Some Diels–Alder Reactions of Naphthacene

JOHN S. MEEK, FREDERICK M. DEWEY,[1a] AND MELVIN W. HANNA[1b]

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received August 27, 1965

Naphthacene has been condensed with ethylene, acrylonitrile, allyl alcohol, methyl acrylate, and acrylamide. The last four reactions gave both possible adducts in almost identical ratios. A slight excess of the adduct having the dienophile substituent *syn* to the benzene ring was obtained in each case.

Many polynuclear aromatic compounds theoretically should undergo a Diels–Alder reaction with maleic anhydride, or similar dienophile, to give two or more isomeric adducts differing in their *exo–endo* or *syn–anti* stereochemistry. About 50 such cases have now been reported and in general only one adduct has been found. This seems to indicate a preferential mode of addition exists. Examples are the condensation of 2 equiv of maleic anhydride with pentaphene[2] and with dibenzo-[*b*,*i*]phenazine.[3] In each case six diadducts may conceivably form; yet only one has been reported, the latter in a yield of over 80%.

In these cases and in almost all of the others, the stereochemistry of the adducts has not been investigated.

Two adducts of maleic anhydride and 2-naphthol have been obtained[4] and structures were assigned on the basis of dipole moments. The major adduct had the anhydride ring *syn* to the benzene moiety. Both maleic anhydride adducts of naphthalene have been obtained and the ratio of the two adducts is reported to be 57:43, and again the major adduct had the anhydride ring as before.[5]

However, the maleic anhydride adduct of 2,3-dimethylnaphthalene has been reported to have the anhydride ring *anti* to the benzene moiety since on warming in methanol the half-ester formed gave a bromo lactone[6] on treatment with sodium carbonate and bromine. Spectroscopic evidence of a second adduct was claimed but it was not isolated.[6]

Pleiadene yielded only one adduct with N-phenylmaleimide and on the basis of its nmr spectrum it was believed to be the *exo* adduct with the maleimide group *syn* to the benzene ring.[7]

Acepleiadylene and acepleiadene each gave only one adduct and that of the former could be hydrogenated to that of the latter and the adducts were assigned the *exo* configuration by analogy.[7]

Maleic anhydride on condensation with 2-nitro-, 2-acetamido-, and 2-dimethylaminoanthracene has given both possible adducts. Structures assigned rest on the dipole moments of the nitro products. As the substituent changed from an electron-attracting to an electron-donating group the major adduct changed from 61% *anti* to 55% *syn*.[8] The effect of the acetamido group is almost indistinguishable from that of the dimethylamino group and little preference is really shown by these substituents.

Results and Discussion

In the present work it was hoped that the bridge hydrogen atoms of 5,12-dihydro-5,12-ethanonaphthacene would be affected differently by the ring currents of the benzene and naphthalene moieties and the nmr spectrum would aid in the elucidation of the structure of the maleic anhydride adduct.

Therefore, ethylene was condensed with naphthacene but the bridge protons could not be separated in the nmr spectrum obtained. The dipole moment of this adduct was 0.1 D.[9] greater than 9,10-dihydro-9,10-ethanoanthracene[10] which is consistent with the observation that the dipole moment of 2,3-dimethylnaphthalene is greater than *o*-xylene.[11] This suggested that the acrylonitrile adducts of naphthacene might be differentiated through their dipole moments.

Condensation of naphthacene and acrylonitrile gave a solid product which was separable into isomeric adducts by fractional crystallization. The lower melting isomer had a dipole moment of 3.38 ± 0.05 D. and the other 3.52 ± 0.05 D.[9] Therefore, the first compound was assigned structure **1a** and the second **1b**, although the differences in the dipole moments are just outside the experimental error. However, the structure assignments were based on their relative magnitudes and not on absolute values.

The nmr spectra of the two isomers confirmed this structural assignment. The aromatic region of the nmr spectrum of 5,12-dihydro-5,12-ethanonaphthacene consisted of a pair of overlapping A_2B_2 patterns from the hydrogens on the two terminal rings, plus a singlet from the uncoupled and magnetically equivalent C_6 and C_{11} hydrogens. This singlet appeared at τ 2.38. In the spectrum of the lower melting isomer **1a**, the A_2B_2 part of the aromatic region changed appreciably but the singlet from C_6 and C_{11} protons remained at τ 2.35. In the spectrum of the higher melting isomer, however, the intensity of the singlet at τ 2.30 was reduced to one-half of its original value and a new singlet at τ 2.16 appeared with equal intensity. This corresponds to a downfield shift of 0.140 ppm.

This result conclusively shows that the higher melting isomer has the structure **1b**. A consideration of the Dreiding model shows the center of the carbon–nitrogen triple bond lies over the proton at the 11 position. The magnetic anisotropy of the nitrile group consequently causes a downfield shift of this proton. A calculation of the expected downfield shift using dis-

(1) (a) National Science Foundation Predoctoral Fellow, 1963–1965; (b) Alfred P. Sloan Fellow, 1965–1967.

(2) E. Clar, *Ber.*, **65**, 503 (1932).

(3) J. A. VanAllan, R. E. Adel, and G. A. Reynolds, *J. Org. Chem.*, **27**, 2873 (1962).

(4) K. Takeda and K. Kitahonoki, *J. Pharm. Soc. Japan*, **71**, 860 (1951); *Chem. Abstr.*, **46**, 8073*g* (1952).

(5) K. Takeda, K. Kitahonoki, M. Sugiura, and Y. Takano, *Chem. Ber.*, **95**, 2344 (1962).

(6) P. Yeats and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960).

(7) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3051 (1965).

(8) F. Kaplan and J. Conroy, *J. Org. Chem.*, **28**, 1593 (1963).

(9) T. S. Gilman, University of Colorado, unpublished work.

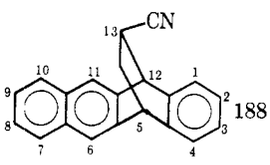
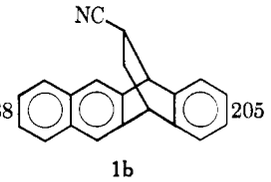
(10) D. D. Tanner and T. S. Gilman, *J. Am. Chem. Soc.*, **85**, 2892 (1963).

(11) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, pp 292, 415.

tances and angles calculated from Dreiding models (R = 3.88 A, θ = 78°, and a value of the magnetic anisotropy[12] of 16.5 × 10^{-6} cm^3/mole) gave a value of 0.136 ppm, in excellent agreement with the experimentally observed shift of 0.140 ppm.

Treatment of each nitrile with acid and then methanol gave the related methyl esters **2a** and **2b**. Condensation of allyl alcohol and naphthacene led to a mixture from which one adduct was readily obtained. The isomeric adduct **3b** was obtained by reduction of **2b**. The Diels–Alder reaction of naphthacene and acrylamide gave two different amides of almost identical melting points and one of these on dehydration with phosphorus pentoxide produced **1a**. (See Table I).

TABLE I

Ratio of a to b	Compd	Mp, °C	Compd	Mp, °C
>1:1	$-CONH_2$ **4a**	268	$-CONH_2$ **4b**	267
	$\downarrow P_2O_5$			
54:46 ± 1	 **1a**	188	 **1b**	205
	$\downarrow$ HCl, CH_3OH		$\downarrow$ HCl, CH_3OH	
57:43 ± 1	CO_2CH_3 **2a**	169	$-CO_2CH_3$ **2b**	184
			$\downarrow LiAlH_4$	
57:43 ± 2	$-CH_2OH$ **3a**	162	$-CH_2OH$ **3b**	153

With both possible adducts now on hand, gas–liquid partition chromatography, utilizing the half-height method,[13] was used to analyze the raw reaction mixtures coming from the Diels–Alder reactions of acrylonitrile and methyl acrylate at 130–160°, and allyl alcohol at 208°. The amides were not volatile enough for this type of analysis and infrared was used instead.

It is to be noted that despite the differences in temperatures at which the adducts were prepared the relative ratio of **a** to **b** isomers showed almost no variation and the isomer with the substituent *syn* to the benzene moiety predominated in each case. When **1b** was heated with acrylonitrile under conditions leading to its formation it was not converted into its isomer nor was the amide **4b** isomerized in boiling xylene. Therefore, the product composition is due to kinetic control and the energy needed to reach the transition state leading to one isomer is almost identical with that leading to the other adduct.

The slight difference appears to reside in the diene rather than the dienophile. Kaplan and Conroy,[7] as noted above, found a greater variation by changing the diene system and keeping the dienophile constant. They noted for their 2-substituted anthracenes "that the transition state containing the maleic anhydride fraction above the electron rich aromatic ring is more stable than the other possibility." This would lead one to predict that the major adducts of naphthacene should be **1b**, **2b**, **3b**, and **4b** instead of the isomers found.

Kaplan and Conroy point out that with the ratios of adducts found for their system the free energies of activation of the two possible transition states differ only by approximately 200 cal/mole. Their ratio of the adducts of 2-acetamido and 2-dimethylamino anthracene, the ratio for those of naphthalene[5] and the ones reported above for naphthacene are almost identical.

In the naphthacene adducts there seem to be no steric or electronic factors which would lead one to predict the formation of one adduct to predominate markedly and one really should expect an approximately 50:50 mixture. Such is the case with almost all the systems so far reported. The most likely exception would be the Diels–Alder reaction of the benzoquinolizium cation where isomeric adducts were sought but not found.[14]

Experimental Section

Preparation of 5,12-Dihydro-5,12-ethanonaphthacene.—A slurry of 1.90 g of naphthacene and 0.1 g of hydroquinone in 50 ml of toluene was placed in a 0.5-l. stainless steel reaction bomb which was then charged with ethylene at about 300 psi. The reaction mixture was heated at 200–225° for 41 hr during which time the pressure rose to 550 psi. After being removed from the bomb the toluene was evaporated and the product was dissolved in benzene. This solution was then passed through an alumina column. The colorless fractions were combined and crystallized from benzene to give 0.91 g (43%), mp 168–172°. Two additional recrystallizations from benzene gave the analytical sample, mp 170–172°.

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93,80; H, 6.26.

The infrared spectrum showed a strong doublet at 13.30 and 13.53 μ.

The nmr spectrum, run in deuteriochloroform, showed a very closely grouped set of lines at τ 8.24 (ethano hydrogens) and what appeared to be a poorly resolved triplet at 5.68. The areas under these peaks were in the ratio of 2:1. The aromatic region was complex and consisted of a pair of overlapping A_2B_2 spectra plus a fairly sharp singlet at τ 2.38. Concentrations were about 0.1 M, and TMS was used as an internal reference.

The dipole moment was measured by Professor T. S. Gilman and a tentative value of 0.95 D. was obtained in comparison with 0.81 D. published for 9,10-dihydro-9,10-ethanoanthracene.[9]

Addition of Acrylonitrile to Naphthacene.—A mixture of 8.5 g of naphthacene (0.037 mole), 20 ml of freshly distilled acrylonitrile (approximately 0.5 mole), and 0.1 g of hydroquinone was heated in a sealed tube at 160–164° for 3 hr. The resulting brown solution was washed from the tube with benzene and a small amount of insoluble solid was removed by filtration. Examination of the infrared spectrum of the solid showed that it was polymeric material and it was discarded. The solution was extracted three times with water to remove acrylonitrile and once with saturated sodium chloride solution and dried over calcium chloride. After filtration of the solution the solvent was evaporated and the resulting brown oil was chromatographed on an alumina (Merck, acid washed) column 5.6 cm in diameter and 56 cm long. The mixture was added to the column in carbon tetrachloride, developed with carbon tetrachloride–benzene mixtures, and eluted with benzene and ether. Careful inspection of the infrared spectra of the fractions indicated that no separation was accomplished. The two isomers were then separated by frac-

(12) G. S. Ready and J. H. Goldstein, *J. Chem. Phys.*, **39**, 3509 (1963).

(13) S. Dal Nogare and R. S. Juvet, Jr., "Gas–Liquid Chromatography," Interscience Publishers, Inc., New York, N. Y., 1962, p 255.

(14) C. K. Bradsher and T. W. G. Solomons, *J. Am. Chem. Soc.*, **80**, 933 (1958).

tional recrystallization from ethyl acetate–petroleum ether (bp 60–70°) mixtures and methanol. The total yield of crystalline products was 8.93 g (85%). The melting point of *syn*-13-cyano-5,12-dihydro-5,12-ethanonaphthacene[15] (**1a**) was 185–188°; *anti*-13-cyano-5,12-dihydro-5,12-ethanonaphthacene (**1b**) had mp 203.5–206°.

Anal. Calcd for $C_{21}H_{15}N$: C, 89.64; H, 5.37; N, 4.97. Found (for **1a**): C, 89.37; N, 5.47. Found (for **1b**): C, 89.46; H, 5.36.

The dipole moments of **1a** and **1b** were determined (in benzene at 25.00°) to be 3.38 ± 0.05 and 3.52 ± 0.05 D., respectively.[8]

The infrared spectrum of **1b** showed a nitrile absorption at 4.48 and an absorption at 13.27 μ. The spectrum of **1a**, in addition to the absorption at 4.48, showed absorptions at 13.04 and 13.40 μ.

The nmr spectra of **1a** and **1b** in deuteriochloroform were identical in the τ 5–10 region. The C_{12} hydrogen gave a doublet at τ 5.42 and the C_5 hydrogen a triplet at 5.60. A multiplet centered at τ 7.16 was assigned to the C_{13} hydrogen (α to the CN), and a second multiplet centered at 7.92 was assigned to the two C_{14} hydrogens. The details of the aromatic region of the spectra appear in the discussion section.

Treatment of 0.15 g of **1b** with 1 ml of acrylonitrile (practical) in a sealed tube at 160–166° for 4 hr resulted in no change (vpc analysis).

A second sample of the crude mixture was prepared by heating 0.40 g of naphthacene with 2 ml of acrylonitrile and a pinch of hydroquinone at 160–166° for 3 hr. The mixture was dissolved in benzene and the solution was rapidly passed through a short column of alumina in order to remove any polymeric material. This mixture was then analyzed by vapor phase chromatography on a 1-m column prepared from 0.25-in. copper tubing and packed with QF-1-0065 fluorosilicone, 15% w/w, on Anakrom ABS, 70–80 mesh. Complete separation was not achieved at 224° with a flow of helium of 55 cc/min. Compound **1a** was eluted first, R_t = 34.6 min, followed closely by **1b**, R_t = 37.6 min. The relative areas were determined by the half-height method to be 54 ± 1% **1a**, and 46 ± 1% **1b**. The peaks were identified by adding first **1a** and then **1b** to the mixture and observing which peak area was increased. In order to check the method of area measurement a mixture of 54% **1b** and 46% **1a** was prepared by mixing 6.4 mg of **1b** with 5.5 mg of **1a** and its analysis gave 54% **1b** and 46% **1a**.

Preparation of *syn*- and *anti*-Methyl 5,12-Dihydro-5,12-ethanonaphthacene-13-carboxylate.—A solution of 0.0868 g of **1a** in 40 ml of ether was chilled in an ice bath and saturated with anhydrous hydrogen chloride. To the cold solution was added 2.5 ml of methyl alcohol. After a stream of hydrogen chloride was passed over the solution for 15 min the flask was stoppered and chilled at −40° for 1 day. The hydrogen chloride salt of the imino ether was collected by filtration. Hydrolysis to the methyl ester was accomplished by warming the salt for a few minutes with dilute hydrochloric acid in 50% methanol. The mixture was neutralized with sodium bicarbonate and the product was collected and washed with water. The dry solid weighed 0.0623 g (64%) and melted at 159–165°. Recrystallizations from ethanol and methanol raised the melting point of **2a** to 167.5–169.0°.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.87; H, 5.66.

The infrared spectrum showed a carbonyl absorption at 5.80 and strong absorptions at 8.30, 11.35, 13.02, and 13.35 μ.

A cold solution of 0.14 g of **1b** in dry ether was treated similarly. Crystals of **2b** weighing 0.08 g having a melting point of 175–181° separated from the solution after it had stood for 1 week at room temperature. Three recrystallizations from methanol raised the melting point to 182–184°. A mixture of **2a** and **2b** gave a melting point depression.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.24; H, 5.53.

The infrared spectrum showed a carbonyl absorption at 5.79 and strong absorptions at 8.31 and 13.24 μ.

Addition of Methyl Acrylate to Naphthacene.—A mixture of 0.40 g of naphthacene (1.8 mmoles), 5 ml of methyl acrylate (5.2 g, 0.06 mole), and 0.05 g of *p*-*t*-butylcatechol was heated in a sealed Pyrex tube at 126–135° for 11 hr. The resulting brown oil was washed from the tube with acetone and the solvent was evaporated. The product, a yellow solid mixed with gummy material, weighed 0.64 g and smelled of methyl acrylate. Compound **2b** was eluted first, R_t = 50.2 min, followed closely by **2a**, R_t = 54.5 min. The relative areas were determined by the half-height method to be 57 ± 2% **2a** and 43 ± 2% **2b**.

***syn*- and *anti*-5,12-Dihydro-5,12-ethano-13-naphthacylmethanol.**—A mixture of 3.0 g of naphthacene, 15.5 ml of allyl alcohol, and 0.1 g of hydroquinone was heated in a sealed tube at 149–153° for 20 hr with almost no reaction occurring. Heating for an additional 7 hr at 182° also failed to effect complete reaction. Finally after 60 hr at 202° all but a small amount of naphthacene had reacted. The product, a thick oil, was chromatographed on alumina, but no separation was accomplished. Fractional recrystallization of the mixture from benzene–petroleum ether mixtures gave a small amount of pure *syn*-5,12-dihydro-5,12-ethano-13-naphthacylmethanol (**3a**), mp 161.0–162.5°.

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.33. Found: C, 88.33; H, 6.21.

The infrared spectrum showed an OH absorption at 3.00 and strong absorptions at 9.81, 13.23, and 13.45 μ.

Repeated recrystallizations of the mother liquors failed to yield pure **3b**; therefore, a solution of 0.062 g of **2b** was reduced by lithium aluminum hydride and yielded 0.038 g (68%) of pale yellow crystals of **3b** melting at 150–153°. When **3a** and **3b** were mixed, the melting point was depressed. Recrystallizations from benzene–petroleum ether and methanol gave the analytical sample of **3b** which melted at 150.5–153.0°.

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.33. Found: C, 87.86; H, 6.28.

The infrared spectrum showed and OH absorption at 3.00, medium absorptions at 9.39 and 9.68, and a strong absorption at 13.48 μ.

A mixture of 0.40 g of naphthacene (1.8 mmoles), 5 ml of allyl alcohol, and 0.05 g of *p*-*t*-butylcatechol was heated in a sealed Pyrex tube at 204–208° for 28 hr. Shorter reaction times at lower temperatures left varying quantities of unchanged naphthacene. The brown liquid was washed from the tube with acetone and the solvent was evaporated at reduced pressure. The resulting thick, brown oil, which weighed 0.77 g, was analyzed by vapor phase chromatography as before. Separation was incomplete at 230° with a flow of helium of 80 cc/min. Compound **3a** was eluted first, R_t = 43.6 min, followed by **3b**, R_t = 46.3 min, and the product composition was found to be 57 ± 2% **3a** and 43 ± 2% **3b**.

Addition of Acrylamide to Naphthacene.—A mixture of 2.20 g of naphthacene (9.7 mmoles), 2.06 g of acrylamide (29 mmoles), 0.1 g of *p*-*t*-butylcatechol, and 30 ml of xylene was refluxed for 11 hr. The solvent was evaporated, and the tan product was thoroughly washed with water and dried in a desiccator. The crude yield was 3.17 g, and the product melted at 200–250°. A small sample of the crude product was saved for analysis and the remainder was chromatographed on neutral alumina. A column, 2.3 × 56 cm, was prepared in petroleum ether using a 70:1 ratio of alumina to crude product. The amide mixture was added to the column in chloroform, developed with a graded series of solvents, and eluted with chloroform. The first fractions which contained amide were almost pure *syn*-5,12-dihydro-5,12-ethanonaphthacene-13-carboxamide (**4b**). Several recrystallizations from methanol gave the analytical sample which melted at 265–267°.

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.24; H, 5.72; N, 4.67. Found: C, 84.15; H, 5.69.

The infrared spectrum showed amide I and II bands at 6.05 and 6.20, respectively, and an absorption at 13.25 μ.

After elution of a fraction containing a mixture of **4a** and **4b** almost pure **4b** was eluted. Several recrystallizations from methanol again gave the analytical sample, mp 266.0–268.6°.

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.24; H, 5.72; N, 4.67. Found: C, 84.48; H, 5.87.

The infrared spectrum showed amide I and II bands at 6.05 and 6.20, respectively, and absorptions at 13.15 and 13.50 μ. Inspection of the infrared spectrum of the crude mixture in the 13.0–13.5-μ region and comparison with the spectrum of a 1:1 mixture of **4a** and **4b** indicated that **4a** was present in slightly greater amount.

No change resulted when 0.072 g of **4b** in 4 ml of *p*-xylene was refluxed for 1 day (infrared and melting point).

A 0.23-g sample of **4a** (0.77 mmole) was finely ground and intimately mixed with 0.3 g of phosphorus pentoxide. The dry

(15) The *syn*–*anti* relation is in regard to the relationship of the substituent at the 13 position and the benzene moiety.

mixture was heated on an oil bath at 135–140° for 1 hr during which time it was stirred with a glass rod. After cooling, ice water was carefully added to remove excess phosphorus pentoxide. The aqueous mixture was extracted with ether, the solution was dried over sodium sulfate, and the solvent was evaporated. The yield was 0.20 g (91%), mp 177–183°. The product was dissolved in methanol, decolorized with charcoal, concentrated, and allowed to crystallize. Colorless crystals formed weighing 0.16 g and melted at 183–187°. Recrystallizations from ethyl acetate–petroleum ether and methanol failed to raise the melting point. A mixture melting point with **1a** showed no depression and the infrared spectra of the two were identical.

Reactions of Aziridines. I. A Mechanism of Piperazine Formation from Aziridines[1]

CLARENCE R. DICK

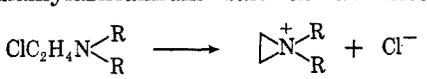
Organic Research Laboratory, Texas Division, The Dow Chemical Company, Freeport, Texas 77541

Received January 6, 1966

The reaction of certain 1-alkylaziridines with alkyl, alkenyl, or benzyl halides as well as with dialkylchloroethylamines has been found to give nearly quantitative yields of the corresponding 1,1,4-trialkylpiperazinium halides. The replacement of the alkyl halides with alkyl *p*-toluenesulfonates resulted in the formation of only poly(1-alkylaziridines). It was concluded that the presence of halide ions was necessary for the formation of piperazines from aziridines. It was also demonstrated that not only halide ions, but a solvent such as acetone was required. The use of water as a solvent resulted in polymer formation. Thus, the necessary presence of halide ions in a solvent of moderate polarity strongly suggests that an SN2 reaction of the halide ion with an intermediate is the product-determining step in the formation of piperazines from aziridines. A mechanism is postulated.

The conversion of aziridines into piperazines has received little attention. Fruton[2] has briefly mentioned the subject in his review of aziridine chemistry, but the reference given for the conversion of 1-methylaziridine into 1,4-dimethylpiperazine appears to be misquoted. Clapp[3] has reported the isolation of piperazine as a by-product from the aminoethylation of phenol with aziridine. More recently, Heine[4] and co-workers reported the conversion of 1-phenylaziridine into 1,4-diphenylpiperazine in 65% yield. No mechanism was postulated.

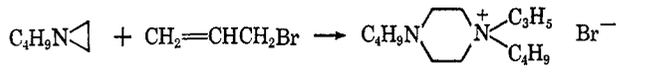
Bartlett[5–7] reported the isolation of 1,1,4,4-tetrasubstituted piperazinium halides from β-chloroethylamines and not aziridines. However, kinetic studies of these reactions by Bartlett strongly support the concept that the chloroethylamine first cyclized to form the 1,1-dialkylaziridinium salt as an intermediate



which underwent further reactions to form the corresponding piperazinium salt. While the aforementioned references demonstrate that aziridines can be considered as precursors of piperazines, a systematic study of this reaction has not been reported.

The reaction of acids or alkylating agents with excess aziridines is generally conceded to produce polyaziridines.[8] However, the data herein presented demonstrate that by the proper choice of conditions one can produce high yields of either a polymer or a piperazine from the same reagents.

The treatment of allyl bromide with a 9-mole excess of 1-*n*-butylaziridine in dry acetone gave a 96% yield of 1,4-di-*n*-butyl-1-allylpiperazinium bromide (reaction 13, Table III) and the excess aziridine was recovered



unchanged. This is the first reported preparation of a 1,1,4-trisubstituted piperazine salt from an aziridine. The structure of this was established by comparison of the infrared spectrum with that of an authentic sample prepared from piperazine, *n*-butyl bromide, and allyl bromide. The mixture melting point showed no depression while the elemental analysis and molecular weights agreed with the proposed structure. Similarly, the reaction of 1-ethylaziridine with ethyl bromide (reaction 3) gave a 99% yield of 1,1,4-triethylpiperazinium bromide whose structure was established in a like manner.

In order to study the role of the alkylating agent in determining the course of this reaction, methyl iodide (reaction 2), methyl *p*-toluenesulfonate (reaction 10), ethyl bromide (reaction 3), and ethyl *p*-toluenesulfonate (reaction 12) were allowed to react with a 9-mole excess of 1-ethylaziridine in acetone at 25°. The reactions of methyl iodide and ethyl bromide resulted in the formation of the corresponding 1,1,4-trialkylpiperazinium halide in 91 and 99% yields, respectively, while the use of methyl and ethyl *p*-toluenesulfonates resulted in the formation of poly(1-ethylaziridine) in 97 and 99% yields, respectively. Infrared analysis indicated that these polymers contained less than 3.0% piperazine rings. These data clearly demonstrate that those alkylating agents which produce halide ions on reacting with aziridines result in piperazine formation, while those producing *p*-toluenesulfonate anions result in polymer as the only product. Thus an anion which is both a good nucleophile and leaving group, such as halide, is necessary for piperazine formation under these conditions. Reaction 10 was therefore repeated (reaction 11) with the addition of 1 mole of sodium iodide per mole of methyl *p*-toluenesulfonate. The

(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1965, Abstract K 93.

(2) J. S. Fruton, "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p 69.

(3) L. B. Clapp, *J. Am. Chem. Soc.*, **73**, 2584 (1951).

(4) H. W. Heine, W. G. Kenyon, and E. M. Johnson, *ibid.*, **83**, 2570 (1961).

(5) P. D. Bartlett, S. D. Ross, and C. G. Swain, *ibid.*, **69**, 2971 (1947).

(6) P. D. Bartlett, J. W. Davis, S. D. Davis, and C. G. Swain, *ibid.*, **69**, 2977 (1947).

(7) P. D. Bartlett, S. D. Ross, and C. G. Swain, *ibid.*, **71**, 1415 (1949).

(8) G. D. Jones in "The Chemistry of Cationic Polymerizations," P. H. Plesch, Ed., The Macmillian Co., New York, N. Y., 1963, Chapter 14; P. E. Fanta in "The Chemistry of Heterocyclic Compounds," Part I, A. Weissberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, Chapter 2.