149°, $[\alpha]_D$ +127°, λ_{max}^{EtOH} 238 mμ, log ε 4.16; *Anal.* found for $C_{18}H_{22}O_2$: C, 79.65; H, 8.38) which upon microbiological dehydrogenation[9] with *Corynebacterium simplex*[10] led in over 60% yield to equilin (VII), m.p. 237–240°, undepressed upon admixture with the natural hormone, $[\alpha]_D$ +295°, λ_{max}^{EtOH} 282 mμ, log ε 3.36. The infrared spectra of synthetic and natural equilin were completely superimposable.

Since the starting material, 19-nortestosterone acetate (I), is prepared[5] from estrone which has been synthesized totally,[11] the above reaction sequence also constitutes a formal total synthesis of equilin (VII).

[9] The feasibility of converting a 19-nor-Δ^4-3-ketosteroid into the corresponding phenol with *C. simplex* already has been demonstrated with 19-norprogesterone (A. Bowers, C. Casas Campillo and C. Djerassi, *Tetrahedron*, **2**, 165 (1958)), and with 19-nortestosterone (S. Kushinsky, *J. Biol. Chem.*, **230**, 31 (1958)).

[10] We are grateful to Dr. Carlos Casas Campillo and staff for the microbiological incubation.

[11] G. Anner and K. Miescher, *Helv. Chim. Acta*, **31**, 2173 (1948); W. S. Johnson, D. K. Banerjee, W. P. Schneider and C. D. Gutsche, THIS JOURNAL, **72**, 1426 (1950); W. S. Johnson, D. K. Banerjee, W. P. Schneider, C. D. Gutsche, W. E. Shelberg and L. J. Chinn, *ibid.*, **74**, 2832 (1952).

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RECEIVED MARCH 29, 1958

INTRAMOLECULAR REACTIONS OF SECONDARY CARBINAMINE NITROSOAMIDES

Sir:

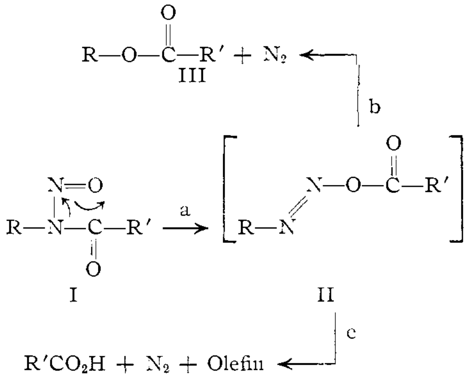
Studies of the nitrosoamide reaction have shown[1] that the reaction proceeds in most cases with partial retention of configuration, and that there is an intramolecular path (b) for the formation of the ester. We now report[2] an oxygen-18 tracer study of reaction b pertinent to the mechanism of the reaction and to the problem of "intramolecular inversion."[3] The nitroso derivatives of N-cyclohexyl and N-1-phenylethylnaphthamides-O-18 were rearranged in various solvents; appropriate controls were run. The esters obtained were cleaved and the O-18 analyses were run in the standard way.[4]

TABLE I

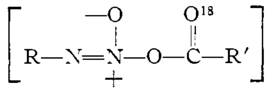
Run	R	Solvent and addend	Retn. of config., %	Atom % excess O-18						
				RNHCOR'	RO_2CR'	$R'CH_2OH$	+ ROH	C/E[a]	(−)ROH	(±)ROH
1	Cyclohexyl	CH_3CO_2H		1.233	0.611	0.798	0.431	65/35		
2	(−) 1-Phenylethyl	Dioxane + CH_2N_2[b]	74	1.232	.622	.656	.545	55/45		
3	(−) 1-Phenylethyl	Dioxane + $2HCO_2H$	80	1.232	.607	.696	.514	58/42	0.536	0.537
4	(−) 1-Phenylethyl	CH_3CO_2H	81	1.232	.592	.843	.372	69/31	0.381	0.380

[a] % in C=O/% in ether position. [b] Equilibrated methyl naphthoate was obtained.

The results (Table I, C/E) show that although "mixing" of the label occurred in reaction b, more than one half of the label remained in the carbonyl group in each case. Simiarly, the reaction of 2-naphthoyl chloride O-18 with the silver salt of N-nitrocyclohexylamine yielded (*via* IV) nitrous oxide



containing 0.0 atom % excess O–18 and cyclohexyl naphthoate with 62% of the O-18 in the carbonyl group. Further information was obtained when

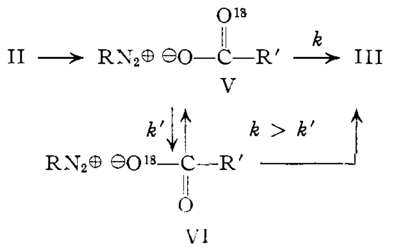


$$\left[\mathrm{R{-}N{=}\overset{\overset{-O}{|}}{\underset{+}{N}}{-}O{-}\overset{\overset{O^{18}}{\|}}{C}{-}R'}\right]$$

IV

optically pure (−)N-(1-phenylethyl)-N-nitroso-2-naphthamide-carbonyl-O-18 was rearranged. The partially racemized ester was cleaved, the 1-phenylethanol obtained was treated with phenyl isocyanate, and the N-phenylcarbamate was fractionally crystallized. Samples of the DL form and the optically pure levorotatory form (corresponding to retention) were thus obtained. Analyses showed that both contained the same amount of O–18 (Runs 3 and 4); the enantiomers are formed with the same distribution of O–18!

A mechanism involving partial mixing of the oxygen atoms prior to the step in which the final configurations are determined accounts satisfactorily for the results; the loss of nitrogen from V or VI could reasonably lead to bond formation on both



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[1] (a) E. H. White, THIS JOURNAL, **77**, 6014 (1955); (b) R. Huisgen, *Ann.*, **601**, 21 (1956); also earlier articles.

[2] Our O-18 results for primary carbinamines were reported in Absts. of the 130th A.C.S. Meeting, September 18, 1956, p. 20-O.

[3] C. E. Boozer and E. S. Lewis, THIS JOURNAL, **75**, 3182 (1953).

[4] W. E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953).

sides of the plane of R⊕ with no further equilibration of the oxygens.[5,6,7] If the step involving the loss of nitrogen is relatively slow, elimination of $R'CO_2H$ apparently can occur, since in the reaction of the nitrosoamide of the methyl ester of alanine, methyl α-diazopropionate was formed.[8]

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(5) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(6) D. B. Denny, *ibid.*, **77**, 1706 (1955).

(7) In the presence of deuterobenzoic acid, the reaction yielded ester containing no significant amounts of deuterium.

(8) Footnote 1a, p. 6013.

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BOOK REVIEWS

The Carbohydrates. Chemistry, Biochemistry, Physiology. Edited by WARD PIGMAN, Department of Biochemistry, University of Alabama Medical Center, Birmingham, Alabama. Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1957. xvii + 902 pp. 16 × 23.5 cm. Price, $20.00.

The present text and reference book represents an exceptionally extensive revision and expansion of "Chemistry of the Carbohydrates," first published in 1948 by Professor Pigman and Dr. R. M. Goepp, Jr. The earlier edition, which was the first extensive general treatise on carbohydrate chemistry in the English language, and which was received enthusiastically by carbohydrate chemists and biochemists, has been brought up to date through 1956 in the current first revision. In contrast to its predecessor, the present text is written by Professor Pigman, also its editor, with the aid of some twenty contributing authors, all active research specialists in some branch of carbohydrate science. In view of the tremendous and rapidly growing literature in this field, this departure gives the present volume greater breadth of scholarship than would be conceivably possible under single authorship. To the editor's credit the divided authorship is completely unobtrusive, and the reader receives a pleasant impression of uniformity and homogeneity on continuing from chapter to chapter through the book, a feeling augmented, perhaps, by the editor's adoption of the new official rules of nomenclature wherever applicable throughout.

The chapter headings in the present volume indicate a generally similar organization to that employed in the earlier edition. The first ten chapters, treating mainly the chemistry of the simple sugars and their derivatives, are revised mainly by expansion to include more recent material. This expansion averages an approximately 23% increase in the number of pages in each of these chapters. The later chapters of the earlier edition, dealing with polysaccharides, have been more extensively changed, and the detailed treatment of starch and cellulose has been abbreviated in favor of more general information regarding plant, bacterial, fungal and animal polysaccharides. In addition, new chapters covering the Identification and Quantitative Determination of Carbohydrates, Photosynthesis and Metabolism of Carbohydrates, and Carbohydrates in Nutrition have been included. Those subjects which now receive more cursory consideration are adequately covered in other monographs, to which reference is always given in the present treatise. In general, frequent references to more detailed treatments help to increase the coverage of the text. The expanded information and scope of the present volume over its predecessor is reflected in an increase in the number of the textual pages from 647 to 817, the pages of author index from 20 to 31 and the number of footnotes from 1834-2994 (representing references to about 4500 individual articles). That the subject index is somewhat less detailed, however, is suggested by its decrease from 80 to 52 pages.

For a text of its size the present volume appears remarkably free from typographical errors. In view of the considerable selection of material from the literature which such a treatise requires, the reader may perhaps disagree occasionally and trivially with the various authors on their emphasis. Similarly, such points as this reviewer found at all objectionable on first reading proved rather unimportant on re-examination in the light of the over-all monumental task of the revision.

Designed as both a textbook and a reference book, this volume fulfills both functions admirably. The general excellence and coverage will ensure its purchase by every practicing organic chemist, biochemist and medical research worker concerned with the chemistry of carbohydrates for a long time to come.

DEPARTMENT OF CHEMISTRY
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Advances in Catalysis and Related Subjects. Volume IX. Edited by D. D. ELEY, Nottingham, England; W. G. FRANKENBURG, Lancaster, Pennsylvania; and V. I. KOMAREWSKY, Chicago, Illinois. Proceedings of the International Congress on Catalysis, Philadelphia, Pennsylvania, 1956. Edited by ADALBERT FARKAS, Houdry Process Corporation, Marcus Hook, Pennsylvania. Academic Press, Inc., Publishers, 111 Fifth Avenue, New York 3, N. Y., 1957. xviii + 847 pp. 16 × 23.5 cm. Price, $16.00.

The ninth volume of "Advances in Catalysis" series consists essentially of the papers presented at the International Congress on Catalysis at Philadelphia in 1956. It is thus different in format and content from the preceding eight volumes which consist of reviews and interpretations of selected sections of the massive literature of catalysis. There is no doubt that the material of volume IX belongs in this distinguished series, because the sum total of these papers represents a thorough and modern review of catalysis as the subject was conceived in 1956. This is indeed a worthy climax to the efforts of the late W. G. Frankenburg and V. I. Komarewsky toward bringing together from world wide sources the best thought on catalytic chemistry. Dr. Eley and Dr. Farkas are to be commended for completing this task with no delay after the death of their editorial collaborators.

Many outstanding scientists specializing in catalysis have contributed to this volume. The organizers of the International Congress on Catalysis are to be congratulated not only for assembling this worthwhile program but for consolidating the achievements of the Congress by securing publication of the papers in this useful form.

The 81 papers and the introductions by Hugh S. Taylor and Eric K. Rideal were contributed by 147 scientists from