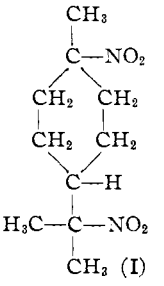
$RR'R''C-NO_2$. This is readily accomplished by using potassium permanganate.

Thus far four amines have been oxidized; the permanganate oxidation of *t*-butylamine has been examined most thoroughly with the result that an 83% yield of pure *t*-nitrobutane has been obtained. Likewise, oxidation of *t*-amylamine gives analytically pure *t*-nitropentane (2-methyl-2-nitrobutane), *t*-octylamine (2-amino-2,4,4-trimethylpentane) yields pure *t*-nitroöctane and from 1,8-diamino-*p*-menthane the corresponding dinitro compound (I) is obtained.



In addition to its simplicity, this new method has the advantage of starting with *t*-carbinamines, substances which have recently become easily accessible.[3,4]

t-Butylamine (100 g.) was added to a stirred mixture of 650 g. of potassium permanganate and 3 l. of water in the course of fifteen minutes. The temperature rose to 45° and, after stirring for eight hours without external heating, the reaction mixture was held at 55 ± 5° for another eight hours. The product was isolated by steam distillation, washed with dilute hydrochloric acid, with water and then dried and distilled. A total of 117 g. (83% yield) of *t*-nitrobutane was collected as eleven fractions (b.p. 127–128°), all of which had $n^{28}D$ 1.3980 and m.p. 25–26°. *Anal.* Calcd. for $C_4H_9NO_2$: C, 46.59; H, 8.80; N, 13.78. Found: C, 46.46; H, 8.74; N, 13.55. Preliminary studies have shown that alkaline hydrogen peroxide is also a useful reagent for this oxidation.

This synthesis now makes *t*-nitroparaffins, *t*-nitrosoparaffins, and related compounds readily available so that for the first time a careful study of the chemistry of these substances is feasible. Such studies have been initiated in this Laboratory.

(3) J. J. Ritter and J. Kalish, THIS JOURNAL, **70**, 4048 (1948).

(4) We thank the Rohm and Haas Company for generous gifts of the amines employed here.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY NATHAN KORNBLUM
LAFAYETTE, INDIANA RAYMOND J. CLUTTER

RECEIVED AUGUST 5, 1954

THE NATURE OF PARTICIPATION OF HYDROGEN IN SOLVOLYTIC REACTIONS

Sir:

The accelerating effect of β-hydrogen atoms on solvolytic reactions is well known. On the basis of rate retardation on substitution of deuterium for hydrogen, the acceleration has been ascribed to elimination-type driving forces in addition to the ordinary ionization process,[1,2] and to a carbonium ion stabilizing hyperconjugation, without reference to olefin formation.[3,4] By analogy to the participation of neighboring nucleophilic substituents, and to certain rearranging systems, the acceleration has been attributed to a similar participation of neighboring hydrogens, with the implication of a non-classical hydrogen bridged carbonium ion.[5]

Since the hydrogens on a methyl group para to a potential carbonium ion center are not eliminated in ordinary carbonium ion reactions and furthermore cannot be involved in bridged structures, we have studied this secondary isotope effect to choose among these alternatives.

Table I shows the results of measuring the rates of acetolysis of methyl-*p*-tolylcarbinyl chloride both with the normal isotope distribution and in the compound heavily deuterated in the α-methyl group (from which elimination may occur), and that deuterated in the *para* methyl group (from which elimination does not occur). The first-order rate constants are the slopes of a least-squares line derived from the titers at equally spaced time intervals according to Guggenheim as described before.[3,4] The maximum deviation of these rate constants from the mean of two or three runs is also shown. A roughly equivalent amount of sodium acetate was added to prevent reversal. It is clear that retardation results from deuterium substitution at both positions; that on the α-methyl group is more effective than that on the *para* methyl group. This constitutes the first example of change in rate produced by isotopic substitution at a point so remote from the seat of the reaction. We believe that this cannot be accounted for on the basis of elimination reactions at any stage, nor is the qualitatively similar nature of the effects at the two positions consistent with the assumption that the hydrogens on the α-methyl group are uniquely effective due to formation of a non-classical bridged ion. The possibility of isotopic exchange in the *para* methyl group of the intermediate carbonium ion is being considered.

TABLE I

RATES OF ACETOLYSIS OF METHYL-*p*-TOLYLCARBINYL CHLORIDE VARIOUSLY DEUTERATED

Compound	% D in CH_3 group	Temp., °C.	$k \times 10^4$ sec.$^{-1}$	$\Delta\Delta F^\ddagger$ per D cal./mole
$CH_3C_6H_4CHClCH_3$	0	50.25	1.14 ± 0.02	
$CH_3C_6H_4CHClCH_3$	0	65.30	6.02 ± 0.01	
$CD_3C_6H_4CHClCH_3$	67	50.25	1.04 ± 0.02	29 ± 7
$CD_3C_6H_4CHClCH_3$	67	65.30	5.61 ± 0.04	23 ± 7
$CH_3C_6H_4CHClCD_3$	80	50.25	0.892 ± 0.01	66 ± 5
$CH_3C_6H_4CHClCD_3$	80	65.30	5.15 ± 0.07	45 ± 5

The last column of Table I, headed $\Delta\Delta F^\ddagger$ per D is calculated from the expression

$$\Delta\Delta F^\ddagger \text{ per D} = \frac{2.303\ RT \log k_H/k_D}{3 \times \%\text{ deuteration}}$$

The errors are estimated assuming a uniform 2% uncertainty in k_H/k_D. While this term is constant within experimental error for deuterium in the

(1) V. J. Shiner, Jr., THIS JOURNAL, **75**, 2925 (1953).

(2) V. J. Shiner, Jr., *ibid.*, **76**, 1603 (1954).

(3) C. E. Boozer and E. S. Lewis, *ibid.*, **74**, 6306 (1952); **76**, 794 (1954).

(4) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

(5) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

para methyl group, in agreement with the results in the 2-pentyl series,[4] the corresponding term for the α-methyl group shows an apparently real temperature dependence. The temperature dependence of this free energy of activation difference is reminiscent of the similar effect observed by Shiner on 2,3-dimethyl-2-chlorobutane[2] and may be connected with the relatively stable olefins or carbonium ions formed in both cases and with the possibility of plural reaction paths.

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE EDWARD S. LEWIS
HOUSTON, TEXAS GALVIN M. COPPINGER

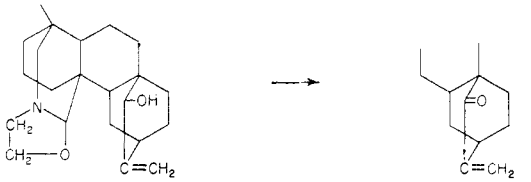
RECEIVED JUNE 17, 1954

THE ACONITE ALKALOIDS. XXVII. THE STRUCTURE OF ATISINE

Sir:

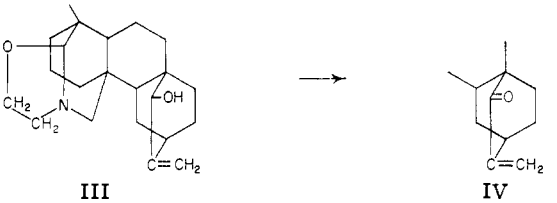
Recently we proposed a structure for atisine[1,2] based on the isolation of 6-ethyl-1-methylphenanthrene from the dehydrogenation of atisine,[3,4] oxoisoatisine[2] and tetrahydroatisine[2] as well as on other studies.[5,6] The formation of tetrahydro and diacyl derivatives suggested the presence of two centers of unsaturation and two hydroxyl groups in the molecule.[3] The diterpenoid structure first suggested[7] was modified and the double bonds placed so as to account for the marked differences in basicity of atisine (*pK* 12.2), isoatisine (*pK* 10) and dihydroatisine (*pK* 8, 2).[2,8] It now appears that a more normal diterpenoid structure better fits the available data. The fact that atisine shows only one C-methyl group[3] and that the lactam group of both oxoisoatisine and oxoisoatisine tricarboxylic acid is unusually resistant to hydrolysis[6] suggests one of the diterpene geminal methyl groups as the site of the lactam group. Wiesner, *et al.*, on the basis of the similarity of the chemistry of atisine and isoatisine to that of veatchine and garryine[9] have recently suggested structures I and III for atisine and isoatisine, though little supporting evidence was presented.[10] We wish to report two series of experiments which support the structures shown for atisine and its derivatives.

Treatment of atisine with chromium trioxide–pyridine complex[11] at 30° furnished an α,β-unsaturated ketone (II) in 60% yield, m.p. 102–103°, $[\alpha]^{31}D$ −27° (*c* 2.33 in chf.). Calcd. for $C_{22}H_{31}NO_2$: C, 77.37; H, 9.15. Found: C, 77.68, 77.60; H, 9.24, 9.32. The ultraviolet spectrum (EtOH) showed $\lambda_{max.}$ 228 mu, ε 9,100; $\lambda_{max.}$ 318 mu, ε 41; $\lambda_{max.}$ 342, ε 61. The infrared spectrum (chf.) showed bands at 3012, 1638 (strong) and 895 cm.$^{-1}$ (>C=CH$_2$); 1702 cm.$^{-1}$ (>C=O), *but the absence of any band attributable to a hydroxyl group.* III showed the absence of active hydrogen. Furthermore, atisine itself showed the presence of *only one active hydrogen.*[12] These data demonstrate that the –NCH$_2$CH$_2$O– in atisine *must be present in a ring*, and not as a free –NCH$_2$CH$_2$OH group as previously maintained.[2,7,13]



I II

That an oxide ring is also present in isoatisine (III) was shown by analogous oxidation of isoatisine with chromium trioxide–pyridine to the α,β-unsaturated ketone (IV), m.p. 159–163°, then 285–295° dec., $[\alpha]^{29}D$ −9.3° (*c* 1.89 in chf.). Found: C, 77.49; 77.50; H, 9.17, 9.34. The infrared spectrum (film from chf.) showed bands at 3077, 1631 (strong) and 884 cm.$^{-1}$ (>C=CH$_2$); 1710 cm.$^{-1}$ (>C=O), *but again the absence of any hydroxyl band in the 3400 cm.$^{-1}$ region.* The Tschugaeff–Zerewitinoff determination was negative.



III IV

Oxidation of atisine with potassium permanganate has given a lactam, the oxoatisine dicarboxylic acid (V).[2,6] Examination of the infrared absorption of its dimethyl ester (VI) reveals bands at 1715 (broad, –CO$_2$Me) and 1639 cm.$^{-1}$ (six-membered lactam) *but no band indicative of a hydroxyl group.*[14] The Tschugaeff-Zerewitinoff determination was negative.

A similar controlled oxidation of isoatisine (III) has furnished oxoisoatisine dicarboxylic acid (VII).[2,6] The infrared spectrum of its dimethyl ester (VIII) shows a band attributable to a hydroxyl group at 3380 cm.$^{-1}$, as well as bands at 1730 (–CO$_2$Me) and 1620 cm.$^{-1}$ (six-membered lactam). Furthermore, hydrogenation of oxoatisine dicarboxylic acid (V) furnished a product identical in all respects with oxoisoatisine dicarboxylic acid (VII) as shown by m.p., rotation, and infrared spectra. These results indicate that in the case of atisine oxidation proceeds

(1) E. S. Stern, "The Aconitum and Delphinium Alkaloids" in "The Alkaloids, Chemistry and Physiology," edited by R. H. F. Manske and H. L. Holmes, Vol. IV, Academic Press Inc., New York, N. Y., 1954, p. 275.

(2) W. A. Jacobs, *J. Org. Chem.*, **16**, 1593 (1951).

(3) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **143**, 589 (1942).

(4) C. F. Huebner and W. A. Jacobs, *ibid.*, **170**, 203 (1947).

(5) L. C. Craig and W. A. Jacobs, *ibid.*, **152**, 651 (1944).

(6) *Ibid.*, **170**, 515 (1947); **174**, 1001 (1948).

(7) L. C. Craig, L. Michaelis, S. Granick and W. A. Jacobs, *ibid.*, **154**, 293 (1944).

(8) O. E. Edwards and T. Singh, *Canad. J. Chem.*, **32**, 465 (1954).

(9) K. Wiesner, *et al.*, *ibid.*, **30**, 608 (1952); *Ber.*, **86**, 800 (1953); *Chem. and Ind.*, **132** (1954).

(10) K. Wiesner, personal communication, Feb. 16, 1954; M. F. Bartlett, Ph.D. Thesis Summary, Univ. of New Brunswick, May, 1954.

(11) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

(12) This test was performed on undistilled atisine. Distillation apparently furnished altered material as shown by a different infrared spectrum from undistilled atisine[8] and by two active hydrogens in the Zerewitinoff test.[5,8]

(13) The ease of opening this ring to furnish –NCH$_2$CH$_2$OH accounts for the ready formation from atisine of dihydroatisine on reduction, a diacetate on acylation, and the formation of glyoxal on treatment with lead tetraacetate. The latter reaction has been cited as proof of the existence of a preformed –NCH$_2$CH$_2$OH group in atisine.[8]

(14) This experiment was suggested to us by Prof. K. Wiesner.[10]