviolet region.

The resulting products were isolated by precipitation with ether and petroleum ether (bp 35–60°) and then recrystallized either directly or after being converted into perchlorate salts for improved solubility. No attempt was made to fractionate the mixture of isomers obtained in the majority of these reactions.

Adduct Structural Considerations.—The longer wavelength ultraviolet absorptions of the adducts of Table I are confined to the 260–275- μ region indicative of the expected cycloaddition of the dienophile across the 9,10 positions of **1**. The possibility that the 1,3-diene adducts, **2c**, **2h**, and **2n**, were formed from 4 + 4 rather than 4 + 2 cycloadditions was excluded by relating **2c** to **2b** (eq 2) and **2n** to **2o** through



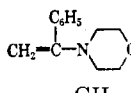
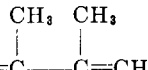



(1) (a) W. E. Bachmann and N. C. Deno, *J. Am. Chem. Soc.*, **71**, 3062 (1949). (b) R. A. Carboni and R. V. Lindsey, *ibid.*, **81**, 4342 (1959). (c) J. Sauer and H. Wiest, *Angew. Chem. Intern. Ed. Engl.*, **1**, 269 (1962). This topic has recently been included in a review, J. Sauer, *Angew. Chem. Intern. Ed.*, **6**, 16 (1967), and in a chapter by R. Huisgen, R. Grashey, and J. Sauer in S. Patai, “The Chemistry of Alkenes,” Interscience Publishers Ltd., London, 1964, p. 739.

(2) K. Alder, *Experientia, Suppl.* **2**, 86 (1955).

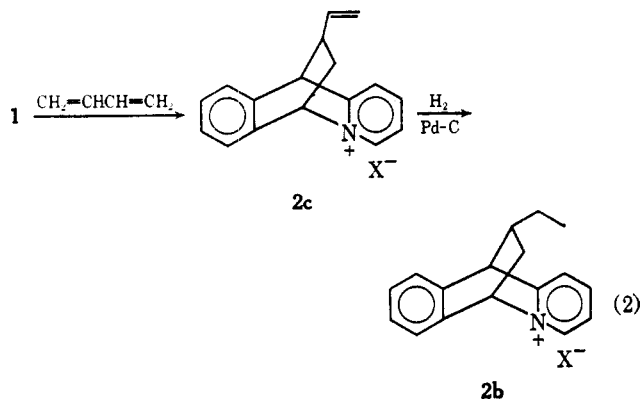
(3) C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **77**, 4812 (1955).

(4) C. K. Bradsher and T. W. G. Solomons, *ibid.*, **80**, 933 (1958).

TABLE I
 ADDUCTS OF 4a-AZONIAANTHRACENE ION (1) AND DIENOPHILES

Adduct	Dienophile	Mp, °C	Reaction conditions			Yield, %	Calcd, %			Found, %		
			Solvent ^a	Temp, °C	Hr		C	H	N	C	H	N
2a ^b	CH ₂ =CH ₂	133-135	A	70	18	93	58.5	4.6	4.6	58.2	4.6	4.4
2b ^c	CH ₂ =CHC ₂ H ₅	248-253	A	70	66	66	64.5	5.7	4.4	64.4	5.9	4.3
2c ^c	CH ₂ =CHCH=CH ₂	164-176	A	70	18	93	60.9	5.0	3.9	61.1	4.8	4.2
2d ^c	CH ₂ =CHCH ₂ OH	174-200	B	100	18	77	60.4	5.0	4.4	60.0	5.0	4.4
2e ^{c,d}	CH ₂ =CHCN	122-127	D	70	48	68	60.1	5.3	7.8	59.7	5.0	8.0
2f ^c	CH ₂ =CHC ₆ H ₅	228-230	B	100	2.5	93	69.2	4.9	3.8	69.1	4.8	4.0
2g ^{b,e}		185 dec	C	25	0.1	84	63.5	5.3	6.0	63.4	5.0	6.3
2h ^b		179-188	B	100	1.5	66	63.1	5.5	3.9	63.2	5.6	3.5
2i ^{b,g}	CH ₂ =C(OEt) ₂ ^h	144-145	C	25	0.1	92	58.6	6.2	3.6	58.6	6.0	3.4
2j ^b	CH ₃ CH=C(OEt) ₂ ⁱ	166-179	C	25	0.1	93	58.6	5.9	3.4	58.4	6.0	3.2
2k ^b	BrCH=C(OEt) ₂ ^j	196-198	C	70	2	100	48.1	4.4	3.0	47.9	4.3	2.9
2l ^b	C ₆ H ₅ CH=C(OEt) ₂ ^k	175-190	C	70	0.1	100	63.6	5.5	2.9	63.1	5.5	2.9
2m ^{b,l}	C ₆ H ₅ CH=CHN(Et) ₂ ^m	116-132	C	25	0.1	91	63.5	6.1	5.9	63.9	6.2	5.6
2n ^b		246	D	25	1.5	94	62.5	4.6	4.1	62.8	4.6	3.8
2o ^b		206-225	D	60	96	76	62.2	5.2	4.0	62.1	5.2	3.8
2p ^b		258-260	B	100	8	69	59.1	5.4	3.8	59.3	5.0	3.7

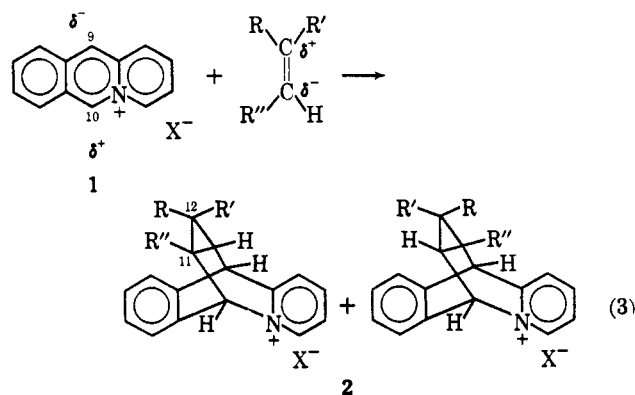
^a Reaction media: A = methanol in an autoclave; B = nitromethane; C = acetonitrile; D = acetonitrile-methanol (3:1 by volume). ^b X⁻ = ClO₄⁻, recrystallized from water. ^c X⁻ = Br⁻, recrystallized from ethanolic ether. ^d Solvated: C₂H₅OH. ^e Solvated: 1/4 H₂O. ^f S. Hünig, K. Hübner, and E. Benzig, *Chem. Ber.*, **92**, 926 (1962). ^g Solvated: 3/4 H₂O. ^h Reference 21. ⁱ S. M. McElvain and W. R. Davie, *J. Am. Chem. Soc.*, **73**, 1400 (1951). ^j F. Beyersted and S. M. McElvain, *ibid.*, **72**, 1661 (1950). ^k S. M. McElvain and M. J. Curry, *ibid.*, **70**, 3781 (1948). ^l Solvated: H₂O. ^m C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).



catalytic reduction of the isolated double bond of 2c and of 2n, and by noting the presence of vinyl methylene absorptions in the nmr spectra of 2c and 2h.

With the exception of 2a, these products can consist of mixtures of isomers owing to positional and/or geometrical isomerism. The distinguishing features of the nmr spectra of the adducts are the resonances of the bridgehead protons (at C-9 and C-10) and of the proton α to nitrogen on the pyridine ring (at C-4). Considering the variety of bridge substituents, the chemical shifts of these protons fall in a fairly narrow range: δ_{C-9H} 5.49 \pm 0.21 (range 5.22-5.86); δ_{C-10H} 6.63 \pm 0.14 (range 6.40-6.95); δ_{C-4H} 9.37 \pm 0.10 (range 9.27-9.64). The multiplicities of these signals are diagnostic in a straightforward manner for the occurrence of both geometrical and positional isomerism. Except for a few cases where peak broadening (due to unknown causes) obscured the line splittings, the multiplicities indicated the presence of *syn*,*anti* isomers with no evidence for positional isomers (eq 3). Thus, 2b-2h are believed to be solely 12-

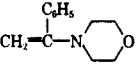


mono, or 12,12-disubstituted 9,10-dihydro-4a-azonia-9,10-ethanoanthracene salts, whereas the ketene acetal adducts, 2i-2l, are solely 12,12-diethoxy derivatives.



This stereoselectivity of addition can be rationalized on the basis that since the 10 position of 1 is known to be attacked by nucleophilic reagents,⁵ it will preferentially attract the negative end of an approaching dienophile. Such a combination of the most probable polarized forms of the dienophile and 1 agrees in general with our orientation results. However, the polarity of the reactant molecules is not thought to be the decisive factor in structural directivity in the diene synthesis,⁶ and, in fact, the above generalization fails with 2e, in that it should be an 11- rather than a 12-cyano derivative, based on the premise that a partial positive charge developed in transition is better

(5) C. K. Bradsher and J. H. Jones, *J. Am. Chem. Soc.*, **81**, 1938 (1959).
 (6) V. Khimii, *Russ. Chem. Rev.*, **31**, 267 (1962).

TABLE II
RELATIVE REACTIVITIES OF DIENOPHILES WITH 4a-AZONIAANTHRACENE BROMIDE

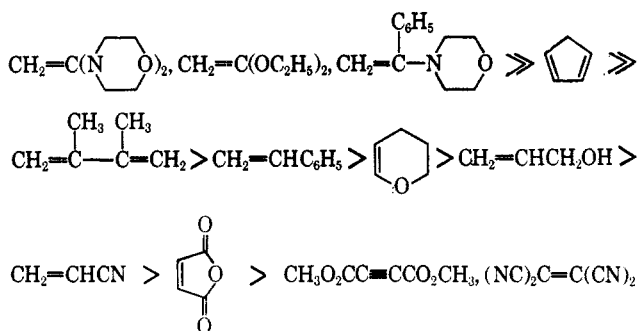
Dienophile	Solvent ^a	Adduct	>75% complete		>90% complete	
			Min	Temp, °C	Min	Temp, °C
$\text{CH}_2=\text{C}(\text{OEt})_2$	A	2i	<4	25	<4	25
	A	2g	<4	25	<4	25
$\text{CH}_2=\text{C}(\text{N} \begin{array}{c} \diagup \text{O} \diagdown \end{array})_2$	A		<4	25	<4	25
	B	2n	35	25	75	25
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	B	2h	>1080	25		
	C		15	100	40	100
$\text{CH}_2=\text{CHC}_6\text{H}_5$	C	2f	30	100	80	100
	C	2p	180	100	360	100
$\text{CH}_2=\text{CHCH}_2\text{OH}$	C	2d	275	100		
$\text{CH}_2=\text{CHCN}$	C	2e	>1080	100		

^a A = acetonitrile, B = nitromethane-methanol (1:1 by volume), C = nitromethane.

accommodated by the β than by the α carbon of acrylonitrile.⁷

Comparative Reactivities.—Considering the reactivity of 1 in relation to its structure, the positively charged nitrogen should produce an electron deficiency in the “diene” portion analogous to that produced by the chlorine atoms of hexachlorocyclopentadiene.¹⁰ This electron withdrawal is obviously quite effective in that it provides another class of compounds which obeys the principle of Diels-Alder reaction with “inverse” electron demand. This is confirmed for 1 by the dienophile activity series shown in Chart I,

CHART I



which was determined on a qualitative basis by spectrophotometric means (see Table II, Experimental Section). The reactions of 1 with the first three highly nucleophilic olefins, representing a ketene aminal, a ketene acetal, and an enamine, are mildly exothermic, with 1 in each case being completely consumed in less than 5 min at 25°. In contrast, reactions of 1 with such electrophilic dienophiles as maleic anhydride and acrylonitrile are quite sluggish, requiring a number of hours at 100° in order to afford modest yields of product. Furthermore, we have not succeeded in obtaining adducts with dimethyl acetylenedicarboxylate or tetracyanoethylene, nor were Brad-

sher and Solomons successful in their attempt to prepare a benzoquinone adduct.⁴

Extension of this study to other azonia polycyclic ring systems has also been made, often with predictable success, based on an assessment of the known reactivity of their polycyclic hydrocarbon counterpart with maleic anhydride. Thus the difficulty encountered in preparing a maleic anhydride adduct of naphthalene⁸ is paralleled by our inability to obtain a ketene diethylacetal adduct of 2,3-dimethyl-4a-azonianaphthalene bromide (3).⁹ On the other hand, naphthalenes bearing electron-donating substituents, such as methyl groups, react much more readily with maleic anhydride than does naphthalene itself,¹⁰ which suggests that the reactivity of azonianaphthalene toward nucleophilic dienophiles would be enhanced by electron-withdrawing substituents. This was substantiated. Anhydride 5, prepared from betaine 4,¹¹ reacts readily with cyclopentadiene and styrene to give 6 and 7, respectively. The first example is particularly interesting in that it involves cyclopentadiene as a precursor to a substituted maleic anhydride (Scheme I).

Considering more complex ring systems, dibenz[*a,c*]anthracene¹² is known to be less reactive than benz[*a*]anthracene¹³ which, in turn, is less reactive than anthracene toward maleic anhydride. Similarly, the reactions of ketene diethylacetal with the two isomeric azoniabenzanthracene perchlorates, 8 and 10,¹⁴ (Scheme II) are slower than with azoniaanthracene perchlorate, 1, but far more rapid than with azonia-dibenz[*a,c*]anthracene perchlorate, 12.¹⁴ The latter cycloaddition requires an elevated temperature (80°) and a large excess of dienophile in order to proceed at an appreciable rate. Again the cycloadditions occur

(8) M. C. Kloetzel and H. L. Herzog, *J. Am. Chem. Soc.*, **72**, 1991 (1950).

(9) O. Westphal, K. Jann, and W. Heffe, *Arch. Pharm.*, **294**, 37 (1961).

(10) M. C. Kloetzel, R. P. Dayton, and H. L. Herzog, *J. Am. Chem. Soc.*, **72**, 273 (1950).

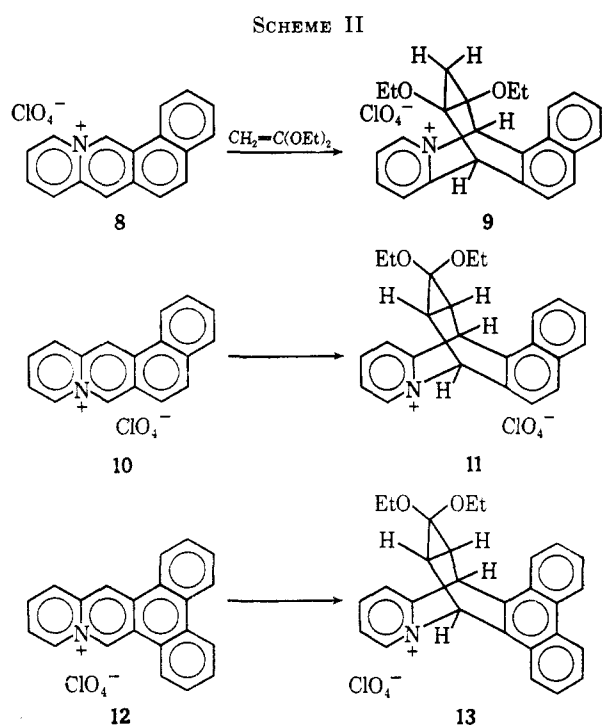
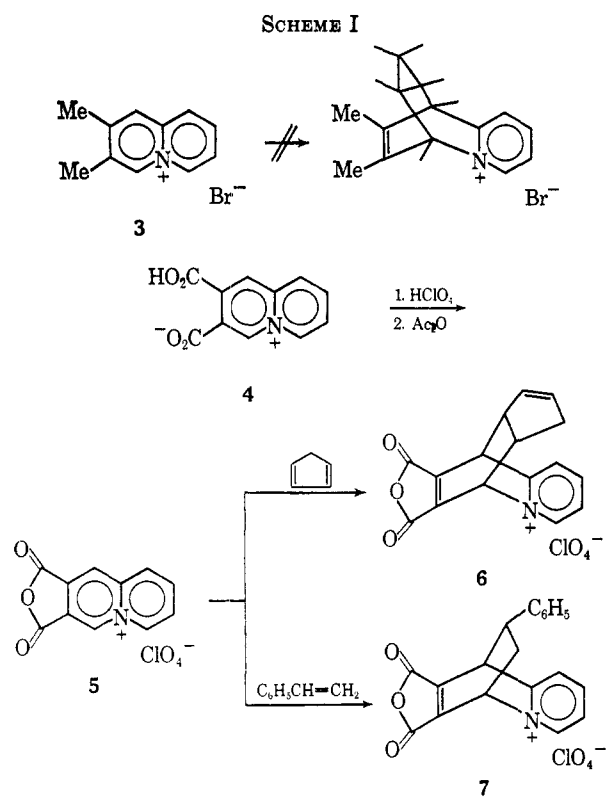
(11) C. K. Bradsher and M. W. Barker, *J. Org. Chem.*, **29**, 452 (1962).

(12) E. Clar and L. Lombardi, *Ber.*, **65**, 1411 (1932).

(13) E. Clar, "Polycyclic Hydrocarbons," Vol. 1, Academic Press Inc., New York, N. Y., 1964, p 311.

(14) C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **78**, 2459 (1956).

(7) For example, in 1,3-dipolar additions, acrylonitrile and styrene add stereospecifically but with opposite orientations to phenyl azide: G. D. Buckley, *J. Chem. Soc.*, 1850 (1954); S. M. Gurvich and A. P. Terent'ev, *Sb. Statei Obshch. Khim. Akad. Nauk SSSR*, **1**, 401 (1953).

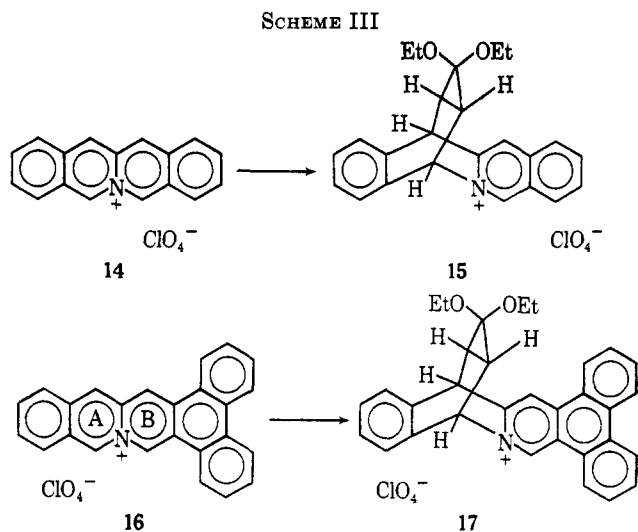


stereospecifically, each giving an adduct having the ethoxyl groups in a position nonadjacent to the quaternary nitrogen.

Naphthalene reacts with maleic anhydride at a faster rate than anthracene.¹⁵ Analogously, adducts **15** and **17** (Scheme III) were produced from rapid, stereospecific cycloadditions of ketene diethylacetal to azonianaphthacene perchlorates, **14**¹⁶ and **16**, respectively. The conclusion that the addition occurred

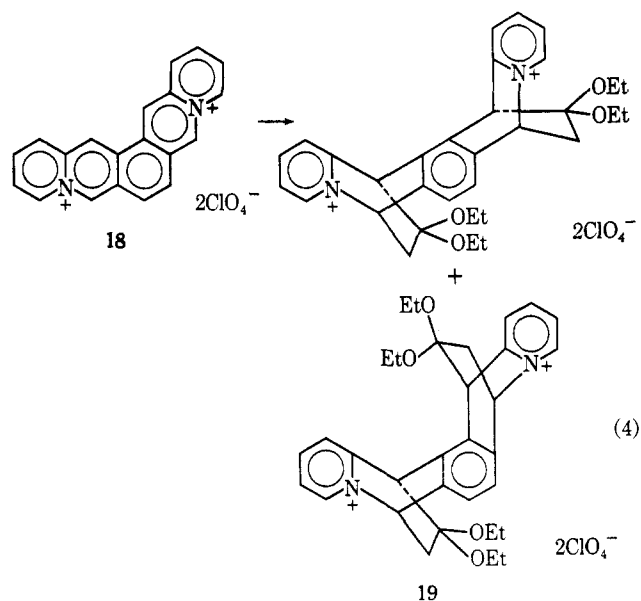
(15) E. Clar, *Ber.*, **65**, 513 (1932).

(16) C. K. Bradsher and T. W. G. Solomons, *J. Am. Chem. Soc.*, **82**, 1808 (1960).



across ring A rather than ring B in **16** is based on the long-wavelength ultraviolet absorption of **17** (λ_{\max} 372 $m\mu$) compared to those of **13** (λ_{\max} 296 $m\mu$) and **15** (λ_{\max} 348 $m\mu$). A comparison of the reactivity of **14** and **1** toward ketene diethylacetal was not made, owing to the rapidity of both of these reactions.

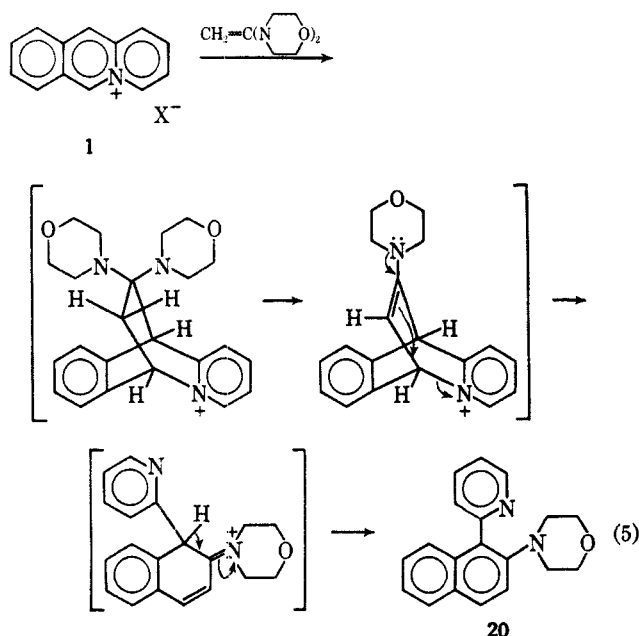
Maleic anhydride adds across both the 5,14 and 8,13 positions of pentaphene.¹⁷ Similarly, 4a, 8a-diazonia-pentaphene diperchlorate, **18**,¹⁸ and ketene diethylacetal combine to give a 1:2 adduct consisting of a mixture of two isomers (**19**) even though the individual additions are stereospecific. Presumably this results from the olefin adding from the same and from opposite sides of the diazoniapentaphene salt, as shown in eq 4.



With one exception, the adducts derived from the more reactive dienophiles were easily isolated in good to excellent yields as stable, crystalline salts. The exception occurred in the cycloaddition reaction (eq 5) between 1,1-dimorpholinoethylene and **1** ($X^- = \text{ClO}_4^-$). The only product isolated, and one which crystallized directly from the reaction mixture, proved to be not a 1:1 adduct, but rather, the new 2-mor-

(17) E. Clar, *Ber.*, **64**, 2194 (1931).

(18) C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **29**, 856 (1964).



pholine-1-(2-pyridyl)naphthalene (20). This compound presumably results from the loss of morpholine from the initially formed 12,12-dimorpholino adduct to give an intermediate enamine which then undergoes an interesting ring opening to form 20.

Facile and somewhat similar transformations have also been observed with the bicyclic ketones derived from the ketene acetal-azonia polycyclic adducts. Our particular interest in this area of research accounts for the emphasis of this paper on the synthesis of the precursor ketene acetal adducts, and will be described in detail in a subsequent communication.

Experimental Section¹⁹

4a-Azoniananthracene Salt Adducts (Table I).—In a typical experiment, a mixture of 2.78 g (0.01 mole) of 4a-azoniananthracene bromide monohydrate (1, $X^- = Br^-$)³ and 4.10 g (0.05 mole) of 2,3-dimethylbutadiene in 200 ml of nitromethane was heated under reflux for 1.5 hr. Analysis of aliquots withdrawn during the course of reaction by observing the 399- $m\mu$ absorbance of 1 indicated that 25% of 1 remained at the end of 15 min, 10% at the end of 40 min, and none at the end of 1.5 hr. Evaporation of the solvent *in vacuo* gave a syrup which was dissolved in a minimum amount of hot water and then treated with solid sodium perchlorate. Adduct 2h (2.35 g, 66%) crystallized from solution as white needles; $\lambda_{max}^{CH_2CN}$ 265 $m\mu$ ($\log \epsilon$ 3.68). The nmr spectrum had absorption at δ 0.87 and 0.98 (singlets, of relative area 1:2) and at 1.80 and 1.83 (singlets, of similar but less easily measured relative areas). These are assigned to the 12- CH_3 and the allylic CH_3 , respectively, the multiplicity arising from *syn,anti* isomerism. Two multiplets centered at 2.17 and 2.42 are assigned as the center strong peaks of the AB part of an ABX spectrum; the outer weak lines are obscured by the allylic CH_3 peaks on the one side and by the residual DMSO- d_6 peaks on the other side. The X part of this pattern appears as a broadened triplet at 6.58. The total pattern represents the absorption of the bridge methylene (C-11) and the bridgehead proton at C-10. The vinyl $=CH_2$ absorption is a pair of broad singlets at 4.57 and 4.69. The C-9 bridgehead is a sharp singlet at 5.30. The aromatic protons, except one, absorb in a complex multiplet extending from 7.2 to

(19) Melting points (uncorrected) were determined on a Thomas-Hoover apparatus. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrometer. Nmr spectra were determined with a Varian A-60 spectrometer on samples, unless otherwise stated, in dimethyl sulfoxide- d_6 solution with tetramethylsilane (TMS) as internal standard. Chemical shifts are recorded as parts per million to lower field from TMS ($\delta = 0$).

8.8; the pyridyl proton α to N^+ appears as a complex multiplet centered at 9.3.

Qualitative data on the reactivities of a number of other dienophiles with 1 were obtained in the same manner and are summarized in Table II. It was necessary to use several different solvents for these reactions, since at 25°, 1 ($X^- = Br^-$) has limited solubility in nitromethane alone, and because the first three dienophiles of Table II react at an appreciable rate with both nitromethane and methanol.

Reduction of Adduct 2n to Adduct 2o and Adduct 2c to Adduct 2b.—A mixture of 2n (3.46 g, 0.01 mole), 1.00 g of 10% palladium on charcoal, and 150 ml of methanol was hydrogenated at 25° and 60 psi (initial pressure) in a Parr shaker. The theoretical hydrogen consumption occurred within 25 min and then stopped. Filtration, followed by removal of the solvent, gave a white crystalline solid which was identical with 2o, as shown by superimposable X-ray powder diagrams and infrared and nmr spectra.

Adduct 2c was related to adduct 2b by an analogous reduction.

Anhydride 5.—Compound 4¹¹ (4.77 g, 0.022 mole), prepared by the nitric acid oxidation of 5,8-dihydroxy-4a-azoniananthracene bromide,²⁰ was dissolved in 25 ml of warm 72% perchloric acid. Upon cooling of the solution, 2,3-dicarboxy-4a-azonianaphthalene perchlorate (5.16 g, 74%) crystallized as white plates, the crystallization being completed by the addition of ethanol and ether. Anhydride 5, mp 213–215° (4.37 g, 93%), was then obtained by heating 5.00 g of the diacid in 50 ml of boiling acetic anhydride for 3 min, followed by refrigeration of the mixture for 1 hr at 5°.

The infrared spectrum showed the characteristic anhydride carbonyl absorptions at 1790 and 1850 cm^{-1} .

Anal. Calcd for $C_{11}H_8ClNO$: C, 44.1; H, 2.0; N, 4.7; Cl, 11.9. Found: C, 43.6; H, 2.4; N, 5.0; Cl, 11.7.

Adduct 6.—To a solution of 2.00 g (0.067 mole) of 5 in 200 ml of acetonitrile–nitromethane (1:1 by volume) was added 2.0 g of cyclopentadiene. After standing at room temperature for 30 min, adduct 6 (1.34 g, 55%), mp 240° dec, was precipitated as white crystals by the addition of 500 ml of ether and 300 ml of petroleum ether. Infrared absorption peaks in the 1700–2000- cm^{-1} region were found at 1790 and 1860 cm^{-1} .

The nmr spectrum had absorption at 2.31 (broad m, 2 H), 3.27 (broad m, 2 H), 5.22 (d, 1 H, C-1 bridgehead), 5.67 (m, 2 H, olefinic), 6.45 (d, 1 H, C-4 bridgehead), 7.7 to 8.8 (m, 3 H, Ar H), 9.28 (d, 1 H, H α to N^+).

Anal. Calcd for $C_{16}H_{12}ClNO$: C, 52.5; H, 3.3; N, 3.8; Cl, 9.7. Found: C, 52.9; H, 3.3; N, 3.8; Cl, 9.5.

Hydrolysis of anhydride 6, by heating for 5 min at reflux a solution of 3.00 g of 6 in 150 ml of water, gave 1.90 g of a betaine as white needles, mp 250–260° dec. The nmr spectrum had absorptions at 2.1–3.8 (broad complex multiplet of 4 H area, assigned to the bridge CH and the allylic methylene), 5.58 (d, 1 H, the C-1 bridgehead), 5.79 (broadened d, 2 H, olefinic), 6.68 (broadened d, 1 H, C-4 bridgehead), 7.8–8.8 (m, 3 H, aromatic), and 9.06 (d, 1 H, aromatic H α to N^+). The appearance of the peak for the H α to N^+ on the aromatic ring as a doublet of multiplets suggests that only one of the two possible isomers has been formed, and this is supported by the appearance of the peaks for the bridgehead protons as doublets instead of pairs of doublets.

Anal. Calcd for $C_{16}H_{12}NO_4$: C, 67.9; H, 4.6; N, 5.0; neut equiv, 283. Found: C, 68.3; H, 4.7; N, 4.8; neut equiv, 281.

Adduct 7 was prepared by heating on a steam bath for 18 hr a mixture of 5 (2.00 g) and styrene (2.0 g) in 100 ml of nitromethane. Dilution of the reaction mixture with ether gave 7 as a crystalline solid. It was characterized as the betaine, mp 250–270°, obtained after its hydrolysis. The nmr spectrum had absorptions at 2.3 (1 H, broad, featureless peak), 3.4 (2 H, broad, featureless peak), 5.31 and 5.53 (each a doublet of 2.5 H, separation, total area 1 H, C-1H), 6.28 (m, 2 H), 7.18 (m) and 7.46 (broad s) (total area 4 H, this area distribution suggests that the C-4 bridgehead is in the 7.2–7.5 region), 7.8–8.6 (m, 3 H), 9.37 (triplet of multiplets, 1 H). The two separate absorptions for the C-1 bridgehead proton and the character of the absorption for the H α to N^+ on the aromatic ring indicate the presence of *syn* and *anti* isomers.

(20) D. L. Fields, J. B. Miller, and D. D. Reynolds, *J. Org. Chem.*, **30**, 252 (1965).

TABLE III
 KETENE DIETHYLACETAL-AZONIA POLYCYCLIC ADDUCTS

Adduct	Mp, °C	Reaction conditions			Nmr bridgehead protons, δ , ppm (multiplicity) ^a	Ultraviolet $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$ (log ϵ)	Calcd, %			Found, %		
		Yield, %	Temp, °C	Hr			C	H	N	C	H	N
9 ^b	166-170	89	25	1	...; 6.00 (s)	270 (4.04)	61.1	5.9	2.9	60.9	5.8	3.0
11	190-195 dec	72	25	1	6.85 (m); 6.53 (s)	270 (4.10)	62.0	5.4	3.1	62.1	5.6	3.2
13	>300 ^d	69	80	3	...; 6.60 (s)	256 (4.88)	65.4	5.2	2.8	65.6	5.2	2.8
						274 s (4.39)						
						296 s (4.14)						
15 ^e	185-186	88	25	<0.05	6.70 (m); 5.60 (s)	236 (4.93)	61.4	5.5	3.1	61.6	5.5	3.1
						270 (3.76)						
						281 s (3.73)						
						333 (3.67)						
						330 (3.69)						
						348 (3.72)						
17 ^f	228 dec	84	25	2	6.80 (m); 5.67 (s)	265 (4.68)	67.7	6.1	2.3	67.6	5.8	2.0
						275 (4.82)						
						305 s (4.32)						
						372 (3.62)						
19	250 dec	96	25	1	6.63 (m); 6.01 (s)	268 (4.18)	53.9	5.3	3.9	53.4	5.3	4.3

^a The peaks described as m are, in most cases, very broad singlet peaks, the broadening being ascribed to unresolved multiplicity.

^b Solvated: $1/2\text{CH}_3\text{OH}$. ^c This signal is buried in the aromatic multiplet, as indicated by area measurements. ^d Melting point of

13, owing to retrograde Diels-Alder reaction at ca. 200°. ^e Solvated: $1/4\text{H}_2\text{O}$ after being recrystallized from ethanol-water.

^f Solvated: $(\text{C}_2\text{H}_5)_2\text{O}$.

Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_4 \cdot 1/4\text{H}_2\text{O}$: C, 70.0; H, 4.6; N, 4.3. Found: C, 70.0; H, 5.0; N, 4.2.

Ketene Diethylacetal-Azonia Polycyclic Adducts (Table III).

—In Table III are tabulated physical, analytical, and spectral data for adducts 9, 11, 13, 15, 17, and 19. With the exception of 16, their azonia polycyclic precursors are known compounds prepared by literature procedures cited in the Discussion.

9a-Azoniadibenz[a,c]naphthacene Perchlorate (16), of mp >300°, was prepared using a general cyclodehydration procedure of Bradsher and Beavers,³ by cyclizing 48% hydrobromic acid the quaternary salt derived from 9-bromomethylphenanthrene and 3-(1,3-dioxolan-2-yl)isoquinoline,²⁰ and then converting the resulting bromide salt into the perchlorate salt, 16, by ion exchange: $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$ m μ (log ϵ), 236 (4.62), 261 (4.80), 300 (4.60), 313 (4.66), 333 (4.56), 410 (4.18), 432 (4.36), 456 sh (3.70).

Anal. Calcd for $\text{C}_{25}\text{H}_{15}\text{ClNO}_4$: C, 70.0; H, 3.5; Cl, 8.2; N, 3.3. Found: C, 70.3; H, 3.8; Cl, 8.1; N, 3.2.

Ketene Diethylacetal-*t*-Butyl Alcohol Reagent.—As a matter of convenience, ketene diethylacetal employed in the syntheses of the adducts of Table III was not used as a pure reagent but rather as a *t*-butyl alcohol mixture which was prepared by a modification of a procedure described by McElvain and Kunding.²¹ Thus, a suspension of 200 g (1.78 moles) of potassium *t*-butoxide²² in 500 ml of dry diglyme was placed in a 3-l. pot of a distillation apparatus equipped with a stirrer, dropping funnel, thermometer, and a 14-in. Vigreux column topped by a stillhead, and was heated by an oil bath to 100°. Bromoacetaldehyde diethylacetal²³ (300 g, 1.52 moles) was then added *via* the dropping funnel to the stirred suspension at a rate to maintain a pot temperature of 120-150°, a head temperature of 100-125°, and a continuous codistillation of the ketene diethylacetal-*t*-butyl alcohol product. Approximately 200 ml of distillate was collected over a 45-min period, the pot temperature eventually being raised to a maximum of 160° by means of the oil bath. The pot was then cooled to 50° and ca. 100 ml of additional distillate with a boiling point up to 75° (60 mm) was collected at reduced pressure. The resulting ketene diethylacetal-*t*-butyl alcohol mixture was used without further purification in the synthesis of the adducts of Table III.

Ketene Diethylacetal Cycloaddition Procedure.—The cycloadditions were effected under the reaction conditions indicated in Table III either by shaking on a wrist-action shaker at room temperature, or by heating at reflux (16 \rightarrow 17) a mixture of azonia polycyclic compound and excess ketene diethylacetal

reagent in acetonitrile. The synthesis of adduct 9 is illustrative of this procedure.

In this synthesis, a suspension of 8¹⁴ (10.00 g, 0.033 mole) in 30 g of ketene diethylacetal-*t*-butyl alcohol reagent and 50 ml of acetonitrile went into solution as it reacted while it was shaken for 1 hr on a wrist-action shaker. Analysis of the solution by ultraviolet spectroscopy showed the reaction to be complete, as indicated by the lack of the 358-, 376-, and 395-m μ absorbances of 8. Dilution with 500 ml of ether-petroleum ether (1:1 by volume) gave an oil which subsequently crystallized. One recrystallization from methanol-ether gave analytically pure 9 (13.60 g, 89%) as white needles.

2-Morpholino-1-(2-pyridyl)naphthalene (20).—To a suspension of 5.00 g (0.018 mole) of 1 ($\text{X}^- = \text{ClO}_4^-$) in 20 ml of acetonitrile was added 4.00 g (0.02 mole) of 1,1-dimorpholinoethylene.²⁴ A deep red solution immediately resulted which, by ultraviolet analysis, contained no starting 1. The solution was heated at reflux for 1 min, cooled, and then allowed to stand at room temperature for 15 min, during which time compound 20 crystallized as long white needles. One recrystallization from methanol gave 3.65 g (70%) of 20: mp 171-172°; $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$ m μ (log ϵ), 224 (4.63), 253 (4.43), 290 shoulder (4.00), 340 shoulder (3.53). The nmr spectrum (CDCl_3) had a four-proton A_2B_2 pattern centered at δ 3.13 (morpholino), a nine-proton multiplet (aromatic) at δ 7.0-8.0, and the proton α to nitrogen as a doublet of multiplets at 8.73.

Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}$: C, 78.6; H, 6.2; N, 9.7. Found: C, 78.2; H, 6.2; N, 10.1.

Registry No.—2a, 14728-15-5; *syn* 2b, 14661-83-7; *anti* 2b, 14661-84-8; *syn* 2c, 14661-85-9; *anti* 2c, 14661-86-0; *syn* 2d, 14661-87-1; *anti* 2d, 14661-88-2; *syn* 2e, 14661-89-3; *anti* 2e, 14661-90-6; *syn* 2f, 14661-91-7; *anti* 2f, 14661-92-8; *syn* 2g, 14728-16-6; *anti* 2g, 14669-01-3; *syn* 2h, 14932-18-4; *anti* 2h, 14728-17-7; 2i, 14728-18-8; *syn* 2j, 14754-82-6; *anti* 2j, 14669-02-4; *syn* 2k, 14728-19-9; *anti* 2k, 14669-03-5; *syn* 2l, 14669-04-6; *anti* 2l, 14669-05-7; *syn* 2m, 14669-06-8; *anti* 2m, 14669-07-9; *syn* 2o, 14669-08-0; *anti* 2o, 14669-09-1; *syn* 2p, 14746-14-6; *anti* 2p, 14669-10-4; 5, 14728-20-2; 6, 14728-21-3; 6 (betaine), 14669-11-5; *syn* 7 (betaine), 14754-83-7; *anti* 7 (betaine), 14754-84-8; 9, 14728-22-4; 11, 14728-23-5; 13, 14728-24-6; 15, 14728-25-7; 16, 14728-26-8; 17, 14728-27-9; 19, 14728-28-0; 20, 14746-15-7.

(21) S. M. McElvain, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 506.

(22) Obtained from K & K Laboratories, Inc., Plainview, N. Y.

(23) Obtained from Aldrich Chemical Co., Milwaukee, Wis.

(24) H. Baganz and L. Domaschke, *Chem. Ber.*, **95**, 2095 (1962).