and air was drawn through the solution. T.l.c. (1-propanol) indicated a slow conversion to the disulfide which was essentially complete after 2 days. The solution was concentrated to a sirup which was dissolved in methanol containing a little hydrochloric acid. Ether was added and L-cystinol dihydrochloride (VII) (1.91 g., 67%) crystallized. After recrystallization from methanol–ether it had m.p. 145–146°, $[\alpha]^{25}D$ −108° (*c* 1.0 in methanol).

Anal. Calcd. for $C_6H_{16}N_2O_2S_2 \cdot 2HCl$: C, 25.26; H, 6.36; N, 9.82; S, 22.49; Cl, 24.85. Found: C, 25.09; H, 6.15; N, 9.80; S, 22.66; Cl, 24.57.

L-*S*-2-Amino-3-hydroxypropylthiosulfuric Acid (III).—The Bunte salt III was prepared from L-cystinol dihydrochloride as described previously for the DL-isomer except that sodium sulfite was used instead of ammonium sulfite. The product had m.p. 190–193° dec., $[\alpha]^{25}D$ −31° (*c* 0.62 in water).

Electronic Effects on the Stereochemistry of the Diels–Alder Reaction[1]

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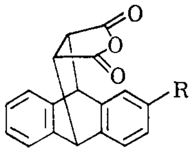
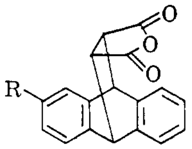
Various 2-substituted anthracenes have been synthesized and their reaction with maleic anhydride investigated. The amounts of the two possible isomers formed, *syn* and *anti*, afforded a medium for the evaluation of the electronic effect on the stereochemistry of the reaction. The results of these studies are discussed.

The Diels–Alder reaction, in which there is the possibility of the formation of more than one product, has been extensively investigated; however, the asymmetrical nature of reacting species has not permitted unequivocal evaluation of the electronic effect in determining the isomer formed.[3] The introduction of a group on the 2-position of the anthracene nucleus permits the formation of two isomeric products in the reaction with maleic anhydride. The amounts of *syn* (I) and *anti* (II) isomers formed would be a function of the substituent. The symmetrical nature of the molecule, except for the substituent, would tend to minimize all other effects which determine the isomer ratio and thus reflect the importance of polar attractive forces in the two possible transition states. The substitution of anthracene in the 2-position rather than the 1-position further removes any steric effect the group may have on the reacting centers.



syn Adduct (I)
a. R = NO_2
b. R = NAc
c. R = $N(Me)_2$



anti Adduct (II)
a. R = NO_2
b. R = NAc
c. R = $N(Me)_2$

The dimethylamino, acetamido, and nitro groups were selected as substituents. The method of Hodgson and Marsden[4] for the replacement of a diazonium group by a nitro group was used to prepare the reported 2-nitroanthracene.[5] Excellent yields of 2-acetamidoanthracene were obtained by the treatment of 2-aminoanthracene with acetic anhydride[6] and lithium aluminum hydride reduction of 2-N,N-dimethylaminoanthracene methiodide in tetrahydrofuran gave 2-N,N-dimethylaminoanthracene.[7]

All Diels–Alder reactions were carried out in refluxing benzene with a ten- to twentyfold excess of freshly sublimed maleic anhydride present. 2-Dimethylaminoanthracene reacted with the appearance of a transient deep red color and the insoluble 2-acetamidoanthracene dissolved slowly as it reacted. The yellow color of the 2-nitroanthracene solution did not intensify as the reaction occurred and disappeared as the reaction approached completion. The relative rates of reaction of 2-nitroanthracene, anthracene, and 2-dimethylaminoanthracene were determined under pseudo first-order conditions similar to those used by Andrews and Keefer.[8]

Compound	k, l./mole sec.
2-Nitroanthracene	0.086×10^{-5}
Anthracene	$.014 \times 10^{-3}$
2-Dimethylaminoanthracene	$.055 \times 10^{-3}$

The spectra of the products exhibited typical succinic anhydride adsorption in the infrared at 5.34 and 5.60 μ.[9] At least one intense band appearing in the spectrum of starting material was completely absent in all cases. The infrared spectra of chloroform, methylene chloride, benzene, or dioxane solutions of pure *syn*- and *anti*-2-nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydrides (Ia and IIa) differed mainly in the 10.0- to 11.0-μ region. Their ultraviolet spectra were similar and as expected for adducts.[10]

The theoretical dipole moments of the two adducts, which contain rigid ring systems free of rotation, were computed from three main components: 9,10-dihydroanthracene (0.4 Debye),[11] succinic anhydride (4.2 Debyes),[12] and nitrobenzene (3.9 Debyes).[13] A value of 7.11 Debyes was obtained for the *syn* adduct and 2.11 Debyes for the *anti* adduct. The measurement of the dielectric constant and refractive index of a series of

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[1] Taken in part from the dissertation of Fred Kaplan presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, September, 1959.

[2] Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio.

[3] J. Martin and R. Hill, *Chem. Rev.*, **61**, 537 (1961).

[4] H. Hodgson and E. Marsden, *J. Chem. Soc.*, 22 (1944).

[5] M. Battegay and P. Boehler, *Compt. rend.*, **203**, 333 (1936).

[6] C. Lieberman and A. Bollert, *Ber.*, **15**, 228 (1882).

[7] A. Bollert, *ibid.*, **16**, 1635 (1883).

[8] L. Andrews and R. Keefer, *J. Am. Chem. Soc.*, **77**, 6284 (1955).

[9] L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 28.

[10] I. Gillet, *Bull. soc. chim. France*, 1135 (1950).

[11] I. Campbell, C. LeFévre, R. LeFévre, and E. Turner, *J. Chem. Soc.*, 404 (1938).

[12] M. Raw and N. Anantanaragan, *Proc. Indian Acad. Sci.*, **5A**, 185 (1937).

[13] L. G. Wesson, "Table of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948, p. 29.

dilute solutions of different concentrations in benzene at a constant temperature[14] established the identities of the adducts.

DIPOLE MOMENT, μ, IN DEBYES

	syn	*Anti*
Calculated	7.11	2.11
Found	6.6 ± 0.9	2.4 ± 1.7

Reduction and acetylation of the *syn*- and *anti*-2-nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydrides (Ia and IIa) to their respective 2-acetamidoanthracene adducts (Ib and IIb) were achieved by the method of Kishi.[15] Major differences occurred in the 10.0-to 11.0-μ region of the infrared spectra of methylene chloride or dioxane solutions of these adducts. The presence of both adducts could not be readily detected in the spectrum of a chloroform solution. The composite spectrum of the *syn* and *anti* adducts was identical with the spectrum of the material obtained from the reaction of 2-acetamidoanthracene with maleic anhydride.

The *syn*-and *anti*-2-dimethylamino-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydrides (Ic and IIc) were obtained by reduction and methylation of the corresponding nitro adducts.[16] The products obtained possessed almost identical infrared spectra in a variety of solvents. The spectra were similar to that of the material obtained from the reaction of 2-dimethylaminoanthracene with maleic anhydride. A difference in chemical shift of the N-methyl peak of the *syn* and *anti* adducts occurred in their nuclear magnetic resonance spectra[17] in deuteriochloroform. The separation of these peaks was enhanced from 2.2 c.p.s. to 8.0 c.p.s. by use of benzene as solvent rather than deuteriochloroform.[18]

Pure *syn* and *anti* adducts of the compounds studied were subjected to reaction conditions for longer periods of time and recovered unchanged. This established that the reaction mixtures obtained were kinetically controlled and that the isomer distribution was a measure of the relative stabilities of the two possible transition states.

The amounts of *syn* and *anti* adducts formed in the reactions of 2-nitroanthracene and 2-acetamidoanthracene with maleic anhydride were determined by quantitative infrared analysis. Comparison of reaction mixture spectra with ones of known concentration confirmed calculated values. Nuclear magnetic resonance spectroscopy was used to analyze the 2-dimethylaminoanthracene–maleic anhydride reaction mixture. Measurement of the relative areas of the two *N*-methyl peaks gave the ratio of the isomers. The following results were obtained:

Group	% *syn*	% *Anti*
NO_2	39 ± 1	61 ± 1
NAc	52 ± 1	48 ± 1
$N(Me)_2$	55 [illegible] 2	45 ± 2

The isomer distribution studies show that the transition state containing the maleic anhydride fragment above the electron-rich aromatic ring is more stable than the other possibility. The ratio of the isomers indicates that the free energies of activation of the two possible transition states differ only by approximately 0.2 kcal. per mole. Many small factors such as the electrostatic interaction[19] of the carbonyl dipole of the maleic anhydride fragment and the greater electron density of one ring can easily account for this small difference.

Although the 2-dimethylaminoanthracene reacts seventy times faster than 2-nitroanthracene the distribution of isomers is not so great. If the dimethylamino group is facilitating a charge transfer of any type, one must assume that the *syn* and *anti* forms resulting from this must be of nearly equivalent energies and do not influence the isomer distribution. It is significant that no major electronic effect be explained in terms of the mechanism of the reaction.

Experimental

Melting points were determined in soft glass capillaries in a Hershberg apparatus and are uncorrected.

Benzin refers to a hydrocarbon solvent boiling at 30–60° and petroleum ether refers to a hydrocarbon solvent boiling at 60–110°. The composition of solvent miztures is described by the volume of the component before mixing.

Analyses were carried out by Dr. S. M. Nagy and his associates at the Massachusetts Institute of Technology, Cambridge, Mass., and Herr W. Manser at the Eidg. Technische Hochschule, Zürich, Switzerland.

2-Aminoanthracene.—The procedure described by Ruggli and Henzi[20] was altered slightly. To a deep red mixture of 200 g. (0.9 mole) of 2-aminoanthraquinone in 1200 cc. of 10% sodium hydroxide solution stirred at room temperature was added 120 g. of zinc dust. The mixture was then brought to a gentle reflux and 25 cc. of 95% ethanol was added to prevent violent foaming. One hundred grams of zinc dust was added every 0.5 hr. until a total of 320 g. (5 moles) was present. After refluxing for 24 hr., the solid material in the brownish yellow mixture was collected and washed with hot water. Soxhlet extraction with acetone removed the 2-aminoanthracene (deep green fluorescence in acetone). Crystallization from hot acetone gave 110 g. (63%) of 2-aminoanthracene; m.p. 236–237°. Recrystallization from toluene afforded 105 g. (60%) of greenish gold plates; m.p. 238–239°; reported[20] m.p. 238°.

2-Anthracenediazonium Cobaltinitrite.—A mixture of 10 g. (0.052 mole) of 2-aminoanthracene and 20 cc. (0.21 mole) of hydrochloric acid (37.5%) was heated on a steam bath in 100 cc. of water for 1 hr. to form the grayish white hydrochloride salt. To this aqueous mixture, maintained below 5°, was added a solution of 4.14 g. (0.06 mole) of sodium nitrite in 25 cc. of water. Additional water (150 cc.) was added slowly to the resulting red mixture to dissolve the insoluble diazonium hydrochloride. After 20 min., sufficient calcium carbonate was added (4 g.) to neutralize any remaining acid. The mixture was filtered under vacuum (to remove insoluble tars and excess calcium carbonate) into a solution of 20.2 g. (0.05 mole) of sodium cobaltinitrite in 500 cc. of water. The resulting red precipitate was collected and washed with cold water and finally with ether.

2-Nitroanthracene.—The solid 2-anthracenediazonium cobaltinitrite was added slowly to a solution of sodium nitrite (10 g.), cupric sulfate (10 g.), and cuprous oxide (4 g.) in 100 cc. of water stirred at room temperature. Foaming occurred upon addition.

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(14) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. 1, Part II, Chap. XXIV, Interscience Publishers, Inc., New York, N. Y., 1949, pp. 1611–1650.

(15) N. Kishi, Japan Patent 4161 (1952); *Chem. Abstr.*, **48**, 5215c (1954).

(16) W. Emerson, U. S. Patent 2,414,031; *Chem. Abstr.*, **41**, 2439b (1949).

(17) Nuclear magnetic resonance spectra were taken with a Varian Associates high resolution spectrometer at 60 megacycles per second. Chemical shifts were measured by the audio-oscillator side-band superposition method with tetramethylsilane as an internal reference in dilute solutions of the compounds examined and are in cycles per second from tetramethylsilane.

(18) J. Pople, W. Schneider, and H. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 422–432.

(19) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 716.

(20) P. Ruggli and E. Henzi, *Helv. Chim. Acta*, **13**, 409 (1930).

After 3 hr. the precipitate was collected and washed with water. Soxhlet extraction of the precipitate with ether yielded a deep red solution. After extraction with 3 *N* hydrochloric acid and 5 *N* sodium hydroxide, the ethereal solution was dried over anhydrous sodium sulfate. Evaporation to dryness yielded 3 g. of red solid. The material was dissolved in a minimum amount of benzene and placed on a chromatography column of aluminum oxide (Woelm, nonalkaline, activity I) prepared in petroleum ether. Elution with 60% petroleum ether–40% benzene removed anthracene. After its complete removal (absence of its characteristic blue fluorescence in solution), a bright yellow band was eluted with benzene. The material obtained upon evaporation of the benzene was crystallized from a hot acetone–petroleum ether mixture twice yielding 1.4 g. (12% from 2-aminoanthracene) of bright yellow needles of 2-nitroanthracene; m.p. 181–182°; reported[5] m.p. 171–172°.

2-Acetamidoanthracene.—Acetic anhydride (35 cc.) and 8.0 g. (0.042 mole) of 2-aminoanthracene were refluxed for 3 hr. The brown solution was cooled to 5° and the resulting white precipitate collected. After the solid material was washed with saturated sodium bicarbonate solution, it was dissolved in hot acetone and placed on a chromatography column of alumina (Fisher, no. A-540) prepared in chloroform. Acetone elution first removed a black impurity. Continued elution with acetone yielded 2-acetamidoanthracene. One crystallization from hot acetone gave 7.7 g. (80%) of light yellow plates of 2-acetamidoanthracene; m.p. 244–245°; reported[21] m.p. 239–240°.

2-N,N-Dimethylaminoanthracene Methiodide.—A mixture of 1.93 g. (0.07 mole) of 2-aminoanthracene and 1.08 g. (0.02 mole) of sodium bicarbonate was heated at 110° in 30 cc. of methyl iodide with a trace of methanol for 8 hr. The precipitate was collected and washed with water and ether. It was then crystallized twice from hot dilute ammonium hydroxide solution yeilding 2.84 g. (73%) of pale yellow plates of 2-dimethylaminoanthracene methiodide; m.p. 227–229°; reported[7] m.p. 215° dec.

2-N,N-Dimethylaminoanthracene.—Three grams (8.56 mmoles) of 2-dimethylaminoanthracene methiodide and 1.50 g. (0.04 mole) of lithium aluminum hydride were refluxed in purified tetrahydrofuran for 4 hr. After decomposition of excess lithium aluminum hydride by the addition of water, the tetrahydrofuran was removed under vacuum. Sodium hydroxide pellets were added to dissolve the aluminum salts and the aqueous layer was extracted with ether. The greenish ethereal layer was dried over anhydrous sodium sulfate and evaporated to dryness, yielding 1.9 g. of a bright yellow solid. The material, dissolved in 60% benzene–40% petroleum ether, was chromatographed over an aluminum oxide (Woelm, almost neutral, activity I) column prepared in petroleum ether. Elution with 40% benzene–60% petroleum ether first yielded anthracene. Continued elution with this solvent mixture gave yellow material. It was crystallized from a benzene–petroleum ether mixture yielding 511 mg. (27%) of yellow needles of 2-dimethylaminoanthracene; m.p. 158–160°; reported[7] m.p. 155°.

Reaction of 2-N,N-Dimethylaminoanthracene with Maleic Anhydride.—A greenish yellow solution of 22 mg. (0.1 mole) of 2-dimethylaminoanthracene in 1 cc. of benzene was added to a refluxing solution of 200 mg. (2.0 mmoles) of freshly sublimed maleic anhydride in 1 cc. of benzene. A deep red color appeared immediately. After 2 hr. the light tan solution was evaporated to dryness and the excess maleic anhydride removed by sublimation at 110° and 10^{-3} mm. The 31.3 mg. (98.5%) obtained was used for quantitative analysis.

Reaction of 2-Acetamidoanthracene with Maleic Anhydride.—A mixture of 34.4 mg. (0.14 mmole) of 2-acetamidoanthracene and 105 mg. (1.1 mmoles) of freshly sublimed maleic anhydride was refluxed in 1.5 cc. of benzene. A deep yellow color resulted as the insoluble 2-acetamidoanthracene slowly went into solution. After 4 hr. the now colorless solution was evaporated to dryness and the excess maleic anhydride sublimed at 110° and 10^{-3} mm. The 49.3 mg. (100%) obtained was used for quantitative analysis.

Reaction of 2-Nitroanthracene with Maleic Anhydride.—1. A yellow solution of 35.1 mg. (0.16 mmole) of 2-nitroanthracene and 100 mg. (1.0 mmole) of freshly sublimed maleic anhydride in 2 cc. of benzene was refluxed for 26 hr. The yellow color still remained. An additional 100 mg. (1.0 mmole) of maleic anhydride was added and the solution refluxed for 30 hr. A faint yellow color still remained. No change in color was observed on continued refluxing or addition of more maleic anhydride. The solvent was evaporated and the excess maleic anhydride removed by sublimation at 110° and 10^{-3} mm. The 49.9 mg. (98.8%) of material obtained was used for quantitative analysis.

2. A solution of 1.079 g. (4.83 mmoles) of 2-nitroanthracene and 5.88 g. (60.0 mmoles) of freshly sublimed maleic anhydride in 50 cc. of benzene was refluxed for 48 hr. The slightly yellow solution was evaporated to dryness. An ethereal solution of the remaining material was extracted with saturated sodium bicarbonate solution to remove excess maleic anhydride. Evaporation of the ethereal layer, after drying over anhydrous sodium sulfate, gave 1.550 g. (100%) of a yellowish white solid. The material, dissolved in 20% acetone–80% benzene, was placed on a chromatography column of silicic acid (Mallinckrodt 100 mesh, no. 2847) prepared in benzene. The column was then washed with petroleum ether to quench any movement caused by the acetone. Elution with benzene first removed traces of impurities. The next fractions contained *anti*-2-nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydride, IIa (identified later), characterized by bands at 10.57 and 10.87 μ in its infrared spectrum in methylene chloride, contaminated with small amounts of the *syn* adduct (Ia), characterized by a band at 10.70 μ. Additional elution with benzene gave fractions consisting of approximately equal amounts of both isomers. Finally, enriched fractions of the *syn* adduct were obtained. The enriched fractions of each adduct were crystallized many times from hot chloroform–petroleum ether until pure adducts were obtained (constant melting point and absence of bands of the other adduct in the infrared spectrum). This procedure gave 437 mg. (28%) of white needles of the *anti* adduct, m.p. 249–250°, and 389 mg. (25%) of white plates of the *syn* adduct, m.p. 279–280°. The adducts were crystallized four times more from hot acetone–petroleum ether and still possessed the same melting points and infrared spectra. These materials were used in the dipole moment determination and quantitative analysis.

Anal. [*anti*-2-Nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydride (IIa)]. Calcd. for $C_{18}H_{11}O_5N$: C, 67.29, H, 3.48; N, 4.36. Found: C, 67.25; H, 3.59; N, 4.47. Ultraviolet spectrum (methanol): λ_{max} 279.5 mμ, ϵ 8000.

Anal. [*syn*-2-Nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydride (Ia)]. Calcd. for $C_{18}H_{11}O_5N$: C, 67.29; H, 3.48. Found: C, 67.19; H, 3.45. Ultraviolet spectrum (methanol): λ_{max} 282 mμ, ϵ 8900.

Dipole Moment Determination.—The *syn*- and *anti*-2-nitroanthracene–maleic anhydride adducts have been described previously. A series of dilute benzene (b.p. 80.0–80.2°, $n^{25}\text{D}$ 1.4981) solutions were prepared.

The dielectric constant measuring apparatus[22] was maintained at 25°. The bridge measuring circuit consisted of a 300-kc./sec. oscillator, two equal resistors, two fixed capacitors, a variable capacitor, and a detection system. The cell was of brass and approximately 3.5 in. in diameter and 2 in. in height and contained a variable and a fixed capacitor. The variable capacitor was a micrometer–electrode system type[23] adapted for liquids.

Refractivities were measured on an Abbe refractometer and were referred to the sodium D line at 25°.

DIPOLE MOMENT, $\mu = 0.0128[(P_2 - R_2)T]^{1/2}$

	P_2	R_2	μ
anti Adduct	219 ± 110	100 ± 109	2.40 ± 1.71
syn Adduct	988 ± 141	101 ± 114	6.58 ± 0.88

Reductive Acetylation of *syn*- and *anti*-2-Nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic Anhydrides (Ia and IIa) to *syn*- and *anti*-2-Acetamido-9,10-dihydroanthracene-9,10-*endo*-α,β succinic Anhydrides (IIa and IIb).—A solution of 26.0 mg. (0.081 mmole) of the *anti*-2-nitroanthracene–maleic anhydride adduct in 5 cc. of acetic anhydride and 0.5 cc. of glacial acetic acid was stirred in an atmosphere of hydrogen in the presence of Raney nickel for 3 hr. at 70°. A white solid was obtained after removal of the catalyst by filtration and evaporation of the filtrate. Extraction of this solid with chloroform gave 28 mg. of material. This material, dissolved in chloroform, was filtered through a

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(21) P. Fedorov, *Izv. Akad. Nauk, USSR, Otd. Khim. Nauk,* **582** (1951); *Chem. Abstr.,* **46,** 8077f (1951).

(22) We are indebted to Mr. William B. Westphal of Insulation Research Laboratory, Massachusetts Institute of Technology, Cambridge, Mass., for the use of his apparatus.

(23) A. von Hippel, "Dielectric Materials and Applications," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 50.

small column of silicic acid prepared in chloroform. Ether elution yielded 26 mg. (96%) of material whose infrared spectrum (dioxane) possessed all major bands present in the spectrum of the material obtained from the reaction of 2-acetamidoanthracene with maleic anhydride except one at 10.70 μ. The material was crystallized to a constant melting point from an acetone–benzene mixture by slowly boiling off the acetone. The white plates obtained changed at 146°, became amorphous at 160°, and liquid at 166°. Ultraviolet spectrum (methanol): λ_{max} 253 mμ, ϵ 16,000; λ_{max} 287 mμ, ϵ 1500.

Anal. Calcd. for $C_{20}H_{15}O_4N$: C, 72.06; H, 4.54; N, 4.20. Found: C, 71.85; H, 4.62; N, 4.26.

Reductive acetylation of the *syn* adduct yielded material which possessed in its infrared spectrum all bands present in the spectrum of the material obtained from the reaction of 2-acetamidoanthracene with maleic anhydride except one at 10.80 μ. Crystallizations from acetone–benzene gave white needles, m.p. 149–150°. Ultraviolet spectrum (methanol): λ_{max} 253 mμ, ϵ 16,000; λ_{max} 287 mμ, ϵ 1500.

Anal. Calcd. for $C_{20}H_{15}O_4N$: C, 72.06; H, 4.54; N, 4.20. Found: C, 72.53; H, 4.73; N, 4.01.

Reductive Methylation of *syn*- and *anti*-2-Nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic Anhydrides (Ia and IIa) to *syn*- and *anti*-2-Dimethylamino-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic Anhydrides (Ic and IIc).—A solution of 128 mg. (0.4 mmole) of the *anti*-2-nitroanthracene–maleic anhydride adduct in 5 cc. of 95% ethanol, 0.5 cc. of glacial acetic acid, and 0.4 cc. of 36% formaldehyde solution was hydrogenated in the presence of 15 mg. of Adam's catalyst. An uptake of 55 cc. of hydrogen (expected for $-NO_2$ to $-N(CH_3)_2$, 49 cc.) occurred over a period of 24 hr. The solution was evaporated to dryness after removal of the catalyst. The material was extracted with aqueous ether. The ethereal extract, after drying over anhydrous sodium sulfate and evaporation, yielded 107 mg. of material. The white solid was refluxed in 30 cc. of benzene for 20 min. After evaporation of the solvent, 105 mg. (82%) of material was obtained whose infrared spectrum was almost identical with that of the material obtained from the reaction of 2-dimethylaminoanthracene with maleic anhydride. Crystallizations from a methylene chloride–petroleum ether mixture afforded off-white plates, m.p. 208–209°. Ultraviolet spectrum (methanol): λ_{max} 270 mμ, ϵ 12,000; λ_{max} 310 mμ, ϵ 24,000.

Reductive methylation of the *syn* adduct required a longer period of time. The infrared spectrum of the material obtained (79%) was similar but not identical with that of the *anti* adduct. No major difference existed.

Reaction Mixture Analysis.—The ratio of adducts obtained from reaction mixtures of 2-nitroanthracene and 2-acetamidoanthracene with maleic anhydride were determined by quantitative infrared analysis. A variation of the "cell in-cell out" method[24] was used. A constant incident intensity (100% transmission) and zero reading (0% transmission) were obtained in the 10.5- to 11.0-μ region for all samples. Beer's law for a two-component system was used to calculate the composition of the mixture.

The 2-nitroanthracene-maleic anhydride reaction mixture was found to be composed of 39.2% of the *syn* adduct and 60.8% of the *anti* adduct. The 10.57- and 10.87-μ bands of the *anti* adduct and the 10.70 μ band of the *syn* adduct were utilized for the analysis. The 2-acetamidoanthracene–maleic anhydride reaction mixture contained 52.0% of the *syn* adduct absorbing at 10.70 μ and 48.0% of the *anti* adduct absorbing at 10.80 μ. Analyses were performed on solutions of known concentration similar to those of the unknowns using the same technique. The analyses were in good agreement and accurate to 0.3%.

The composition of the reaction mixture of 2-dimethylaminoanthracene and maleic anhydride was determined by analysis of its nuclear magnetic resonance spectrum in benzene solution. The *N*-methyl peaks of the *syn*- and *anti*-dimethylamino adducts appeared at 141 and 149 c.p.s., respectively. The relative areas of the two peaks were determined. The mixture was composed of 45% of the *anti* adduct and 55% of the *syn* adduct. The method of analysis was accurate to 2%.

Attempted Equilibration of *syn*- and *anti*-Adducts.—The infrared spectrum of 5 mg. of pure *syn*- or *anti*- adduct in 0.5 cc. of benzene was recorded. The infrared spectrum of the solution after refluxing for 1 week was identical with that of starting material. To this solution was added 10 mg. of maleic anhydride. After refluxing the solution for 24 hr., no change was observed in the spectrum. No change occurred in the nuclear magnetic resonance spectra of the 2-dimethylaminoanthracene adducts.

Kinetic Data.—Benzene solutions of known concentration (0.00469 *M* anthracene, 0.000158 *M* 2-dimethylaminoanthracene, 0.000184 *M* 2-nitroanthracene—all with 1.2806 *M* maleic anhydride) were placed in a 1-cm. quartz spectrophotometric cell. Five minutes were allowed for complete mixing to occur before initial readings were taken. Measurements of optical density were made with a Beckman DU spectrophotometer at 420 mμ. Only starting material was found to absorb at this wave length. The values of the rate constants, *k*, were determined from the first-order rate expression $k = 2.303 \log (ODi/ODt)/(MA)t$.

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[24] *Perkin-Elmer Instrument News*, **II**, **3**, 6 (1951).

Reactions of Ethylene Diisothiocyanate with Primary and Secondary Amines[1]

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Ethylene diisothiocyanate (I) reacts with an excess of aqueous methylamine and ethylamine to give 1-methyl- and 1-ethylthiocarbamylimidazolidine-2-thione (Va, b). The phenyl analog (Vc) has been obtained upon addition of aniline to I in acetone solution, whereas the reverse mode of addition yielded the substituted ethylenedithiourea (II). Structures Va, b, and c have been prepared by independent syntheses. Reaction of I with excess aqueous dimethylamine and pyrrolidine gave almost exclusively the ethylenedithioureas; with excess of aqueous piperidine, a mixture of bis- and monoadduct was formed. The monoadducts could be conveniently obtained from all the secondary amines studied, by adding them to I in acetone solution. The properties of these monoadducts are consistent with the structures 1-dialkyl- and 1-alkylenethiocarbamylimidazolidine-2-thione, similar to those of Va, b, and c.

Ethylene diisothiocyanate (I) has been reported to react with aqueous ammonia forming ethylenedithiourea (II. R = R' = H) and a monoadduct for which structure III has been formulated.[2] Alkylene dithioureas had been obtained previously by treating I with aniline,[3] as well as by treating the homolog $(CH_2)_4(NCS)_2$ with ammonia, methylamine, and aniline,[4] and $(CH_2)_6(NCS)_2$ with aziridine.[5]

The structure of the monoadduct formed by the reaction of I with ammonia currently is being elucidated in our laboratories by X-ray diffraction.[6] In this

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[1] Part of this work has been treated in a preliminary communication: F. D'Angeli and A. Bandel, *Tetrahedron Letters*, **1**, 5 (1961).

[2] G. D. Thorn and R. A. Ludwig, *Can. J. Chem.*, **32**, 872 (1954).

[3] A. Ya. Yakubovic and V. A. Klimova, *J. Gen. Chem. USSR* (Eng. Transl.), **9**, 1777 (1939); *Chem. Abstr.*, **34**, 3685 (1940).

[4] J. v. Braun and G. Lemke, *Ber.*, **55**, 3552 (1922).

[5] A. G. Bayer, British Patent 753, 247; *Chem. Abstr.*, **51**, 9681 (1957).

[6] Unpublished work.