atoms one at a time than in a concerted fashion. This seems to indicate that structural reorganization is the costly factor in this reaction, and that the *preferred mechanism will be that requiring the least structural reorganization* (principle of least motion[51]). Carried to its extreme the principle of least motion predicts that most base- (or solvent)-initiated 1,2- or 1,3-elimination reactions will proceed by two-stage mechanisms and that the concerted mechanism will be relatively rare.[52] This prediction can be broadened to include all reactions where two (or more) bonds are formed and two (or more) bonds are broken.

Our conclusion is that two types of nucleophilic bimolecular concerted reactions may actually be myths ($\mathrm{S_N2'}$ reactions and base-initiated 1,3 eliminations) and that this mechanistic pathway may be much less common than has been assumed heretofore for other reactions in which two (or more) bonds are formed and two (or more) bonds are broken (such as 1,2-elimination reactions).

I express my appreciation to the National Institutes of Health (Public Health Service Grant No. CA-07351 from the National Cancer Institute) and to the National Science Foundation (NSF GP 4208 and GP 7065) for support of this work. I also wish to express my gratitude to my collaborators in this work: R. L. Arnold, J. B. Biranowski, M. W. Carlson, P. W. R. Corfield, E. Doomes, R. R. Frame, R. W. Hemwall, E. B. Hoyt, Jr., B. B. Jarvis, T. G. Mecca, S. Meyerson, D. A. Schexnayder, R. G. Scamehorn, W. A. Springer, J. G. Strong, M. M. Vestling, J. M. Williams, Jr., and K. C. Yee.

---

(51) See J. Hine, *J. Org. Chem.*, **31**, 1236 (1966), and *J. Amer. Chem. Soc.*, **88**, 5525 (1966), for a discussion.

(52) There is strong evidence to indicate that base-initiated 1,2-elimination reactions with simple secondary alkyl halides are concerted,[53] but the status of the much more numerous elimination reactions where the hydrogen atom is rendered more acidic by the presence of an electron-withdrawing group in the 2 position or the tendency of the halogen to ionize is increased by the presence of an electron-releasing group at the 1 position is not so clear. Such reactions may well be stepwise.

(53) See, for example, R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968).

Petroleum Nitrogen Compounds and Oxygen Compounds

LLOYD R. SNYDER*

Union Research Center, Union Oil Company of California, Brea, California

Received February 25, 1970

Petroleum technologists have an obvious interest in the chemical structure of their basic raw material. However, concern for what petroleum is— and how it was formed—extends well beyond the oil industry. Its considerable abundance in the earth's crust along with oil shale and coal accounts for part of this broad interest. As the "molecular fossils" of ancient plant deposits, petroleum provides an intriguing link between the plant biochemistry of today and that of 100 million years ago. The apparent alteration of this original plant mass in the course of geological time has raised basic questions as to the kinds of chemistry that could have been involved in the formation of petroleum. As our knowledge of the composition of petroleum increases, moreover, we should receive fresh insights into the lipid composition of present plants.

The distillable fraction of petroleum is composed mainly of hydrocarbons, with variable amounts of sulfur compounds as the principal other constituents. Lesser amounts of nitrogen compounds and oxygen compounds make up the balance. Despite their smaller concentrations, these nitrogen and oxygen compounds play an important role in the science of petroleum. Their greater reactivity compared with that of the hydrocarbons makes them more sensitive indicators of the physicochemical environment of petroleum during its long storage in the ground. Similarly their greater structural complexity provides more stringent checks on proposed relationships between petroleum components and past or present plant constituents.

Finally, nitrogen compounds are important to the petroleum refiner. They poison many refining catalysts and cause undesirable deposits in finished products such as gasoline and jet fuel. A knowledge of the nature of these nitrogen compounds should prove useful in the development of processes for their removal and of additives for their control. Although the composition of the hydrocarbons and sulfur compounds in petroleum has been understood in general terms for about 15 years (*e.g.*, see ref 1), a similar understanding of the nitrogen compounds and oxygen compounds has unfolded only during the past 2 years. It is this story which shall now concern us.

The structural range of petroleum hydrocarbons is illustrated in Figure 1 as a three-dimensional, continuous array. Generally each of the compound types implied by Figure 1 occurs in a given petroleum as a continuous homologous series. Figure 2 diagrams the two main families of sulfur compounds found in petroleum, the sulfides and thiophenes. Other sulfur compound types (mercaptans, polysulfides, etc.) occur, but in generally smaller concentrations. Numerous individual hydrocarbons and sulfur compounds have been identified in petroleum (see ref 2). Within a given

---

* Recipient of the 1970 American Chemical Society Award in Petroleum Chemistry, sponsored by Precision Scientific Company.

(1) (a) F. W. Melpolder, R. A. Brown, and T. A. Washall, *Anal. Chem.*, **26**, 1904 (1954); (b) H. E. Lumpkin and B. H. Johnson, *ibid.*, **26**, 1719 (1954).

(2) (a) M. A. Bestougeff in "Fundamental Aspects of Petroleum Geochemistry," B. Nagy and U. Colombo, Ed., Elsevier, Amsterdam

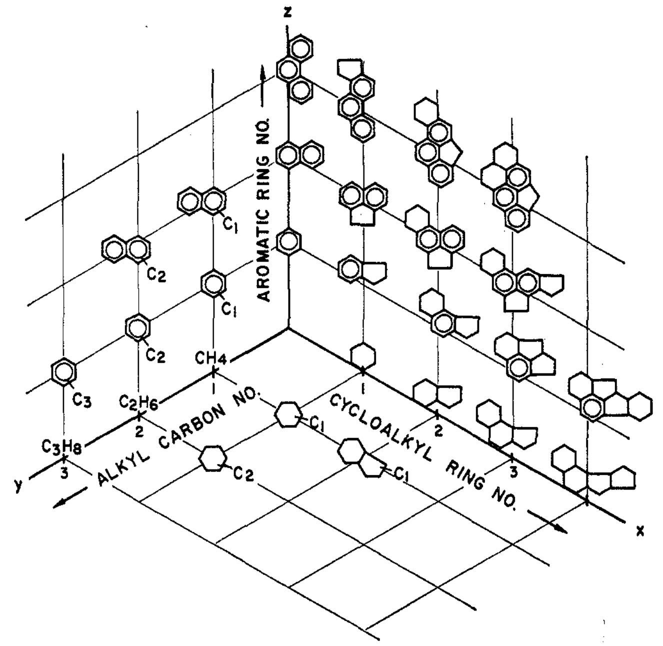


Figure 1. Petroleum hydrocarbons: their structural range.

homologous series all of the possible isomers are usually found at the beginning of the series. As molecular weight increases, however, certain structures begin to predominate while other isomers are essentially absent. Among the hydrocarbons many of the favored isomers have been found to be structurally related to certain plant constituents or their reaction products.[2a,3] These observations have played an important role in establishing a biological origin for petroleum. Likewise, any discontinuity in diagrams such as those of Figure 1 or 2 provides important information on the origin or history of petroleum. We will examine several examples which involve nitrogen or oxygen compounds.

With the advent of high molecular weight mass spectrometry in the early 1950's, an overall picture of the hydrocarbons and sulfur compounds in petroleum soon became available. Adsorption chromatography was used to separate the sample into fractions of differing aromatic ring number (*i.e.*, along the z axis of Figure 1). For each of the resulting fractions the mass spectrometer could provide an analysis in terms of components defined by the number of cycloalkyl rings and total carbon number (*i.e.*, along the x and y axes of Figure 1). This approach simultaneously provided comparable information on the composition of the sulfur compounds present in the sample, and such analyses have been essentially routine within the petroleum industry for many years.

A similar approach to overall analysis of the nitrogen and the oxygen compounds (N,O compounds) has proved more difficult for the following reasons. This group of compounds is considerably more complex than the hydrocarbon–sulfur compound fraction, consisting of about ten major families *vs.* only three for the hydrocarbons plus sulfur compounds (Figures 1 and 2a, b). N,O compounds are difficult to isolate from the hydrocarbons and sulfur compounds present in 5-fold to 100-fold excess. Separations of individual N,O compound classes from each other are more difficult than in the case of hydrocarbon and sulfur compound types. The N,O compounds are concentrated into the higher boiling fractions of petroleum, where separation and analysis are more complicated for all classes of petroleum compounds. Finally, these compounds are more susceptible to alteration and loss during handling. Despite these problems, by 1967 the application of classical techniques had resulted in the isolation and identification of a large number of individual N,O compounds.[2b,4] Most of these compounds are low molecular weight acids or bases (pyridines, quinolines, carboxylic acids, phenols). Because the bulk of petroleum N,O compounds are concentrated into higher boiling fractions, however, these pure compound studies have provided only limited insight into the overall composition of petroleum.

In 1961 our laboratory turned its attention to the composition of the N,O compounds in petroleum. Our ultimate goal was to determine which N,O types are present and in what relative concentrations, and to account for all the N,O compounds in the total distillate from a representative petroleum. Limited attempts of this sort had been made before 1961 and were to be repeated in different laboratories during the next six years,[5] but these investigations provided at best only partial answers. A fresh approach to the analysis of these N,O compounds was required, one which recognized and dealt with the special problems listed above. Because of the great complexity of the N,O compound fraction and its dilution by large amounts of hydrocarbons and sulfur compounds, we felt that major attention should be given to the separation scheme used. We also anticipated that high-resolution mass spectrometry (*i.e.*, 1 in 10,000 or higher) would play a most important part in our overall analytical scheme. Mass spectrometers with this capability had been reported prior to 1961, and their unique potential for analyzing complex N,O compound fractions was readily apparent at an early date.[6] In addition to improved separation plus high-resolution mass spectrometry, we were also counting on the many techniques which had proved useful in previous studies of petroleum composition: elemental and colorimetric analysis, titration, infrared (ir), ultraviolet (uv), and nmr spectroscopy, etc.

By 1966 we had largely completed work on our separation scheme, and this coincided with the installation in our laboratory of a high-resolution mass spectrom-

---

1967, pp 77–108; (b) G. Costantinides and G. Arich in ref 2a, pp 109–175.

(3) I. R. Hills, G. W. Smith, and E. V. Whitehead, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13**, B5 (1968).

(4) H. L. Lochte and E. R. Littman, "The Petroleum Acids and Bases," Chemical Publishing Co., New York, N. Y., 1955.

(5) (a) C. La Lau, *Anal. Chim. Acta*, **22**, 239 (1960); (b) N. N. Bezinger, M. A. Abdurakhmanov, and G. D. Gal'pern, *Petrol. Chem. USSR*, **1**, 13 (1962); (c) D. M. Jewell and G. K. Hartung, *J. Chem. Eng. Data*, **9**, 297 (1964); (d) I. Okuno, D. R. Latham, and W. E. Haines, *Anal. Chem.*, **37**, 54 (1965); (e) L. R. Snyder and B. E. Buell, *Anal. Chim. Acta*, **33**, 285 (1965).

(6) H. E. Lumpkin, *Anal. Chem.*, **36**, 2399 (1964).

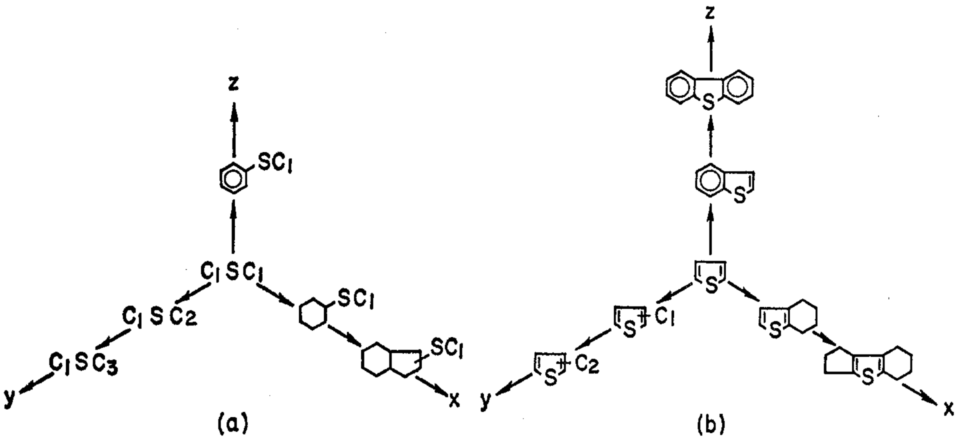


Figure 2. Petroleum sulfur compounds.

eter. At this point we began our long-planned study of the N,O compounds in petroleum.

Separation of N,O Compound Types

A separation scheme for the analysis of petroleum N,O compounds must aim at the isolation of individual families (*e.g.*, pyridines, furans, phenols, etc.) and the further separation of each family into its benzologs (*e.g.*, pyridines, quinolines, benzoquinolines, etc.). It should also be possible to predict which compound types will be recovered in a given fraction, as this considerably simplifies subsequent compound type identification. At an early stage of our study we recognized that the techniques of ion exchange and adsorption chromatography offered unique advantages with respect to our separation goals. These two procedures provide pronounced separation by compound type with little differentiation on the basis of relative cycloalkyl substitution or molecular weight (the latter is provided by subsequent mass spectral analysis). We therefore concentrated initially on a general understanding of adsorption and ion exchange as they apply to petroleum separations.

In the case of ion exchange the work of Munday and Eaves[7] had established its general value in isolating petroleum acids and bases. Since the pK_a values of most simple compound types are known, it is straightforward to predict which compound types will be found in a given ion-exchange fraction and what separations by ion exchange are in principle possible (for a review of the pK_a values of likely petroleum constituents, see ref 8). The major problem in applying ion exchange to the separation of petroleum N,O compounds proved to be an experimental one: the need for open-structured resins which provide ready exchange of high molecular weight (200–1000) acids and bases. Fortunately the commercial macroreticular resins introduced soon after our project began were found to give useful ion-exchange separations of petroleum distillates of all molecular weights.

Prior to 1960 the principles of separation by adsorption chromatography were poorly understood, and the applications of this technique in petroleum analysis were on an essentially empirical basis. Work reported since then has greatly advanced our fundamental understanding of adsorption chromatography (for a recent review see ref 9), and the extension of this information to petroleum separations quickly followed. It became possible to predict accurately the relative separation of various petroleum compound types on different adsorbents,[8] and this in turn suggested the coordinated use of several adsorbents within a single separation scheme (see below and Figure 3). Numerous comparisons have since been made between experimental and predicted separation order in the adsorption chromatography of petroleum hydrocarbons and N,O compounds,[10,11] and the results fully verify the accuracy of such predictions. As a result predictions of separation sequence could be used to advantage in aiding the identification of separated N,O compound types in our study, much as retention volumes and R_f values are used in the chromatographic identification of pure compounds. Interestingly, it is even possible to reassess the results of earlier workers and to show in several cases that reported identifications of petroleum constituents are inconsistent with the separations used to isolate these compounds.[10]

On the basis of the above considerations and additional experimental work we designed the overall separation scheme of Figure 3 for the separation of petroleum N,O compound types (for a detailed discussion, see ref 11 and 12). Its application to a series of petroleum distillates has shown excellent separation of N,O compound types in the 200–500° boiling range and useful, but somewhat poorer, separations of still higher boiling distillates. Initial chromatography on silica (Figure 3) provides clean-cut separation of the hydrocarbons plus thiophenes and furans (S_0) from sulfides

---

[7] W. Munday and A. Eaves, *World Petrol. Congr., Proc., 5th, 1959*, Paper 9, Sect. V (1960).

[8] L. R. Snyder and B. E. Buell, *J. Chem. Eng. Data*, **11**, 545 (1966).

[9] L. R. Snyder, "Principles of Adsorption Chromatography," Marcel Dekker, New York, N. Y., 1968.

[10] L. R. Snyder, *Anal. Chem.*, **38**, 1319 (1966).

[11] L. R. Snyder and B. E. Buell, *ibid.*, **40**, 1295 (1968).

[12] (a) L. R. Snyder, B. E. Buell, and H. E. Howard, *ibid.*, **40**, 1303 (1968); (b) L. R. Snyder, *ibid.*, **41**, 314 (1969); (c) *ibid.*, **41**, 713 (1969).

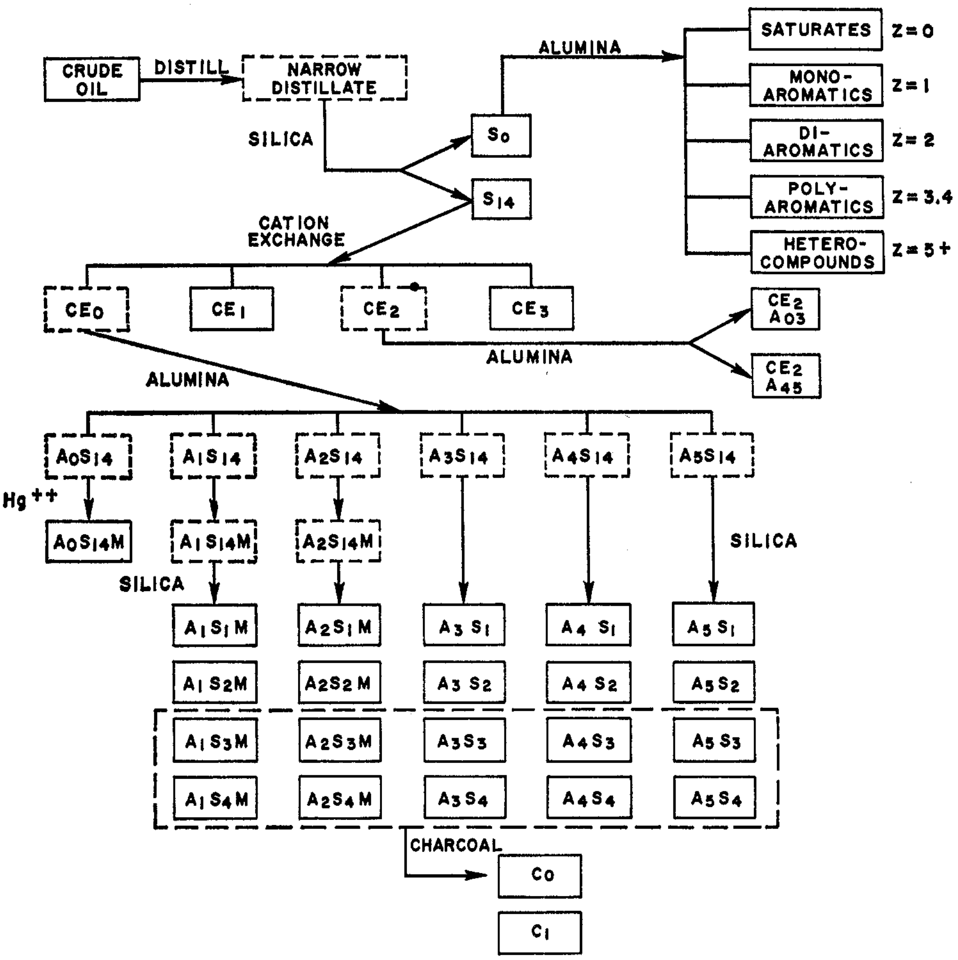


Figure 3. A separation scheme for the separation of petroleum N,O compound types.[11,12]

and other N,O compounds (S_{14}).[13] Further separation of S_0 on alumina provides fractions of increasing aromatic ring number ($z = 0$, saturated hydrocarbons; $z = 1$, single-aromatic-ring compounds, etc.), and this facilitates the mass spectral analysis of the furan derivatives in S_0. Fraction S_{14} is next separated by cation-exchange chromatography into fractions of varying basicity: CE_0, $pK_a < -2.5$; CE_1, $pK_a \approx -2.5$; CE_2, $-2.4 \leq pK_a \leq 2$; CE_3, $pK_a \leq 2$. CE_2 is further separated on alumina, providing a split between the indoles and amides in this fraction. The nonbasic fraction CE_0 is the most complex of these ion-exchange fractions, and it is further subjected to a double separation on alumina and silica. The intermediate separation by Hg^{2+}-impregnated resin removes the sulfides present in the first three alumina fractions.[14] The compounds in the 21 fractions from separation on alumina and silica increase in polarity in moving diagonally down and to the right of Figure 3 ($A_0S_{14}M$ least polar, A_5S_4 most polar). Acidic compounds are held preferentially on the basic adsorbent alumina, so that relative acidity increases in moving to the right and upward in Figure 3 (A_5 fractions most acidic, S_4 fractions largely neutral). These two-dimensional trends in fraction polarity and acidity result in a good dispersion of petroleum N,O compound types across these 21 fractions. The aliphatic N,O compounds in petroleum are largely neutral, so these compounds concentrate into the later eluted fractions from silica (surrounded by dashed line in Figure 3). These aliphatic compounds can be separated from aromatic N,O compounds by charcoal chromatography. Charcoal, unlike the polar adsorbents alumina and silica, does not preferentially adsorb polar compounds but does separate compounds on the basis of the number of aromatic rings present in the molecule. For this reason charcoal is also used to separate the CE_3 fraction into pyridines, quinolines, and benzoquinolines.

High-Resolution Mass Spectral Analysis

The value of high-resolution mass spectrometry in the analysis of petroleum N,O compounds is best illustrated with an example. In Figure 4 a partial mass spectrum is shown of the $A_{03}CE_2$ fraction (indoles concentrate) from a 200–370° distillate. This spectrum was obtained under low ionizing voltage conditions at a resolution of about 1 in 10,000. The principal peaks in

---

(13) The fraction symbols (S_0, CE_1, etc.) of Figure 3 are discussed in ref 11; S, A, CE, C, and M refer to fractions from silica, alumina, cation-exchange resin, charcoal, and mercury-impregnated cation-exchange resin, respectively. The subscripts refer to successively eluted fractions, using selected solvents for each fraction (0 eluted first).

(14) It can be predicted that sulfides present in the A_{02} fractions do not contain N or O (*i.e.*, they are not N,O compounds), but they do interfere with the subsequent determination of N,O compounds in these fractions.

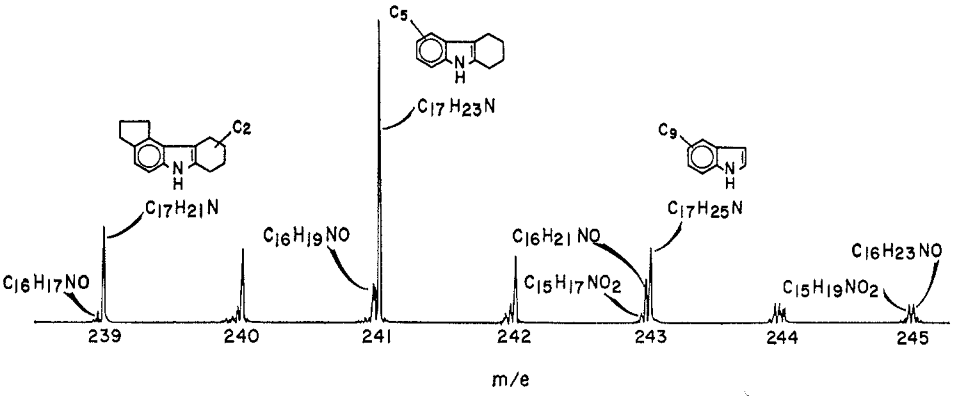


Figure 4. Partial mass spectrum of the $A_{03}CE_2$ fraction from distillate 2.

the spectrum correspond to the unfragmented molecular ions of aromatic compounds. Aliphatics (if present) show low ion intensities with extensive fragmentation under these conditions.

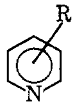
Exact mass measurement of the peaks of Figure 4 permits the assignment of the empirical formulas shown. All of the compounds in this fraction contain a single nitrogen atom per molecule, so that the major peaks fall on odd integral mass numbers. Peaks on even mass numbers arise from a heavy isotope of carbon or hydrogen in the molecule and can be ignored. Besides providing the empirical formula and relative concentration (peak height) of each molecular ion, high-resolution mass spectrometry provides separation of peaks of similar mass (*e.g.*, the triplet at m/e 243 of Figure 4). This is important in petroleum analysis, where a given fraction often contains more than one compound type.

The individual components of a petroleum compound class can be represented by the general formula C_nH_{2n+z} plus additional atoms of S, N, or O; *e.g.*, $C_nH_{2n+z}N$ for the indoles of Figure 4, with z ranging from -9 (alkyl indoles) to -17 (indoles with four cycloalkyl rings). Variations in z correspond to structural change along the x and/or z axis of Figure 1, while variation in n reflects movement along the y axis. The largest observed value of z for a particular compound type (*e.g.*, -9 for the indoles of Figure 4) is useful in defining its molecular structure, since this value of z corresponds to the simplest derivatives of the class (no cycloalkyl substitution and a minimum number of aromatic rings). Similarly the smallest observed value of n defines the empirical formula of the unsubstituted compound or *nucleus* ($n = 8$ for the alkylindoles), so long as the boiling range of the sample overlaps the boiling range of this compound.

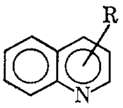
To our knowledge no one has yet reported a resolution greater than about 1 in 20,000 in the mass spectral analysis of petroleum fractions.[15] Within this limit certain molecular ions cannot be resolved: ions differing by the substitution of N for CH_2, or SH_4 for C_3. Exact mass measurement, which is accurate to within a few parts per million, can still be used to identify the principal component in these unresolved doublets. Where both components are present in significant amounts, this technique also furnishes a rough estimate of their relative concentrations (see ref 12c). Although a resolution of 1 in 50,000 or even 1 in 100,000 would have proved useful in the present study, its lack did not seriously impede the final analysis. Ultra-high-resolution mass spectrometry should prove useful in the detailed characterization of petroleum residues boiling above 500°, however.

Analysis of a California Petroleum Distillate

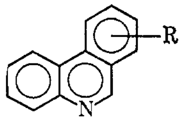
The petroleum studied (from the Wilmington oil field) was selected primarily for its high nitrogen content. It was first distilled into the six fractions of Table I, and fractions 2–5 were analyzed for all N,O compound types present in significant amounts.[12,16] Fraction 1 contained only traces of N,O compounds, and fraction 6 was too complex for detailed analysis by the present scheme. A condensed summary of these analyses is given in Table I. Bases titrable in glacial acetic acid comprise one-third to one-fifth of the total N,O compounds in each distillate fraction and are concentrated into fraction CE_3 (Figure 3). The mass spectral analysis of this fraction shows a series of aromatic nitrogen compounds beginning with $C_nH_{2n-5}N$ and extending (in the higher boiling distillates) to $C_nH_{2n-31}N$. Titration of CE_3 in acetonitrile and in acetic anhydride indicates weak bases ($pK_a \sim 5$) which do not acetylate, *i.e.*, tertiary aromatic amines. Separation of CE_3 on charcoal yields three distinct compound types which can be identified from their characteristic uv spectra: pyridines ($C_nH_{2n-5}N$; **1**), quinolines ($C_nH_{2n-11}N$; **2**), and phenanthridines ($C_nH_{2n-17}N$; **3**). These results agree with the findings of other workers, who have identified a large number of individual pyridines and quinolines in petroleum.[2b,4] Phenanthridines and benzo[*h*]quinolines have also been reported.[5c]



1



2



3

---

[15] Higher resolution is attainable with pure compounds, since instrumental sensitivity can be traded for resolution in this case.

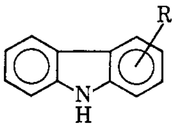
[16] L. R. Snyder, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **15**, C43 (1970).

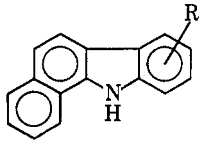
Table I
N,O Compound Types in Distillates from the Wilmington, Calif., Petroleum

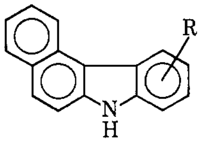
Compound type	% (wt) in each distillate[a] No. 2 (200–370°)	No. 3 (370–450°)	No. 4 (450–540°)	No. 5 (540–700°)
Aromatic Compounds[b]				
Pyridines (**1–3**)	0.6	2.7	5.0	8.2
Indoles (**4–10**)	0.3	4.5	6.1	15.2
Amides (**11, 12**)	0.2	1.2	2.1	9.3
Benzofurans (**17–19**)	0.5	1.1	1.8	3
Dihydrobenzofurans (**20**)	0.1	0.1	0.1	
Phenols (**21, 22**)	0.3	1.0	1.3	1.2
Polyfunctional compounds[c] (**15, 16, 25, 26**)	0.003	0.1	0.4	8.1
Aliphatic Compounds				
Carboxylic acids	0.5	1.7	1.3	4
Neutral oxygen compounds				
Monofunctional (**28, 29**)	0.5	0.6	1.7	2.2
Polyfunctional (**30**)	0.0	0.1	0.6	1.1
Total N,O compounds	(3.0)	(13.2)	(21.0)	(52)
Distillate yields (% (wt) of petroleum)	25.7	16.5	13.7	17.9

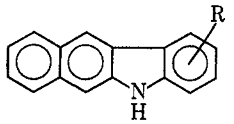
[a] Fractions 1 (200° minus) and 6 (700° plus) were not analyzed in detail; fraction 6 contains 95% N,O compounds. [b] Plus higher benzologs (*e.g.*, pyridines include quinolines, benzoquinolines, etc.). [c] Does not include sulfur groups (N,S, or O,S compounds).

Another important family of aromatic nitrogen compounds is found in fractions CE$_1$ and A$_{34}$S$_{23}$ (*i.e.*, A$_3$S$_2$, A$_3$S$_3$, A$_4$S$_2$, and A$_4$S$_3$), beginning with $C_nH_{2n-15}N$ and extending to $C_nH_{2n-29}N$ (mass spectral analysis). Some overlap of this series of compounds into adjacent fractions is observed. Fractions CE$_1$ and A$_{34}$S$_{23}$ show the characteristic uv maxima of the alkylcarbazoles ($C_nH_{2n-15}N$, **4**) (with a pronounced maximum at 292 nm) and a sharp ir band at 2.88 μ (N–H). Further separation of CE$_1$ (and other fractions) on alumina yields strongly adsorbing fractions whose uv spectra match those of the 1,2-benzcarbazoles ($C_nH_{2n-21}N$; **5**) and 3,4-benzcarbazoles (**6**). The 1,2 isomers are present in roughly 6-fold greater concentration than the 3,4-benzcarbazoles, while the 2,3 isomers are absent altogether (more about this shortly). Previous workers (see ref 2b) have isolated carbazole from petroleum, and one study[5e] showed that carbazoles and benzcarbazoles were present in every petroleum analyzed.

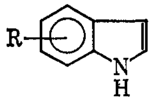

4


5

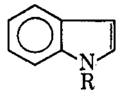

6

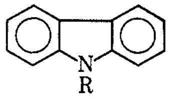

7 (absent)

Aromatic nitrogen compounds beginning with $C_nH_{2n-9}N$ and extending to $C_nH_{2n-21}N$ are found in small amounts in the various distillates. These compounds are concentrated into the weakly adsorbing alumina fraction (A$_{03}$) from CE$_2$, and are very weak bases (pK_a ~ 0) which can be titrated in acetic anhydride. The uv spectrum of this fraction matches that of the alkylindoles ($C_nH_{2n-9}N$; **8**), and this assignment is confirmed by colorimetric analysis (reaction with *N*,*N*-dimethyl-*p*-aminobenzaldehyde). Indoles have been reported as petroleum constituents by previous workers, usually on the basis of inconclusive evidence.

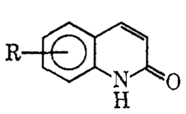

8

Small amounts of aromatic nitrogen compounds falling mainly on the $C_nH_{2n-11}N$ to $C_nH_{2n-17}N$ series are found in the A$_{12}$S$_{14}$ fractions. These are believed to be mainly *N*-alkylindoles (**9**) and carbazoles (**10**), but the evidence is largely indirect. The latter compound types are predicted to concentrate into the A$_{12}$S$_{14}$ fractions. Other simple nitrogen compound types (nitriles, amines, non-nitrogen-substituted indoles and carbazoles) can be ruled out on the basis of separation predictions and the absence of characteristic ir absorption bands. Most of the carbazoles and about half of the indoles in these distillates are of type **4** and **8**, rather than N-alkyl substituted.

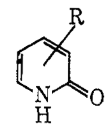

9


10

Aromatic compounds with an atom of both nitrogen and oxygen in the molecule are found concentrated into CE$_2$, with some overlap into CE$_1$, CE$_3$, and the more strongly adsorbing neutral fractions (*e.g.*, A$_5$S$_4$). These begin at $C_nH_{2n-5}NO$ and extend to $C_nH_{2n-29}NO$; they are mainly very weak bases (pK_a ~ 0). Fractions in which this series of compounds is present exhibit ir bands in the amide region (5.9–6.1 μ), and the integrated intensity of these amide bands correlates quantitatively with the concentrations of this family of compounds determined by mass spectrometry. On this basis, and in view of their weak basicity, we conclude that these compounds are mainly aromatic amides or amide-like compounds (*e.g.*, 4-quinoline, 3-acetylindole). The 2-quinolones ($C_nH_{2n-11}NO$; **11**) have



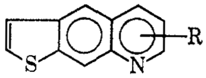
11



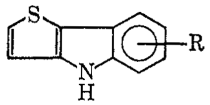
12

been reported in a previous petroleum[17] and were also isolated from the present petroleum. The beginning of this family of compounds at $C_nH_{2n-5}NO$ suggests the presence of the next lower benzolog, the 2-pyridones **12**. Other aromatic amides are also present in these distillates, but their structures have not yet been determined. Several distinct amide bands can be observed in addition to the pyridone/quinolone band at 6.08 μ. A band at 6.00 μ appears to be associated with a series of compounds which begin at $C_nH_{2n-15}NO$ and have a unique uv spectrum.[12b] Individual compounds of this series have been isolated from another petroleum.[18]

Aromatic compounds with an atom of both nitrogen and sulfur in the molecule are found in small amounts in distillate fraction 4 and in substantial amounts in fraction 5. Most of these compounds concentrate into fraction CE_3 with the pyridine bases, but a smaller quantity occurs together with the carbazoles in fractions CE_1, $A_{34}S_{23}$, etc. Both of these series of compounds begin at about $C_nH_{2n-15}N$, but the poor mass spectral resolution of these compounds from corresponding sulfur-free nitrogen compounds makes this somewhat uncertain. On the basis of the separation characteristics of these two classes (*i.e.*, comparison with predictions) and their empirical formulas, the basic compounds appear to be thiophenoquinolines ($C_nH_{2n-15}NS$; **13**) and the nonbasic compounds thiophenoindoles ($C_nH_{2n-15}NS$; **14**). However, these assignments must be regarded as speculative.

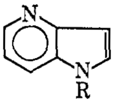


13

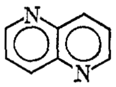


14

Aromatic compounds with two nitrogen atoms per molecule are found in traces in distillate fraction 3, in minor amounts in fraction 4, and in substantial quantities in fraction 5. These concentrate into fraction CE_3 and fall on the series $C_nH_{2n-8}N_2$ through $C_nH_{2n-20}N_2$. Infrared data do not indicate the presence of N–H groups. On the basis of their separation sequence and empirical formulas, these compounds could consist of the N-substituted azaindoles ($C_nH_{2n-8}N_2$; **15**), azaquinolines ($C_nH_{2n-10}N_2$; **16**), and higher benzologs.



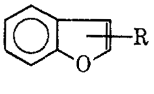
15



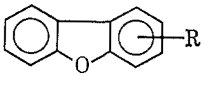
16

Traces of compounds beginning with $C_nH_{2n-11}NO_2$ and extending through $C_nH_{2-n17}NO_2$ were found in the $A_{23}CE_2$ fractions from distillates 2 and 3. No satisfactory structure has yet been found which explains the empirical formulas and separation sequence. Aliphatic compounds which contain nitrogen appear to be absent from the present distillates; aromatic nitrogen compounds as determined by mass spectral analysis quantitatively account for all the nitrogen in fractions from each of the distillates studied.

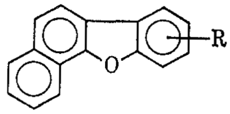
A family of aromatic oxygen compounds concentrates into the hydrocarbon–sulfur compound fractions from S_0. These begin at $C_nH_{2n-10}O$ in the z = 2 fraction and $C_nH_{2n-16}O$ in the z = 3–5+ fractions. The only oxygen compounds which are sufficiently weakly adsorbing to be found in these fractions are the furan derivatives, confirming the presence of the benzofurans ($C_nH_{2n-10}O$; **17**) and dibenzofurans ($C_nH_{2n-16}O$; **18**).



17



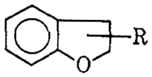
18



19

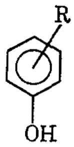
A sharp jump in concentration at the $C_nH_{2n-22}O$ series in the z = 4+ fraction suggests that the naphthobenzofurans (**19**) are also major furan types. A similar, less pronounced jump at $C_nH_{2n-28}O$ likewise hints at the dinaphthofurans. Individual dibenzofurans have been isolated from a previous petroleum.[19]

Small amounts of aromatic compounds beginning at $C_nH_{2n-8}O$ are found in the A_1S_{14} fractions of distillation fraction 2 and the A_2S_{14} fractions of distillate 3. The uv spectra of these fractions closely resemble those of the alkyl-1,2-dihydrobenzofurans (coumarans, $C_nH_{2n-8}O$; **20**), which are predicted to concentrate into these fractions. The ir spectra of these fractions are free from bands due to carbonyl or hydroxyl groups.

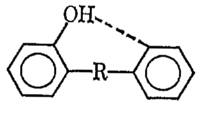


20

Another series of aromatic oxygen compounds beginning at $C_nH_{2n-6}O$ and extending to $C_nH_{2n-28}O$ concentrates into fractions $A_{45}S_{14}$. These are very weak acids which titrate in pyridine (pK_a $\sim$ 9), and they show sharp ir bands at 2.76 (free OH) and 2.82 μ (intramolecularly hydrogen bonded OH). The uv spectra of these fractions, when freed of carbazoles by charcoal chromatography, are characteristic of alkylphenols (**21**). A sharp jump in concentration occurs at $C_nH_{2n-14}O$ in some fractions, and this jump correlates with enhanced intramolecular hydrogen bonding be-



21



22

---

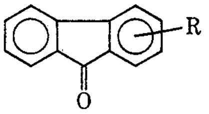
(17) E. C. Copelin, *Anal. Chem.*, **36**, 2274 (1964).

(18) J. R. Fox, private communication.

(19) F. F. Yew and B. J. Mair, *Anal. Chem.*, **38**, 231 (1966).

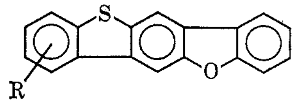
tween an OH group and an aromatic ring (2.82-μ band intensity). This suggests the presence of phenylalkylphenols ($C_nH_{2n-14}O$; **22**). The naphthols are present in only minor amounts (or not at all) in the present petroleum. Individual phenols have been identified in other petroleums.[2b]

Fluorenones (**23**) have been identified in another petroleum from the Wilmington oil field (see ref 2b), but aromatic ketones were not found in significant amounts in the present petroleum.

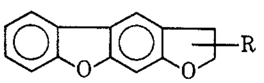


23 (not found)

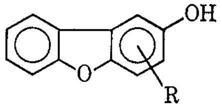
Several polyfunctional aromatic oxygen compounds were observed in trace amounts (0.02–0.06% (wt)) in distillate 5 of Table I. Since these were present in very small concentrations in the final fractions, structural assignments were based on the mass spectrally determined empirical formulas and the position of those compounds in the separation scheme of Figure 3. A series of homologs beginning with $C_{18}H_{10}OS$ was found in the $z = 5+$ fraction of S_0. Only furan or thiophene functional groups are weakly enough adsorbing to be found in this fraction, suggesting benzothiophenodibenzofurans (**24**). Compounds beginning at $C_nH_{2n-18}O_2$ and extending to $C_nH_{2n-28}O_2$ are found in the $A_{12}S_4$ fractions. The benzofuranocoumarans (**25**) are one of the few compound types with two oxygen atoms per molecule which are predicted to concentrate into these fractions. Two series of compounds are found in the A_5S_{24} fractions, beginning at $C_nH_{2n-16}O_2$ and $C_nH_{2n-6}OS$. These are probably phenol derivatives because of their position in the separation scheme, and structures **26** and **27** are likely possibilities. Inferential evidence favoring structures **24**–**27** is their structural resemblance to simpler petroleum compounds: the furans, thiophenes, coumarans, and phenols.



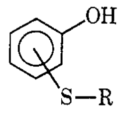
24



25



26



27

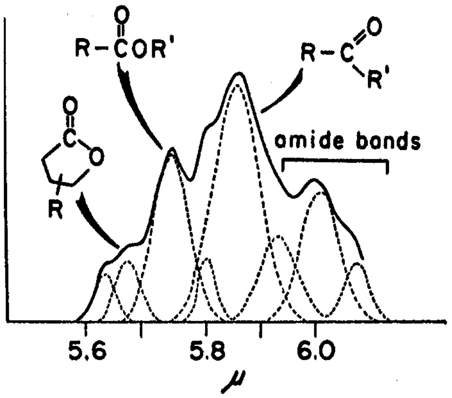
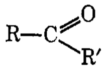
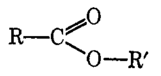


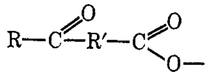
Figure 5. Partial ir spectrum of A_3S_4 fraction from distillate 4.



28



29



30

A significant part of the $A_0S_{14}M$ and $A_{15}S_{34}$ fractions consists of neutral aliphatic oxygen compounds, and these are concentrated into the C_0 fractions from charcoal separation. The ir spectra of these fractions show several distinct bands in the carbonyl region, as illustrated in Figure 5. An ester band at 5.75 μ and/or a ketone band at 5.88 μ are in all cases most intense, from which we conclude that aliphatic ketones **28** and esters **29** are the main constituents. Monofunctional aliphatic oxygen compounds (*e.g.*, **28**, **29**) are predicted to concentrate into the A_{03} fractions, and difunctional compounds (*e.g.*, **30**) in the A_{45} fractions. These assignments are confirmed by the 2-fold greater carbonyl absorptivity (integrated absorbance of peaks falling between 5.6 and 5.9 μ) of the A_{45} fractions. The oxygen contents of these various $A_{15}S_{34}C_0$ fractions correlate well with their ir analysis in terms of mono- or difunctional ketones and esters. Several individual aliphatic ketones have been isolated from petroleum (see ref 2b), and the presence of esters in other petroleums has been confirmed by saponification and ir studies.[20] A minor ir band at 5.68 μ (Figure 5) suggests small amounts of γ-lactones, and one compound of this class (oxyallobetul-2-ene) has been isolated from petroleum.[2b]

Carboxylic acids are a common constituent of petroleum, and a large number of aliphatic carboxylic acids have been identified in petroleum.[2b,4] This group of compounds is lost in the separation scheme of Figure 3, being irreversibly adsorbed on alumina. They can, however, be recovered by other techniques (*e.g.*, ion exchange, base extraction). A systematic study of the carboxylic acids from another petroleum has been reported recently by Seifert, *et al.*[21] These workers have reported a wide variety of aromatic and nitrogen- or sulfur-containing carboxylic acid types in addition to the alkane- and cycloalkanecarboxylic acid types found by previous workers. The studies of Seifert, *et al.*, are based on extensive separation, chemical reaction, and high-resolution mass spectrometry.

Despite these recent advances in our understanding of the N,O compounds in petroleum, much remains to be learned. The various subtypes in the amide and aliphatic oxygen compound classes need to be further characterized, particularly with respect to unassigned ir bands. Detailed structures for the polyfunctional and sulfur-containing aromatic N,O compounds (*e.g.*, **13**–**16**, **24**–**27**) should be confirmed. Although these compounds are minor constituents of distillates 2–4 of Table I, they probably account for most of the N,O

---

(20) G. I. Jenkins, *J. Inst. Petrol., London*, **51**, 313 (1965).

(21) (a) W. K. Seifert and R. M. Teeter, *Anal. Chem.*, **41**, 786 (1969); W. K. Seifert, R. M. Teeter, W. G. Howells, and M. J. R. Cantow, *ibid.*, **41**, 1638 (1969); W. K. Seifert and R. M. Teeter, *ibid.*, **42**, 180 (1970).

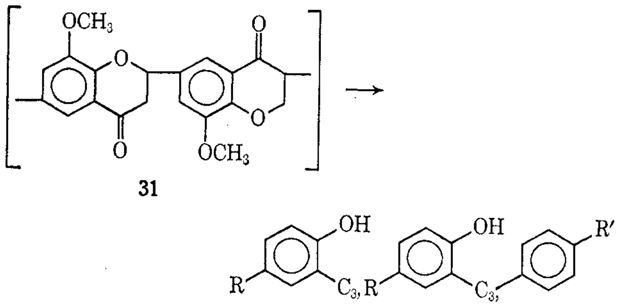
compounds in the distillation residue and hence about half of all N,O compounds in the original petroleum. Finally, information comparable to that summarized in Table I is needed for a series of petroleums of different geological age and environment.

Structural Relationships Among the Petroleum N,O Compounds

Certain general trends can be recognized in the analytical data of Table I (for a detailed discussion, see ref 16). The total concentration of N,O compounds in each distillate fraction increases sharply with fraction boiling point. With increased boiling point there is also a marked tendency toward increasing aromaticity and polyfunctionality of these compounds. It is likely that the distillation residue (fraction 6) is composed mainly of aromatic, polyfunctional N,O compounds.

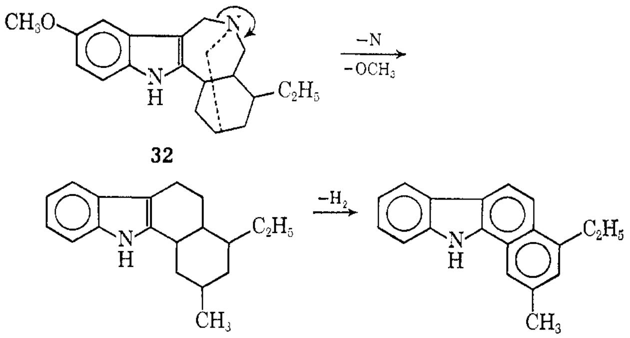
As in the case of the hydrocarbons and sulfur compounds (Figures 1 and 2) each N,O compound type exists as a continuous series of compounds of varying carbon number and cycloalkyl substitution. Within a particular family of compounds, structural variation along the z axis (as in Figures 1 and 2) can take different forms. In the pyridine benzologs the single aromatic ring of pyridine itself is followed by successive ring fusions to yield the quinolines, phenanthridines, and (presumably) larger condensed ring structures. This pattern is the same as that observed in the hydrocarbon and thiophene derivatives. The furan and pyrrole families differ in that the single-ring members (furans and pyrroles) are totally absent from the Wilmington petroleum, and the two-ring members (benzofurans, indoles) are present in small concentrations (relative to three-ring and four-ring derivatives). These structural trends in the furan and pyrrole families parallel the relative reactivities toward acid environment of the individual compound types, furans > benzofurans > dibenzofurans ≈ naphthobenzofurans; pyrroles > indoles > carbazoles ≈ benzcarbazoles, suggesting that the smaller ring compounds may have been present in petroleum originally but were selectively destroyed during storage and migration.

In the phenol family structural variation along the z axis appears to take place by phenyl substitution to yield the phenylalkylphenols, rather than by ring fusion to give the naphthols. This preference for a nonfused two-ring structure is unique among major petroleum families, whether hydrocarbons, sulfur compounds, or N,O compounds. One explanation is that the phenols are derived from plant lignin, which can be regarded as a polymeric derivative of hydroxylated phenylpropane, *e.g.*, **31**.[22] Cleavage of the lignin chain with selective loss of certain oxygen groups would lead to phenols and phenylalkylphenols, but not naphthols. A related hypothesis is that lignin-like fragments of lower molecular weight are present in plants and can be degraded to phenol derivatives in a simpler sequence of reactions.

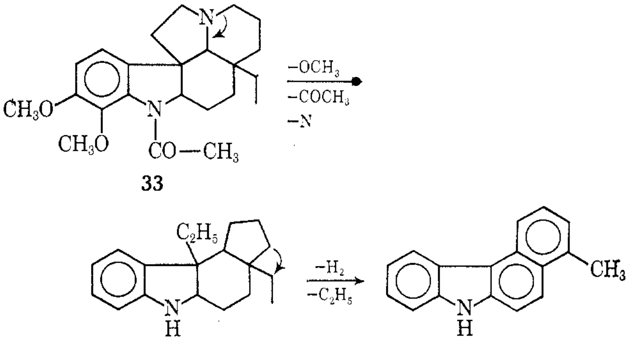


31

We have noted the relative concentrations of the different benzcarbazole isomers: 1,2 > 3,4, with 2,3 absent. This same distribution is found in a wide variety of petroleums,[5c] and it has been attributed[23] to the formation of these compounds from plant alkaloids of similar structure. Thus several plant alkaloids are structurally related to the 1,2-benzcarbazoles, and others are somewhat less obviously related to the 3,4-benzcarbazoles, *e.g.*, ibogaine (**32**) and aspidospermine (**33**). Interestingly, no such structural connections can be drawn between the 2,3-benzcarbazoles and known alkaloids. It is also possible that nonbasic plant constituents which are intermediate in structure between **32** or **33** and petroleum benzcarbazoles are the main benzcarbazole precursors, rather than the alkaloids themselves.

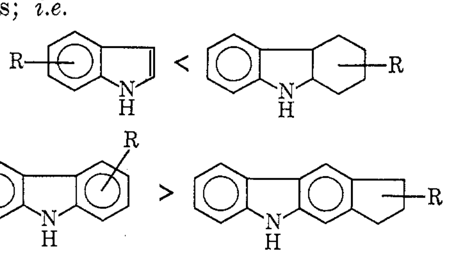


32



33

Among the indoles and carbazoles it is observed[16] that the addition of a cycloalkyl substituent is relatively more favored among the indoles than among the carbazoles; *i.e.*



---

(22) A. Russell, *J. Amer. Chem. Soc.*, **70**, 1060 (1948).

(23) L. R. Snyder, *Nature*, **205**, 277 (1965).

Similar trends are not observed in other petroleum families. In each case a three-ring structure is preferred, and this recalls the presence of the tetrahydro- or hexahydrocarbazole nucleus in certain alkaloids (*e.g.*, aspidospermine (**33**). Again it seems likely that a preference for a given structure in petroleum is rooted in a similar preference for that structure in plants.

A detailed examination of the structural relationships between individual N,O compounds and their precursors in nature will be presented elsewhere.[24]

---

[24] G. C. Speers and E. V. Whitehead, "Crude Petroleum. Organic Geochemistry: Methods and Results," Springer-Verlag, New York, N. Y., in press.

Silyl–Proton Exchange Reactions

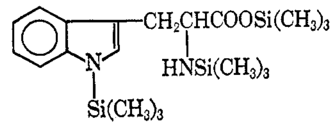
JOHANN F. KLEBE

General Electric Research & Development Center, Schenectady, New York

Received April 27, 1970

Organosilicon compounds are enjoying a rapidly growing appreciation among even those organic chemists and biochemists who are not otherwise particularly concerned with organometallic chemistry. This esteem arises from the fact that a large variety of organic and biologically important substances can readily—and reversibly—be converted into organosilyl derivatives with profoundly changed properties. The "silylation" of organic compounds—the replacement of protons from oxygen, nitrogen, and sulfur, to name the most common cases, by triorganosilyl (most often trimethylsilyl) groups—has the general effect of reducing hydrogen bonding between molecules and thus increasing volatility and solubility.

To illustrate the effect of silylation, the amino acid tryptophan is a high melting, moderately water soluble solid which is insoluble in most organic solvents and has a negligible vapor pressure; it therefore cannot be analyzed by gas–liquid partition chromatography. Its tris(trimethylsilyl) derivative is a liquid which is miscible in all proportions with organic solvents such as benzene; it has a boiling point of 140° (0.2 mm) and is sufficiently thermally stable to allow analysis by glpc. On contact with water, the silyl groups are removed hydrolytically and tryptophan is regenerated.[1]



Silylation has become an important part of gas–liquid partition and thin-layer chromatographic analyses of materials such as carbohydrates, amino acids, Krebs cycle acids, and steroids. A recent review of this field revealed over 800 references to investigations of silylation and its application for analytical purposes.[2]

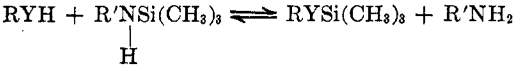
In synthetic applications, silylation of a molecule may increase its reactivity toward attacking reagents, either at the site of the newly introduced silyl substituent or in adjacent positions of the molecule, or the silyl group may serve as protection for sensitive functional groups during a synthesis. This actively growing field encompasses a wide spectrum of organic compounds and reactions.[3]

Methods of Silylation

Two general methods are available for silylations: reactions with chlorosilanes and a tertiary amine as acid acceptor, and exchange reactions with silicon–nitrogen compounds functioning as silyl donors. The classical chlorosilane method employs a very powerful reagent mixture; the removal of hydrochloric acid in the form of its amine salt provides sufficient driving force to displace practically any reactive hydrogen on a heteroatom by silyl. Separation problems stemming from the formation of amine salts and the corrosive nature of the reagents are the drawbacks of this method.

$$\mathrm{RYH} + (\mathrm{CH_3})_3\mathrm{SiCl} + \mathrm{R'_3N} \longrightarrow \mathrm{RYSi(CH_3)_3} + \mathrm{R'_3N\cdot HCl} \quad (1)$$

Silylamines have long been used as alternative silylating agents. This silylation method is based on the relatively slow silyl–proton exchange between the silyl derivative of a low-boiling amine or ammonia[4] and mobile protons of the substrate. The reaction equilibria are shifted toward the product side by distillation of the amine. Although the exchange rates are enhanced by the addition of catalytic amounts of ammonium salts or chlorosilanes,[5] silylations by this method require typically several hours at reflux temperature.



$$\mathrm{RYH} + \mathrm{R'}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\mathrm{Si(CH_3)_3} \rightleftharpoons \mathrm{RYSi(CH_3)_3} + \mathrm{R'NH_2} \quad (2)$$

The most recent addition to the list of silylating agents is the class of silylamides[1,6,7] which combine the

---

[1] J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

[2] A. E. Pierce, "Silylation of Organic Compounds," Pierce Chemical Co., Rockford, Ill., 1968.

[3] For reviews, see L. Birkofer and A. Ritter, *Angew. Chem.*, **77**, 414 (1965); K. Rühlmann, *Z. Chem.*, **5**, 130 (1965); J. F. Klebe, *Advan. Org. Chem.*, in press.

[4] O. Mjörne, *Kem. Tidskr.*, **62**, 120 (1950).

[5] R. Fessenden and D. F. Crowe, *J. Org. Chem.*, **26**, 4638 (1961).