dride. A −300 mesh sample of $VH_{0.87}$ was treated for several hours in a platinum dish with 10% HF. The HF solution then was removed and the product washed in water, alcohol, and finally in ether. An X-ray diffraction powder pattern of the product showed the presence of the f.c.c. vanadium dihydride. Faint lines in the low angle region, however, indicated a small amount of the monohydride. A trace of vanadium oxide also was indicated by faint lines in the diffraction pattern. The value of the lattice constant for the dihydride determined from this film was 4.271 ± 0.002 Å. The formula was found to be $VH_{1.77 \pm 0.05}$ by hydrogen loss *in vacuo*. Vanadium samples of 99.8+ per cent. purity were obtained from the Oregon Metallurgical Company, Albany, Oregon. Additional details of preparation, stability, and physical properties will be given in future publications.

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RECEIVED JULY 24, 1961

REDUCTION OF ISOLATED OLEFINIC BONDS BY MEANS OF *p*-TOLUENESULFONYLHYDRAZINE

Sir:

Prompted by Thiele's early work[1] on azodicarboxylic acid, and other considerations, we recently investigated the decomposition of this substance in the presence of olefinic compounds, with the discovery that reduction of isolated carbon–carbon double bonds occurred.[2] Of the various mechanistic interpretations which might be entertained (including reduction by azomonocarboxylic acid or a related species), involvement of the elusive H_2N_2 or an equivalent is the most direct. We have now found that saturation of isolated olefinic bonds also can be effected through thermal decomposition of another possible H_2N_2 (but not azomonocarboxylic acid) source, *p*-toluenesulfonylhydrazine.[3,4]

Reductions were carried out by heating under reflux a solution of the olefinic component and a 100% excess of *p*-toluenesulfonylhydrazine in diglyme for one hour under nitrogen.[5] As typical results, oleic and elaidic acids were reduced to stearic acid (73% and 70%, respectively, both by infrared analysis and bromine titration); in these runs the sulfur-containing by-products were removed by extraction or by oxidation to the water-soluble sulfonic acid. Reduction of allyl alcohol gave 1-propanol (99%), and cyclohexene gave cyclohexane (98%) (both by vapor phase chromatography). The thermal decomposition of *p*-toluene sulfonylhydrazine should give rise to *p*-toluenesulfinic acid as one of the initial products,[6] and confirmation of this presumption has been obtained by the isolation of the sulfinic acid, along with *p*-tolyl disulfide, from the pyrolysis of the sulfonhydrazide in diglyme.[7]

Thus, the azodicarboxylic acid and *p*-toluenesulfonylhydrazine reduction methods—insofar as they are compatible with the H_2N_2 hypothesis—involve preparation of a species which, although in itself too unstable to be isolated under ordinary conditions,[8] nevertheless can be utilized as a reagent in the presence of a substrate.

We wish to take this opportunity for drawing attention to the general possibilities of carrying out new reactions on organic molecules through the use of unstable neutral inorganic reagents, in the same sense that unstable, unisolated organic entities (such as carbenes) are utilized. This field of investigation would appear to be relatively virgin, in that incorporated into the entire body of organic chemistry are only few such examples—virtually all known reactions involving inorganic reagents are executed by means of "shelf" chemicals of normal stability. Further, within the confines of inorganic chemistry, this device may be useful in providing evidence for the existence of such unstable species.

(1) J. Thiele, *Ann.*, **27**, 127 (1892). Thiele reported that in the decarboxylation of azodicarboxylic acid, carbon dioxide, nitrogen and hydrazine are formed; and he suggested that the hydrazine and nitrogen arise by disproportionation of the unstable diimide. The comment may be made that reduction of azodicarboxylic acid with H_2N_2 would also lead to hydrazine, *via* decarboxylation of the intermediate hydroazodicarboxylic acid.

(2) E. E. van Tamelen, R. S. Dewey and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).

(3) No evidence is available to distinguish between HN=NH and $H_2N\overset{-}{-}\overset{+}{N} \leftrightarrow H_2N\overset{+}{=}\overset{-}{N}$ in this decomposition.

(4) Commercially available from Aldrich Chemical Company, Milwaukee, Wis.

(5) The decomposition of *p*-tosylhydrazine can be accelerated by the addition of hydroxide ion, and to some extent by metal ions. Whether the decomposition is a radical or cyclic process, or involves an α- or β-elimination, is unknown.

(6) The loss of *p*-toluenesulfonylhydrazine by prolonged heating during recrystallization has been observed by C. H. DePuy and D. H. Froemsdorf, *J. Am. Chem. Soc.*, **82**, 636 (1960).

(7) *p*-Toluenesulfinic acid is converted to *p*-tolyl *p*-toluenethiosulfonate in hot aqueous solution (R. Otto and O. V. Gruber, *Ann.*, **145**, 13 (1868)), and the thioester has been converted to *p*-tolyl disulfide in hot aqueous sodium carbonate (E. Fromm, *Ber.*, **41**, 3409 (1908)).

(8) Some evidence for persistence of H_2N_2 at low temperatures has been presented, for example, by S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958).

(9) National Institutes of Health Postdoctoral Fellow.

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RECEIVED JULY 26, 1961

THE STRUCTURE OF NYBOMYCIN

Sir:

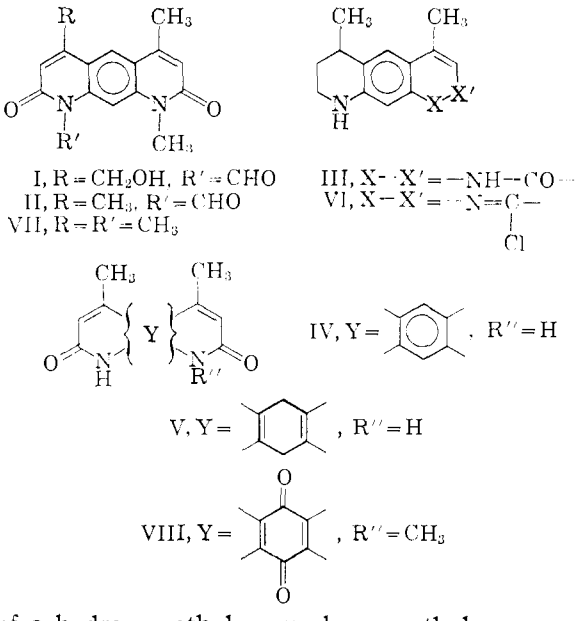
The antibiotic nybomycin has been described in independent reports by Strelitz, Flon and Asheshov,[1] and by Eble, Boyack, Large and DeVries[2]; apart from strong *in vitro* biological activity, its chief characteristics are its thermal stability (m.p. 325–330°) and its extreme insolubility except in concentrated acids. The report by Eble[2] showed the molecular formula of nybomycin to be $C_{16}H_{14}N_2O_4$ (rather than $C_8H_7NO_2$)[1] and established the presence of an aliphatic hydroxyl group. The present report shows the structure of nybomycin to be represented by I.

On treatment with refluxing 47% hydriodic acid (in which nybomycin is soluble), I is converted to deoxynybomycin (II, $C_{16}H_{14}N_2O_3$,[3] dec. >335°), which precipitates from this medium. Deoxynybomycin differs from the parent I by replacement

(1) F. Strelitz, H. Flon and I. N. Asheshov, *Proc. Natl. Acad. Sci. U. S.*, **41**, 620 (1955).

(2) T. E. Eble, G. A. Boyack, C. M. Large and W. H. DeVries, *Antibiotics and Chemotherapy*, **8**, 627 (1958).

(3) Microanalyses are within accepted limits.



of a hydroxymethyl group by a methyl group, as shown by solubility characteristics, by loss of infrared hydroxyl bands at 3350 and 1106 cm.$^{-1}$ and by the nuclear magnetic resonance spectra[4] of the two compounds (I and II), which contain singlets at 3.79 (Ar–CH_2–O–) and 7.04 (Ar–CH_3), respectively.

Under more vigorous reductive conditions (red phosphorus, 47% hydriodic acid, 240°, 1.5 hours) deoxynybomycin is converted to a mixture of three new compounds, III, IV, and V. The n.m.r. spectrum[4] of III ($C_{14}H_{16}N_2O$, m.p. *ca.* 280°) contains three aromatic singlet protons at 1.71, 1.92 and 2.71, an Ar–CH_3 singlet at 7.10, and the groupings N–CH_2–C, Ar–$CHCH_3$–C, and C–CH_2–C—at 6.05 (triplet, J = 5.7 cps.), 6.5 (multiplet) and 8.35 (doublet, J = 5.4 cps.), and 7.6 (multiplet), respectively. That III is an amide is shown by its infrared spectrum (1655 cm.$^{-1}$) and by its conversion in refluxing phosphorus oxychloride to a chlorimine (VI, $C_{14}H_{15}N_2Cl$, m.p. 172–174°), whose n.m.r. spectrum[4] is very similar to that of III and whose ultraviolet spectrum closely approximates that of 6-dimethylaminoquinoline.[5] Compound VI, moreover, is dehydrogenated to a fully aromatic, fluorescent compound whose ultraviolet spectrum is nearly identical with that of published diazaänthracenes.[6] The ultraviolet spectra of VI and its dehydrogenation product thus establish a linear three-ring system for nybomycin and the position of one nitrogen.

Compound IV ($C_{14}H_{12}N_2O_2$) dissolves in sodium hydroxide, where it reacts with dimethyl sulfate to give VII ($C_{16}H_{16}N_2O_2$, darkens >330°). The unusual simplicity of the n.m.r. spectrum of VII establishes the symmetry of the nybomycin nucelus. The spectrum[4] contains singlets at 2.67 (two Ar–H's), at 5.73 (two N–CH_3's), and at 7.10 (two Ar–CH_3's). Comparison of these n.m.r. values with those of model compounds reveals their remarkable similarity to those of 1,4-dimethyl-2-quinolone (Ar–H 2.57, N–CH_3 5.86, Ar–CH_3 7.23), and their divergence from those of N-methylisoquinolones (*e.g.*, N–CH_3 6.46).

The appearance of both N–CH_3 groups at 5.73 establishes the attachment of both nitrogens to the central ring, while the presence of both Ar–CH_3 groups at 7.10 locates them tentatively in the γ-positions of the two pyridone rings, a location substantiated by the two Ar–H protons at 2.67. These assignments are in agreement with the n.m.r. patterns for III and VI (*cf.* above). In distinguishing the formula VII and its 1,8-diazaänthracene nucleus from the alternative 1,5-diazaänthracene formulation, the presence of two Ar–H peaks (singlets, one proton each) at 1.17 and 1.85 in the n.m.r. spectrum of VII is definitive, since the alternative, fully symmetrical, 1,5-diazaänthracene nucleus would require a singlet (two-proton) Ar–H peak for the identical central ring protons. Substantiation of the ring system of VII is provided by the rapid concentrated nitric acid oxidation (steam bath) of II to a red *p*-quinone (VIII, $C_{15}H_{12}N_2O_4$, m.p. *ca.* 330°) with two symmetrical Ar–CH_3 groups (τ 7.05)[4] and two nearly symmetrical Ar–H groups (τ 2.45 and 2.66).

The conversions of II to IV (–CO, $-CH_2$) and of II to VIII (–CO, $-H_2$, $+O_2$) are unusual in that a CO group is lost both on reduction and on oxidation. This is explained readily, however, by the presence of an N–CHO group in II (and in I).[7] The presence of the formamide is further evidenced by increased infrared absorption at 1675 cm.$^{-1}$. Its n.m.r. peak is to be found among the unsplit protons of the aryl region [at 1.64, 2.58, 2.77, and 3.12 (2)] in both I and II; for comparison, the N–CHO proton of N-methylformanilide is found at τ 1.47.

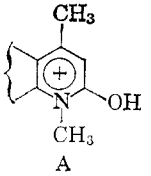
The hydroxymethyl group, found only in nybomycin itself, is located on the same ring as the formyl group by the comparative C–CH_3 values[4] of I (7.10), of deoxynybomycin (7.04, 7.10), and of VII (7.10), also measured relative to an internal N-methylformanilide marker (N–CH_3, 6.70). The exceptional Ar–CH_3 peak (at 7.04), appearing first

(4) All n.m.r. spectra described were obtained on trifluoroacetic acid solutions at 60 Mc., either with a Varian Model V-4300C high resolution instrument or with a Varian Model A-60 spectrometer. An internal tetramethylsilane standard and the audio-oscillator side band technique were employed; the values given refer to the τ scale [G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)].

(5) E. A. Steck and G. W. Ewing, *J. Am. Chem. Soc.*, **70**, 3397 (1948). In this reference the ultraviolet spectra of 6- and 7-aminoquinolines are nearly indistinguishable, while that of 6-dimethylaminoquinoline shows a bathochromic shift and more nearly corresponds to that of VI. Thus, these ultraviolet data only establish the attachment of an amine grouping in the 6- *or* 7-position of VI. The point is resolved below in favor of the 7-position by the n.m.r. spectrum of VII.

(6) N. Ikekawa, *Chem. Pharm. Bull. (Japan)*, **6**, 401 (1958).

(7) An alternative O–CHO grouping is eliminated by the absence of infrared carbonyl absorption above 1665 cm.$^{-1}$ in spectra of I and II. An alternative Ar–CHO group is eliminated by the cited infrared data and by the presence of five C–H singlets in the trifluoroacetic acid n.m.r. spectra of I and II. The surprisingly slow hydrolysis of the formyl group in acid may be explained by the low solubility of II in all but concentrated acids and by the preferential protonation of the N-methylpyridone ring to give a stabilized carbonium ion (A).



A

after loss of the CH_2OH group and found only in the presence of the NCHO group, must be on the formylated ring.

The chemical effect of the N-formyl group is manifest in two novel variations on the reactions above. (1) Further phosphorus–hydriodic acid reduction of IV gives only V, and no III. The ultraviolet spectrum of V shows it to contain the two isolated pyridone nuclei shown.[8] Since no III is formed, the formyl group is apparently required for reduction of the pyridone ring; otherwise, the central ring is the more readily reduced. (2) Treatment of IV and VII with concentrated nitric acid does not give quinones analogous to VIII, but instead gives dinitro compounds.

Acknowledgment.—This investigation was supported in part by a research grant, No. E-1278, from the National Institute of Allergy and Infectious Diseases, Public Health Service. We also wish to express our thanks to Dr. T. E. Eble and the Upjohn Company for a very generous nybomycin sample.

(8) H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942).

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RECEIVED JUNE 26, 1961

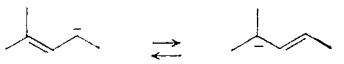
PRODUCTION, STABILIZATION, AND REACTIONS OF SIMPLE HYDROCARBON CARBANIONS. I. ACTIVATION OF C-H BONDS IN HYDROCARBON OLEFINS

Sir:

The production of carbanions from simple hydrocarbons has been the subject of much study.[1] Recently, Price has shown that allyl ethers undergo an anionic isomerization reaction in homogeneous media at mild conditions.[2] We have had a program in this area for some time and these recent results prompt us to communicate our findings concerning the anionic activation of hydrocarbon olefins. We have found that the low temperature, homogeneous, base catalyzed isomerization of hydrocarbon olefins is possible in certain media. In this communique, only the solvent dimethyl sulfoxide will be discussed.

The base used in this research was sublimed potassium *tert*-butoxide. At 55°, a dimethyl sulfoxide solution 1.0 molar in 2-methylpentene-1 and 1.0 molar in potassium *tert*-butoxide was found to yield 2-methylpentene-2. Starting with either 2-methylpentene-1 or 2 methylpentene-2, no 4-methylpentene-1 or *cis* and *trans* 4-methylpentene-2 was observed after 55 hours at 55°. Analyses were performed on a 21 ft. gas chromatographic column of 3% squalane on firebrick. This system was sensitive to 0.1% of the olefin isomers. On starting with 2-methylpentene-2, the product distribution remained constant for hours 15 to 55 at 88.1% 2-methylpentene-2 and 11.9% 2-methylpentene-1.

Although both olefins gave rise to the same isomer distribution, it may be that equilibrium involving the 4-methylpentene isomers would be achieved on longer standing. However, these data clearly show that the rate of base-catalyzed isomerization past a tertiary carbon hydrogen bond (Eq. 1) is much slower than that involving primary–secondary bonds (Eq. 2). This falls in line with

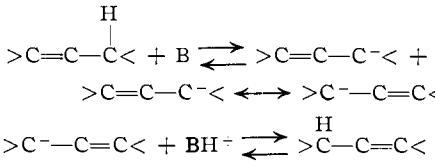

(1)


(2)

the order of carbanion stability, *vis.*, primary > secondary > tertiary. The rate constant at the 1.0 molar base level was 1.2×10^{-4} sec.$^{-1}$. Small amounts of *tert*-butyl alcohol slow the rate appreciably. A solution that is 1.0 molar in potassium *tert*-butoxide, 1.0 molar in *tert*-butyl alcohol and 1.0 molar in olefin has a rate that is $^1/_{100}$ that of the solution not containing any alcohol. This may be interpreted on the basis of complex formation between alcohol and base and the effect is being investigated further.[3] No noticeable conversions were obtained in pure *tert*-butyl alcohol, tetrahydrofuran or 1,2-dimethoxyethane over very long time periods at 55°.

With olefins that may form *cis* and *trans* isomers, the reaction is kinetically controlled and initially gives rise to more *cis* than *trans* olefin. As an example, butene-1 is 96% selective to *cis*-butene-2 at 80% butene-1 conversion. This stereoselective isomerization reaction was discovered by Pines using sodium on alumina although the degree of stereoselectivity was not as marked.[4] The question of the transition state is important. Both Pines and Price arrive at similar activated complexes although the catalysts are different.[2,4] To shed light on this point, tritium tracing experiments were carried out. Although the structure of the transition state is unknown, we have found that the reactant olefin exchanges protons with the solvent at roughly the same rate at which the isomerization reaction proceeds.

In general, it has been postulated[2,4] that the base catalyzed isomerization reaction proceeds via carbanion formation (step 3), rearrangement of the intermediate (step 4) and finally reformation of the isomerized olefin hydrocarbon[1] (step 5).


(3)

(4)

(5)

The question arises as to whether the reaction is strictly intramolecular, a 1–3 shift, or whether the anion abstracts a proton from another olefin or whether it abstracts a proton from the solvent. These three mechanisms can be clearly distinguished by carrying out the isomerization of mixed olefin reagents with one olefin tagged with H^3 in the allylic position. If no H^3 appears in the untagged olefin and the activity of the tagged olefin

(1) H. Pines, "Advances in Catalysis and Related Subjects," Vol. 12, Academic Press, New York, N. Y., 1960.

(2) C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961).

(3) D. J. Cram, *et al.*, *ibid.*, **81**, 5740 (1959).

(4) W. O. Haag and H. J. Pines, *ibid.*, **82**, 389 (1960).

(5) R. Wolfgang and R. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).