was heated under reflux overnight with freshly prepared Raney nickel (approximately 20 g.). The mixture was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was distilled to yield 1.30 g. (80%): b.p. 110° (0.1 mm.); $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 3290 (s) (NH), 1640 (s) (C=O). The infrared spectrum was identical with that of an authentic sample prepared by the method of Bischler and Napieralski.[24]

2-(N-Benzylidenamino)benzo[*b*]thiophene (XVIIa).—A solution of 220 mg. (2.0 mmoles) of benzaldehyde in 1 ml. of ethanol was added to a solution of 300 mg. (2.0 mmoles) of I in 3 ml. of ethanol; the resulting mixture was heated under reflux on a steam bath for 10 min. After the solution had cooled, the resulting product upon recrystallization from ethanol yielded 200 mg. (43%), m.p. 143–145°, $\nu_{max}^{10\%\ CHCl_3}$ (cm.$^{-1}$) 1620 (m) (C=N).

Anal. Calcd. for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; S, 13.51. Found: C, 76.10; H, 4.75; S, 13.76.

2-(N-*p*-Chlorobenzylidenamino)benzo[*b*]thiophene (XVIIb).—A solution of 140 mg. (1.0 mmole) of *p*-chlorobenzaldehyde and 150 mg. (1.0 mmole) of I in 6 ml. of ethanol was heated under reflux for 1 min. on a steam bath to yield, after recrystallization from ethanol, 154 mg. (57%) of yellow needles, m.p. 194–195°, $\nu_{max}^{10\%\ CHCl_3}$ (cm.$^{-1}$) 1615 (m) (C=N).

Anal. Calcd. for $C_{15}H_{10}ClNS$: C, 66.29; H, 3.71; Cl, 13.05. Found: C, 66.18; H, 3.84; Cl, 13.07.

Diazotization of 2-Aminobenzo[*b*]thiophene (I). A. 2-Bromobenzo[*b*]thiophene (XIII).—To 1.50 g. (0.01 mole) of I in 12 ml. of 20% hydrobromic acid was added an aqueous solution of 0.70 g. (0.01 mole) of sodium nitrite at 0°. To the cooled solution was added a solution of 2.16 g. (0.015 mole) of cuprous bromide in 15 ml. of 20% hydrobromic acid. The mixture was allowed to come to room temperature slowly with stirring (2 hr.) and then was steam distilled. The distillate was saturated with sodium chloride and was extracted with three 20-ml. portions of ether. After the combined extracts were dried over magnesium sulfate, the ether was removed by distillation. Distillation of the residue yielded 0.95 g., b.p. 130–145° (17 mm.); the product solidified and was recrystallized from ethanol–water to yield 0.65 g. (31%) of 2-bromobenzo[*b*]thiophene (XIII), m.p. 38–39°. The infrared absorption spectrum was identical with that of an authentic sample prepared by treating 2-thianaphthenyllithium with bromine.[4]

B. 2-Keto-2,3-dihydrobenzo[*b*]thiophene (XVb).—A stirred suspension of 1.50 g. (0.01 mole) of I in a solution of 5 ml. of concentrated sulfuric acid and 10 ml. of water was cooled to below 5°, and a solution of 1.00 g. of sodium nitrite in 5 ml. of water was added. After this solution had been stirred for 5 min., it was added to a hot solution of 10 ml. of concentrated sulfuric acid and 10 ml. of water. This mixture was heated at 115° for 15 min. and then was steam distilled. The distillate was saturated with sodium chloride and was extracted with ether. The ether extracts were combined and dried over magnesium sulfate. After solvent removal, the residue was distilled to yield 0.50 g. (34%), b.p. 130–135° (14 mm.), m.p. 43–45°. The infrared absorption spectrum (neat film) was identical with that of a sample of "2-hydroxythianaphthene" (XVa) prepared by the method of van Zyl, *et al.*[15]

Actually, XVb could be formed by direct acidic hydrolysis. A solution of 2.00 g. (0.014 mole) of I in 100 ml. of 6 *N* hydrochloric acid and 40 ml. of tetrahydrofuran was heated under reflux for 3 days. The oil which formed was extracted with ether (three 40-ml. portions); the ether extracts were washed with saturated sodium chloride solution and dried over magnesium sulfate. After ether removal, the residue was distilled to yield 1.80 g. (90%) of product, b.p. 50–60° (0.05 mm.); crystallization of a sample from petroleum ether (b.p. 30–60°) gave a substance, m.p. 44–45°, identical with that produced by way of the diazotization procedure, as confirmed by the identity of the infrared absorption spectra: ν_{max} (cm.$^{-1}$) 1700 (w) (thiolactone C=O).

(24) A. Bischler and B. Napieralski, *Ber.*, **26**, 1903 (1893).

Acknowledgment.—This investigation was supported in part by an International Fellowship Award in the Petroleum Field (Type D Grant) from the American Chemical Society Petroleum Research Fund, in part by research contract DA-49-193-MD-2049 with the Office of the Surgeon General of the U. S. Army Medical Research and Development Command dealing with antiradiation agents, and in part by funds provided for biological and medical research by the State of Washington Initiative Measure No. 171. We wish to express thanks to Varian Associates for assistance in determination and interpretation of the n.m.r. spectrum of 2-amino[*b*]thiophene (I). One of us (G. W. S.) wishes also to thank Professor S. J. Angyal, University of New South Wales, Professor L. H. Briggs, University of Auckland, and Professor Lloyd M. Jackman, University of Melbourne, for generous professional hospitality.

Acenaphthene Chemistry. VIII.[1,2] The Oxidation of 5-Benzenesulfonamidoacenaphthene with Lead Tetraacetate. Two New Acenaphthene Compounds with Imidol Structures

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The oxidation of 5-benzenesulfonamidoacenaphthene with lead tetraacetate produced a mixture of substances. With the aid of methanol as an extraction solvent there was obtained 2-acetoxy-5-benzenesulfonimido-2a-acenaphthenequinol acetate (V), 2,3-diacetoxy-2a-methoxy-5-benzenesulfonimido-2a,5-dihydroacenaphthene (VI), 5-benzenesulfonamidoacenaphthylene (VII), and benzenesulfonamide.

Derivatives of acenaphthene in which the acenaphthene nucleus is a part of a quinoid structure have not been studied extensively. Rowe and Davies[3] reported what they believed to be the dioxime of 4,5-acenaphthenequinone, but this product, described as a brown, amorphous, infusible powder has not been adequately characterized. An acenaphthene compound with an *o*-imidol structure, 4,5-acenaphthenequinonedibenzenesulfonimide (I), has been described.[4]

An acenaphthene with a related structure was recently reported by Wittig, Reppe, and Eicher.[5] They described the structure II which was obtained by treating acenaphthylene with trityl sodium and trapping the intermediate with triphenylboron, followed by hydrolysis of this intermediate.

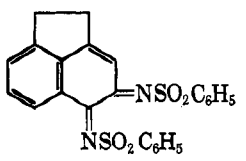
(1) Paper VII: H. J. Richter and W. C. Feist, *J. Org. Chem.*, **26**, 3133 (1961).

(2) This work was supported by Public Health Service Research Grant CA 02997-6 from the National Cancer Institute, National Institutes of Health, and by a Shell Oil Co. Fellowship.

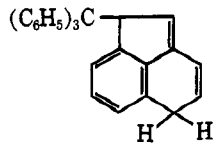
(3) F. M. Rowe and J. S. H. Davies, *J. Chem. Soc.*, **117**, 1344 (1920).

(4) H. J. Richter and B. C. Weberg, *J. Am. Chem. Soc.*, **80**, 6446 (1958).

(5) G. Wittig, H. G. Reppe, and T. Eicher, *Ann.*, **643**, 47 (1961).

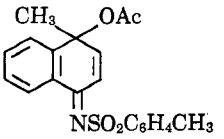


I

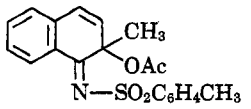


II

Adams and co-workers[6,7] studied the oxidation of 1-(*p*-toluenesulfonamido)-4-methylnaphthalene and 1-(*p*-toluenesulfonamido)-2-methylnaphthalene with lead tetraacetate and reported the formation of 1-(*p*-toluenesulfonimido)-4-methyl-4-naphthoquinol acetate (III) and 1-(*p*-toluenesulfonimido)-2-methyl-2-naphthoquinol acetate (IV), respectively.



III



IV

It has also been shown[8] that lead tetraacetate oxidized the benzenesulfonamides of 1- and 2-naphthylamine to 1-benzenesulfonimido-1,4-naphthoquinone and 2-benzenesulfonamido-1,4-naphthoquinone.

In some preliminary work concerned with the preparation of acenaphthenes with a quinoid structure, Weberg[9] briefly examined the oxidation of 5-benzenesulfonamidoacenaphthene with lead tetraacetate. Two products were reported, but no structures could be assigned that agreed with the analytical data. In view of the known acenaphthenes with a quinoidal structure and the formation of quinoid substances by the oxidation of sulfonamides with lead tetraacetate, the oxidation of 5-benzenesulfonamidoacenaphthene with this reagent was re-examined.

In the study described in this paper the crude oxidation product was separated into two fractions by trituration with methanol at room temperature. The insoluble fraction was separated into two components, V, white needles, m.p. 174–175°, and VI, white prisms, m.p. 141–143°, by fractional crystallization from methanol. The less soluble fraction, V, showed absorption at 1550 cm.$^{-1}$ indicating the presence of a C=N and acetate C=O absorption at 1735 cm.$^{-1}$. The analytical results were in accord with $C_{22}H_{19}NO_6S$ which required the introduction of two acetoxy groups.

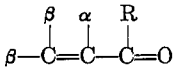
Samples of 1-(*p*-toluenesulfonimido)-4-methyl-4-naphthoquinol acetate (III) with a *p*-imidol acetate chromophore and 1-(*p*-toluenesulfonimido-2-methyl-2-naphthoquinol acetate (IV) with an *o*-imidol structure were prepared.[6,7] The ultraviolet absorption spectrum of III showed a maximum at 281 mμ and IV showed maxima at 302 and 367 mμ. The ultraviolet absorption of V (maximum at 270 mμ and a shoulder at 310 mμ) was interpreted to eliminate the possibility of an *o*-imidol structure since the maxima in this system are at longer wave lengths.

When subjected to catalytic reduction, the white needles V lost acetic acid to form a new white solid (Va) which was unstable to heat. A benzene solution of this substance became yellow at temperatures above 40°. The infrared spectrum indicated an N—H (3220 cm.$^{-1}$) and an acetoxy C=O (1735 cm.$^{-1}$) and the elemental analyses were in accord with the formula $C_{20}H_{17}NO_4S$, which would agree with the loss of one acetoxy group.

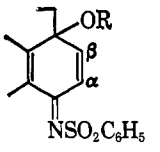
When a solution of Va in acetic acid was refluxed, it was quantitatively converted into a yellow substance VII which proved to be identical with the yellow needles obtained by chromatography of the methanol-soluble fraction of the crude oxidation product. The yellow product VII resulting from the decomposition of Va and that obtained from the methanol-soluble fraction of the crude oxidation were catalytically reduced to 5-benzenesulfonamidoacenaphthene, which on dehydrogenation with chloranil re-formed VII, which is thus shown to be 5-benzenesulfonamidoacenaphthylene.

Attempts to convert the white prisms VI into a known derivative of acenaphthene were not successful. Compound VI is not formed from V, as a pure sample of V was recovered quantitatively unchanged after 48 hr. stirring with an excess of lead tetraacetate and isolated with the aid of methanol under the same conditions employed in the original oxidation. The elemental analysis suggested $C_{23}H_{21}NO_7S$ which corresponds to 5-benzenesulfonamidoacenaphthene with the introduction of a methoxy and two acetoxy groups. The infrared spectrum indicated a normal acetate[10a] by an absorption at 1730 cm.$^{-1}$, a vinylic type acetate[10b] by absorption at 1705 cm.$^{-1}$, and a carbon–nitrogen double bond with a peak at 1570 cm.$^{-1}$. No absorption peak characteristic of the N–H was present.

The ultraviolet absorption (282 mμ) and the C=N absorption in the infrared indicate a *p*-imidol system. It has been noted[11] that, when a parent chromophoric system in the steroids is altered by changing the substituents attached to the systems, a definite and predictable shift of the absorption maximum is observed. Thus, the parent conjugated ketone system,



where R is alkyl or a ring residue and α and β are hydrogen, consistently exhibits an absorption maximum at 215 mμ. The substitution of OR or $OCOCH_3$ for hydrogen at the α-position causes a bathochromic shift of 10 mμ, and at the β-position 12 mμ from the original absorption of the parent system. The chromophore present in the *p*-imidol system of V is quite similar, differing only in that a carbon–nitrogen double



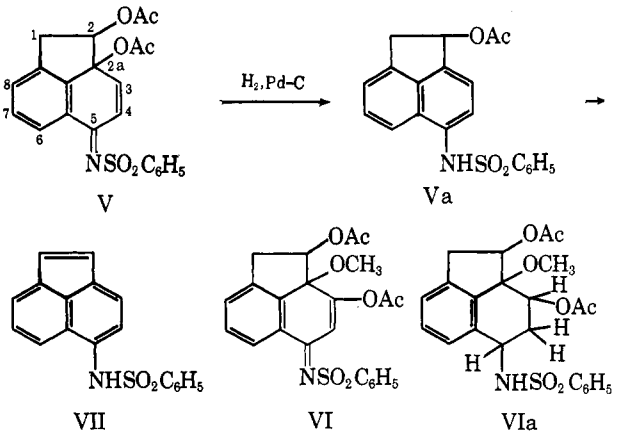
bond has replaced the carbonyl group. If the substitution of $OCOCH_3$ for hydrogen at the β-position would cause a bathochromic shift of 12 mμ from the absorption maximum of the parent system, an absorption at 282 mμ would be required. This was observed with

(6) R. Adams and J. E. Dunbar, *J. Am. Chem. Soc.*, **78**, 4774 (1956).
(7) R. Adams and E. L. DeYoung, *ibid.*, **79**, 705 (1957).
(8) H. J. Richter and R. L. Dressler, *J. Org. Chem.*, **27**, 4066 (1962).
(9) B. C. Weberg, Ph.D. Thesis, University of Colorado, 1958.
(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y.: (a) p. 179; (b) p. 171.
(11) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp. 15–19.

VI. An acetoxy group in the β-position would also account for vinylic acetate absorption at 1750 cm.$^{-1}$ in the infrared. The two acetoxy groups in VI indicated by the analysis are then in the 2- and 3-positions. A rearrangement of an acetoxy group in a *p*-imidol acetate has been reported. Adams and DeYoung[7] report that treatment of 1-(*p*-toluenesulfonimido)-4-methyl-4-naphthoquinol acetate (III) with mineral acid formed 1-(*p*-toluenesulfonamido)-3-acetoxy-4-methylnaphthalene.

Since the *p*-imidol system requires a substituent at the 2a-position, the structure VI is indicated. This could be formed from a substance present in the crude oxidation mixture during the isolation using methanol. It gave a positive test for methoxy.[12] Catalytic reduction of VI formed white needles, m.p. 150–152°, but elemental analysis did not support a reasonable structure. However, the infrared spectrum revealed the presence of N–H with absorption at 3300 cm.$^{-1}$. Absorption in the acetate carbonyl region is confined to one peak at 1735 cm.$^{-1}$ characteristic of the normal ester and thus indicating the destruction of the vinylic acetate. The ultraviolet spectrum showed absorption maxima only at wave lengths shorter than 290 mμ and in general seemed to be quite similar to substances with a benzene nucleus. Most acenaphthene derivatives exhibit an ultraviolet maximum at *ca.* 290 mμ or higher and acenaphthene itself exhibits maxima at 288 mμ and at a wave length greater than 320 mμ. 5-Benzenesulfonamidoacenaphthene shows a principal absorption maximum at 301 mμ.

These data would suggest the complete reduction of one ring of the acenaphthene nucleus. This would be consistent with the assignment of the methoxy at 2a as in structure VI, since elimination of methanol does not occur so readily as the elimination of acetic acid. The structure proposed for this reduction product is VIa. This substance may be expected to be rather unstable owing to the possibility of eliminating acetic acid, methanol, and/or benzenesulfonamide. This potential instability may account for the unsatisfactory analysis obtained.



V Va VII VI VIa

The remaining product isolated from the oxidation of 5-benzenesulfonamidoacenaphthene proved to be benzenesulfonamide as shown by a comparison of the infrared spectra and a mixture melting point determination with an authentic sample. This could result from solvolysis of a substance containing the benzenesulfonamido group. Adams[13] and co-workers have reported similar results in their studies of quinonedibenzenesulfonamides.

In the structures for V and VI the bridge acetoxy has been placed at the 2-position; however, the evidence presented thus far would apply equally well if this group were in the 1-position. A firm assignment was made by an examination of the n.m.r. spectra of V and VI utilizing 1-acetoxyacenaphthene as a model compound.

1-Acetoxyacenaphthene exhibited a typical ABX pattern, in which the methinyl (X) proton peaks were centered at τ 3.49 and the methylene (AB) protons gave rise to a complex of eight peaks from τ 7.17 to 6.30.

Since the methinyl proton in the model is α to both acetoxy and benzo moieties, a similar chemical shift would be expected if the acetoxy were in the 1-position in compounds V and VI. However, V exhibited a doublet at τ 4.09 (J = 4 c.p.s.) and a series of 11 peaks between τ 6.70 and 5.85. For compound VI a triplet at τ 4.12 (J = 8.5 c.p.s.) and a series of 12 peaks between τ 6.95 and 5.38 were observed. This suggests the methinyl protons in V and VI are deshielded primarily by an α-acetoxy with a small effect due to the acetoxy or methoxy at the 2a position and not by a vicinal aromatic ring. Therefore, the acetoxy has been assigned the 2-position.

The difference in multiplet absorption patterns for the methinyl protons suggests a difference in stereochemistry for the two rigid systems V and VI; however, no data are now available that would allow assignment of stereochemistry.

Experimental Section

Oxidation of 5-Benzenesulfonamidoacenaphthene with Lead Tetraacetate.—Finely ground 5-benzenesulfonamidoacenaphthene (6.18 g., 0.02 mole) was suspended in 100 ml. of glacial acetic acid, and with stirring an excess of lead tetraacetate (53.16 g. 0.12 mole) was added in one portion. The color changed from yellow to a final dark orange. After stirring for 105 min. the excess lead tetraacetate was destroyed by adding 15 ml. of ethylene glycol. The resulting orange–brown solution was poured into cold water and yielded a light yellow solid which was collected on a filter, washed with 700 ml. of water, and air dried. The crude product (7.7 g.) was treated with 15 ml. of methanol and allowed to stand for 1 hr. at room temperature. The resulting mixture was separated by filtration giving 4.78 g. of insoluble material and a dark brown filtrate.

The insoluble fraction was leached with 100 ml. of boiling methanol and there remained 1.7 g. of crude 2-acetoxy-5-benzenesulfonimido-2a-acenaphthenequinol acetate (V). Crystallization from methanol (decolorizing carbon) gave white needles: m.p. 174–175°; ν_{max}^{KBr}, in cm.$^{-1}$, 1735 (acetate C=O), 1630, 1590, 1550, 1450, 1370, 1320 (SO_2), 1235 (shoulder), 1215, 1200 (shoulder), 1153 (SO_2), 1090, 1040, 962, 923, 912, 828, 812, 788, 777, 765, 709, and 689; λ_{max}^{MeOH}, in mμ (ϵ), 27 0(6700) and 310 (shoulder) (2700).

Anal. Calcd. for $C_{22}H_{19}NO_6S$: C, 62.10; H, 4.50; N, 3.29. Found: C, 62.48; H, 4.68; N, 3.32.

The methanol extract was reduced to *ca.* one-fifth of its original volume by heating on the steam bath. On standing it deposited 1.95 g. of impure 2,3-diacetoxy-2-methoxy-5-benzenesulfonimido-2a,5-dihydroacenaphthene (VI). White prisms were obtained upon recrystallization (decolorizing carbon) from methanol: m.p. 141–143°; ν_{max}^{KBr}, in cm.$^{-1}$, 3060, 2890, 2600, 1750 (vinylic acetate), 1730 (acetate), 1605, 1570 (C=N), 1450, 1370, 1315,

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 116.

(13) R. Adams and W. Reifschneider, *Bull. soc. chim. France*, 23 (1958).

1305, 1250 (shoulder), 1225, 1160 (SO_2), 1115, 1090, 1070, 1040, 1020, 988, 968, 937, 880, 827, 785, 777, 760, 720, and 691; λ_{max}^{MeOH}, in mμ (ε), 282 (18,400).

Anal. Calcd. for $C_{23}H_{12}NO_7S$: C, 60.65; H, 4.65; N, 3.08. Found: C, 60.42; H, 4.65; N, 3.05.

The dark brown filtrate, resulting from treatment of the crude oxidation product with methanol, and the residual methanolic liquor remaining after isolation of crude white products V and VI were combined and the solvent was evaporated under a current of air. The remaining brown glass (3.78 g.) was chromatographed on alumina. Benzenesulfonamide (0.9 g.) was obtained from the fractions eluted with ether and 5-benzenesulfonamidoacenaphthylene (VII), 0.58 g., was recovered using 10% methanol in ether. Crystallization of VII from benzene–petroleum ether (b.p. 85–100°) gave yellow needles: m.p. 154–155°; ν_{max}^{KBr}, in cm.$^{-1}$, 3290 (NH), 1485, 1430, 1350, 1325 (SO_2), 1295 (olefin CH), 1230, 1165 (SO_2), 1150, 957, 876, 836, 813, 768, 719, 700 (olefin CH), and 685.

Anal. Calcd. for $C_{18}H_{13}NO_2S$: C, 70.34; H, 4.26; N, 4.56. Found: C, 70.19; H, 4.24; N, 4.51.

Catalytic reduction of VII (0.2 g.) in the Parr hydrogenator (10% palladium on charcoal and absolute ethanol solvent) gave 0.2 g. of 5-benzenesulfonamidoacenaphthene as shown by identical spectra and no depression in a mixture melting point.

2-Acetoxy-5-benzenesulfonamidoacenaphthene (Va).—Two grams of V suspended in 100 ml. of absolute ethanol was placed in the Parr hydrogenator with 200 mg. of 10% palladium on charcoal, and the mixture was shaken for 18 hr. under a hydrogen pressure of 43 p.s.i. Removal of the catalyst by filtration gave a water-clear solution, and evaporation of the solvent *in vacuo* yielded 1.72 g. (99.5%) of the white product Va. In attempting to crystallize this material it was found to be very temperature sensitive and developed considerable yellow coloration at the boiling point of benzene. A satisfactory method of crystallization required the solution of the substance in a minimum of benzene at 40°, the addition of petroleum ether to incipient cloudiness, and cooling in the refrigerator. White microcrystals deposited: m.p. 147–148°; ν_{max}^{KBr}, in cm.$^{-1}$, 3220 (NH), 1735 (acetate C=O), 1590, 1500, 1450, 1415, 1390, 1370, 1355, 1320 (SO_2), 1235, 1165 (SO_2), 1090, 1048, 1019, 938, 890, 820, 798, 782, 770, 752, 732, 693 (shoulder), and 686.

Anal. Calcd. for $C_{20}H_{17}NO_4S$: C, 65.38; H, 4.67; N, 3.81. Found: C, 65.38; H, 4.88; N, 3.72.

When a solution of 0.65 g. of Va in 10 ml. of glacial acetic acid was refluxed for 5 hr., a yellow solution was formed which, when poured into cold water, gave 0.58 g. (100%) of 5-benzenesulfonamidoacenaphthylene (VII). The infrared spectrum of the purified material was identical with that of the yellow needles from the methanol-soluble fraction of the original oxidation mixture (*vide supra*) and of the compound prepared by an independent route (*vide infra*). Mixture melting point determinations showed no depression.

5-Benzenesulfonamidoacenaphthylene (VII).—One gram of 5-benzenesulfonamidoacenaphthene was suspended along with 0.8 g. of chloranil in 20 ml. of xylene. The mixture was refluxed for 24 hr. and gave a dark brown solution which contained a brown solid. Forty milliliters of benzene was added to dissolve all solids; the solution was filtered and then chromatographed on alumina. The fractions eluted with acetone yielded 0.26 g. of VII. Crystallization from benzene–petroleum ether gave yellow needles, m.p. 152–154°. The infrared spectrum was identical with that of the product VII obtained from the oxidation of 5-benzenesulfonamidoacenaphthene, and mixture melting points showed no depression.

Reduction of 2,3-Diacetoxy-2a-methoxy-5-benzenesulfonimido-2a,5-dihydroacenaphthene (VI).—Catalytic reduction of VI at 41 p.s.i. of hydrogen in the Parr apparatus gave a product which resisted crystallization and exhibited a broad melting point range.

Using platinum oxide (100 mg.) as the catalyst, 1 g. of VI was suspended in 50 ml. of absolute methanol plus 5 ml. of glacial acid, and the mixture was placed under 41 p.s.i. of hydrogen in the Parr hydrogenator. After shaking for 24 hr. the mixture was filtered and the solvent was evaporated (*in vacuo*), leaving 1 g. of a cream-colored glass. Crystallization from benzene–petroleum ether gave white needles: m.p. 150–152°; ν_{max}^{KBr}, in cm.$^{-1}$, 3300 (NH), 3070, 2900, 2680, 1735 (acetate C=O), 1490, 1450, 1408, 1370, 1320 (SO_2), 1260, 1238, 1165 (SO_2), 1137, 1110, 1095, 1070, 1028, 963, 942, 931, 915, 897, 798, 762, 751, 718 and 684; λ_{max}^{MeOH}, no peaks between 290 and 380 mμ. Analysis indicated the product was not a chemical entity as a reasonable empirical formula could not be calculated from the analytical data.

Anal. Found: C, 62.40; H, 5.42; N, 2.70.

All n.m.r. data were obtained on a Varian A-60 spectrometer. The spectra of V and VI were obtained using methylene chloride and deuterioacetone solutions. 1-Acetoxyacenaphthene was used as the neat liquid.

Ten π-Electron Nitrogen Heterocyclic Compounds. II. Bromination of Imidazo[1,2-*a*]pyridines

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Received June 14, 1965

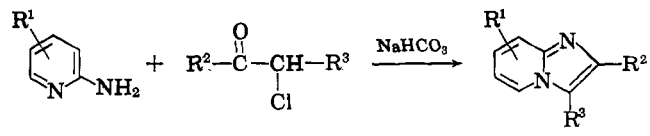
Bromination of several imidazo[1,2-*a*]pyridines has been shown to occur at position 3, in agreement with predictions based on frontier-electron calculations.

In the first paper of this series,[1] we reported the analysis of the n.m.r. spectra of some imidazo[1,2-*a*]-pyridines and some results of HMO calculations on this system.

We have now calculated the total π-electron, as well as the frontier-electron densities of several imidazo[1,2-*a*]pyridines (Table I). Both of the indices suggest that electrophilic substitution (on carbon) should occur at position 3. While the total π-electron densities predict almost equally probable substitution at several other positions (see Table I), the frontier-electron distribution suggests quite strongly that the most preferred position of substitution is position 3.

It is of interest to investigate a typical electrophilic substitution reaction in order to compare the experimental results with the prediction of the two different reactivity indices.

The compounds were prepared by the reaction sequence shown below.



We decided to study the bromination[2] of some selected imidazo[1,2-*a*]pyridines, since it is well established that the substitution of a bromine for hydrogen does not significantly alter the chemical shift positions

(1) W. W. Paudler and H. L. Blewitt, *Tetrahedron*, **21**, 353 (1965).

(2) 2-Phenylimidazo[1,2-*a*]pyridine has previously been brominated: V. K. Matveen, *Bull. Acad. Sci. USSR, Classe sci. math. nat., Ser. Chem.*, 1005 (1936).