matic protons, two of which show different chemical shifts.

The above analytical and spectral data have led us to assign structure VI to this substance. The n.m.r. strongly supports this assignment. The formation of VI can be readily explained if one considers firstly that the 2-acetamido group can readily tautomerize, and secondly that the thiazolyl and phenyl groups can and do undergo free rotation readily. Under these conditions, the initial dehydration step can occur to form intermediate A which is then favorably disposed to undergo a second dehydration to form VI. We have named this compound 4-methyl-2-thia-3,6,10c-triazoaceanthrylene. (See Scheme II.)

### Experimental

**2-Amino-4-(2-nitro phenyl)thiazole Monohydrobromide (II).**—A solution of 2-nitro-ω-bromoacetophenone[8] (24.4 g., 0.1 mole) in ethyl alcohol (250 ml.) was treated with 7.6 g. of thiourea and the reaction mixture was heated under reflux for 4 hr. On cooling and addition of ethyl acetate to the concentrated reaction solution crystals appeared which were collected. Three recrystallizations from ethyl alcohol–ethyl acetate gave 20 g. of pure material, m.p. 179–180°.

*Anal.* Calcd. for $C_9H_8BrN_3O_2S$: C, 35.77; H, 2.66; N, 13.91. Found: C, 35.90, H, 2.91; N, 13.83.

**2-Amino-4-(2-aminophenyl)thiazole Monohydrobromide (III).**—A solution of 2-amino-4-(2-nitrophenyl)thiazole monohydrobromide (15.1 g., 0.05 mole) in 100 ml. of alcohol was shaken with hydrogen under pressure (45 lb./in.²) at room temperature using 6 g. of 10% palladium–charcoal catalyst. After the theoretical amount of hydrogen was taken up, the catalyst was filtered off and washed with 100 ml. of methanol. The washings were combined with the filtrate; the solution was evaporated to dryness to afford 12 g. of crystalline residue. Recrystallization with methanol–ethyl acetate gave a pure material, m.p. 224–225°.

*Anal.* Calcd. for $C_9H_{10}BrN_3S$: C, 40.16; H, 3.72; N, 15.50. Found: C, 39.95; H, 3.67; N, 15.46.

**2-Acetamido-4-(2-acetamidophenyl)thiazole (IV).**—The base from above salt (5.7 g.) was dissolved in tetrahydrofuran (80 ml.) and treated with pyridine (4.7 ml.). This solution was warmed to 40° and treated with 4.5 g. of acetyl chloride and boiled under reflux for 2 hr. The solvent was removed under reduced pressure; the residue was suspended in water. The suspension was extracted with ethyl acetate. The organic extract was dried over anhydrous sodium sulfate and evaporated to dryness. This gave 5.0 g. of diacetamide which was recrystallized from methanol–ethyl acetate to yield pure white crystals, 242–243°.

*Anal.* Calcd. for $C_{13}H_{13}O_2N_3S$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.48; H, 4.85; N, 15.34.

**4-Methyl-2-thia-3,6,10c-triazoaceanthrylene (VI).**—2-Acetamido-4-(2-acetamido phenyl)thiazole (2.0 g.) was treated with 6 ml. of phosphorus oxychloride. The reaction mixture was warmed on the steam bath for 12 min. and later boiled under reflux for 1.5 hr. The excess of phosphorus oxychloride was distilled under reduced pressure on the steam bath and the residue was carefully diluted with water (125 ml.). The gummy suspension was washed with ethyl acetate. The aqueous extract was made basic with 2 *N* sodium hydroxide solution (50 ml.) and the suspension was extracted with ethyl acetate (500 ml.). This extract was dried over anhydrous sodium sulfate and evaporated to dryness (0.8 g.). On chromatography on chromatoplates, the following fractions were obtained: fraction A, 5-cm. movement, 250 mg., highly crystalline, m.p. 208–209°; fraction B, 8-cm. movement, 140 mg., residue not crystalline; fraction C, 9-cm. movement, 140 mg., residue amorphous. Recrystallization of fraction A from ethyl alcohol gave pure material, m.p. 214–215°, which remained unchanged on repeated recrystallizations.

*Anal.* Calcd. for $C_{13}H_9N_3S$: C, 65.26; H, 3.79; N, 17.57; S, 13.38; mol. wt., 239.23. Found: C, 65.07; H, 3.76; N, 17.35; S, 13.55; mol. wt., 249.

(8) H. Gevekoht, *Ann.*, **221**, 327 (1883).

## Mass Spectrometry for Structure Determination. Simple Nitrogen Heterocycles

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A number of recent studies[1-6] have demonstrated the utility of mass spectrometry in organic structure determinations. The method basically consists of the identification of modes of fragmentation which are characteristic of certain structural features. A careful study of the fragmentation patterns of related known compounds and application of the information so obtained to the spectrum of the unknown sample reveals structural information concerning the unknown.

As a basis for extension of the technique, we have examined the mass spectra of twenty simple nitrogen heterocyclic compounds, fourteen of which have not previously been reported. The instrument used in this work was a Consolidated Engineering Corp. mass spectrometer Model 21-102, modified to perform as the Model 21-103C, with the exception that the original four-coil magnet has been retained. Additionally, the instrument has been modified for high temperature sample introduction and automatic mass to charge ratio ($m/e$) marking.

The complete spectra obtained are too lengthy for reproduction here, but they have been submitted for distribution through Committee E-14 of the American Society for Testing Materials.[7] The purpose of this note is to point out certain features which are thought to have general structural significance. The structures of the fragments discussed are postulated from the standpoint of the driving force for their formation. This driving force is usually the formation of a very stable molecule or ion.[1] Rearrangement processes were in evidence and were particularly common when migration of hydrogen atoms was involved.[2] Since there are frequently several different fragments formed by different modes of fragmentation or rearrangement that can appear at the same $m/e$ ratio, the absence of a peak may be of more conclusive diagnostic significance than the appearance of a peak.

As shown in Table I, a significant (greater than 5%) $m/e$ of 28 was present in the spectra of all compounds investigated except 2-methylcarbazole. Owing to the

(1) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, and references therein.

(2) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960.

(3) J. L. Courtney and J. A. Shannon, *Tetrahedron Letters*, **1**, 13 (1963), and references therein.

(4) F. W. McLafferty, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1961.

(5) T. Nakano and C. Djerassi, *J. Org. Chem.*, **26**, 167 (1961).

(6) J. H. Beynon and A. E. Williams, *Appl. Spectry.*, **13**, 101 (1959); **14**, 27 (1960).

(7) These spectra have also been deposited as Document number 7914 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $6.25 for photoprints or $2.50 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

TABLE I
RELATIVE INTENSITIES OF DISCUSSED FRAGMENTS[a]

| Compounds | $N_2^+$ | $CNH_2^+$ | $C_3H_3^+$ | M–HCN | M–$C_2H_4$ | M–$C_2H_3O$ |
|---|---|---|---|---|---|---|
| 2-Methylcarbazole | | | 5 | | | |
| Imidazole | | 48 | | 80 | | |
| 2-Ethylbenzimidazole | | 11 | 12 | 5 | | |
| Indole | | 11 | 10 | 38 | | |
| 3-Acetylindole | | 9 | 6 | | | 100 |
| Pyrrole | | 84 | 84 | 64 | | |
| 1-Methylpyrrole | | 17 | 37 | | 28 | |
| 1-Phenylpyrrole | | 9 | 26 | | 52 | |
| 3-Acetyl-2,4-dimethylpyrrole | | 17 | 15 | | | 100 |
| 2-Methylpyrazine | | 23 | 34 | 56 | | |
| 2,5-Dimethylpyrazine | | 18 | 46 | 10 | | |
| 2,6-Dimethylpyrazine | | 25 | 67 | 6 | | |
| Pyrazole | 49[b] | 49[b] | 29 | 60 | | |
| 3-Methylpyrazole | 44[b] | 44[b] | 11 | 10 | | |
| 3,5-Dimethylpyrazole | 23 | | 33 | | 6 | |
| Indazole | 14[b] | 14[b] | 12 | 33 | | |
| 2-Aminopyrimidine | | 45 | 13 | | | |
| 4,6-Dimethylpyrimidine | | 29 | 54 | 29 | | |
| 3-Amino-1,2,4-triazole | 100[b] | 100[b] | | 28 | | |
| 4-Amino-1,2,4-triazole | 100[b] | 100[b] | | 5 | | |

[a] Intensities are given in per cent of base peak and are listed only if they are greater than 5%. [b] Combination of both $N_2^+$ and $CNH_2^+$.

improbability of intermolecular collisions, $N_2^+$ may be considered a significant contributor only when nitrogen atoms are adjacent in the molecule. Therefore, with the exception of such molecules, $CNH_2^+$ appears to be the main contributor to a *m/e* of 28. Of the compounds investigated, pyrrole had the largest *m/e* of 28 attributed to $CNH_2^+$. This might be anticipated, as this fragment may be formed in two ways from pyrrole and does not require rearrangement for formation. Owing to the many possible rearrangements that could occur, it does not seem feasible to make structural predictions based on the appearance of a *m/e* of 28. However, the absence of such a *m/e* of 28 could be of value. For example, based on this investigation, the absence of a *m/e* of 28 would eliminate the possibility of adjacent nitrogen atoms in a given nitrogen heterocyclic compound. Additionally, the possibility of an unsubstituted ring nitrogen atom between two carbon atoms with two hydrogen atoms attached to the C–N structure would be eliminated.

Another positive ion which appeared in significant amount was $C_3H_3^+$, which is most probably the cyclopropenium cation.[4] A peak at a *m/e* of 39 appeared in the spectra of all molecules examined in which there were three or more carbon atoms in a chain with at least three hydrogen atoms among them. A comparison of the values for the *m/e* of 39 for the various compounds studied and their structures demonstrates clearly the correlation between the number of ways a fragment may form and its probability of formation. For example, it is interesting to note that the per cent of the base peak for the $C_3H_3^+$ fragment of 2,6-dimethylpyrazine was almost twice that of the 2-methylpyrazine. Such comparisons cannot, of course, be made between unrelated compounds. The high stability of the carbazole ring structure is reflected in a lower degree of fragmentation than is observed in the pyrazines. Again, the widespread appearance of the *m/e* 39 peak makes its absence in a given spectrum especially important. Based on this investigation, the nonappearance of a significant *m/e* of 39 indicates the absence of a three-carbon chain with at least three hydrogen atoms attached.

Formation of the neutral molecule HCN was indicated several times during this investigation as a driving force for the formation of a positive ion[6]; however, the formation pattern fails to be consistent enough for correlation. This apparent inconsistency also is present in the pattern of formation of the neutral $C_2H_4$ molecule.

A consideration of the effects produced by the presence of an acetyl group on a nitrogen heterocyclic ring, as evidenced by both data obtained in this study and other reported spectra,[6] reveals that a correlation may be established. It may apparently be concluded that no acetyl group is present on a given nitrogen heterocyclic ring if a significant parent ion minus 43-*m/e* peak is not present in the spectrum.

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## 8,9,10,11-Tetrahydro-12*H*-benzo[5,6]quinoxalino-[2,3-*e*][1,4]diazepin-12-ones. Examples of a New Heterocyclic Ring System

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The present note describes the preparation of several 8,9,10,11-tetrahydro-12*H*-benzo[5,6]quinoxalino-[2,3-*e*][1,4]diazepin-12-ones (Va–e), examples of a hitherto unreported heterocyclic ring system. The products are shown in Table III.

The first member of the new series, 8,9,10,11-tetrahydro-12*H*-benzo[5,6]quinoxalino[2,3-*e*][1,4]-diazepin-12-one (Va), was prepared by the sequence shown. Treatment of ethyl cyanoacetate with 2-amino-