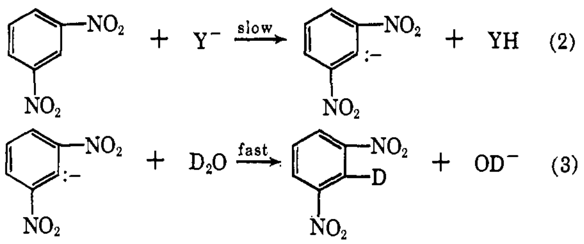
ing abstraction of hydrogen by the Brønsted base, followed by fast protonation by solvent of the resulting carbanion (eq 2-4). (3) Since the reaction medium



$$YH + OD^- \rightleftharpoons Y^- + HOD \qquad (4)$$

in some of these exchange processes ($Y^- = OD^-$, PhO^-, $S_2O_3{}^{2-}$) was strongly colored (deep red or purple) it is possible that the anion was partly tied up in the form of Meisenheimer adducts; on the other hand the colors may only be indicative of charge-transfer complexing. Detailed equilibrium studies with respect to complex formation, coupled with kinetic studies on the exchange process, will be required to separate these effects. The studies relevant to these factors are under active consideration.

Acknowledgment. This research was supported by a grant (PRF 1841 A-4) from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

E. Buncel, A. W. Zabel
Department of Chemistry, Queen's University,
Kingston, Ontario, Canada

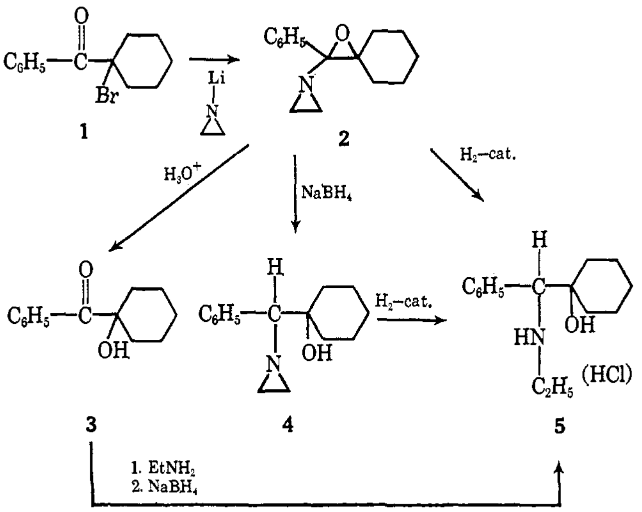
Received October 24, 1966

Epoxyamines. A New Functional Group in Organic Chemistry

Sir:

We wish to report the preparation and rearrangement of a new class of organic compounds, the epoxyamines. Although the concept of this unusual functional group has been invoked as an intermediate in several instances,[1-3] isolation and complete characterization of an example previously had not been accomplished.[4] The apparent inaccessibility of these compounds had been attributed to their high reactivity and to the possibility of facile rearrangements.[1,2]

We have now isolated a stable crystalline epoxyamine, 2-(1-aziridinyl)-2-phenyl-1-oxaspiro[2.5]octane (**2**), by the action of the lithium salt of ethylenimine[5] on α-bromocyclohexyl phenyl ketone[6] (**1**) in ether at room temperature. Evaporative distillation (bath temperature 90–100° (0.01 mm)) of the crude product gave 70–75% of **2**, bp 90–95° (0.001 mm), n^{24}D 1.5870, which could be crystallized from pentane; mp 20–22°. The infrared spectrum was devoid of any hydroxyl and carbonyl absorptions but had strong peaks at 1025 and 1045 cm^{-1}. The nmr spectrum ($CDCl_3$) was consistent with structure **2**, showing aromatic protons from τ 2.45 to 2.85 and aliphatic protons from τ 7.8 to 9.0 in the ratio 5:14.



Hydrolysis with 2 *N* hydrochloric acid converted **2** into the known α-hydroxycyclohexyl phenyl ketone[6] (**3**) in 90% yield. Reduction of **2** with sodium borohydride in methanol gave 1-[α-(1-aziridinyl)benzyl]-cyclohexanol (**4**) (60%), mp 113–114°. Hydrogenation of **4** in ethanol at atmospheric pressure using 10% palladium on carbon as catalyst yielded 1-(α-N-ethylaminobenzyl)cyclohexanol (**5**), characterized as its hydrochloride (85%), mp 223–224° dec. This amino alcohol **5** was also formed in 80% yield by direct hydrogenation of **2** in methanol using the same catalyst. The structure of **5** was confirmed by its formation from the sodium borohydride reduction of α-hydroxycyclohexyl phenyl ketone N-ethylimine, which in turn was made from ethylamine and **3** in the presence of potassium carbonate.

When heated to the reflux temperature in *o*-dichlorobenzene for 15 hr under a nitrogen atmosphere, **2** rearranged with ring expansion to give 2-(1-aziridinyl)-2-phenylcycloheptanone (**6**) in 35–38% yield, the remainder of the material being an intractable resin. This rearrangement was particularly interesting, since according to a previous postulate[7] α-(1-aziridinyl)-cyclohexyl phenyl ketone (**7**) would have been the expected product. To show that **7** was not an intermediate in the transformation of **2** to **6**, **7** was prepared by the general method[8] involving the action of ethyl-

---

(1) C. L. Stevens, P. Blumbergs, and M. Munk, *J. Org. Chem.*, **28**, 331 (1963), and references cited therein.

(2) A. Kirmann and H. I. Joschek, *Bull. Soc. Chim. France*, 3483 (1963).

(3) A. Hassner and P. Catsolacos, *J. Org. Chem.*, **32**, 549 (1967).

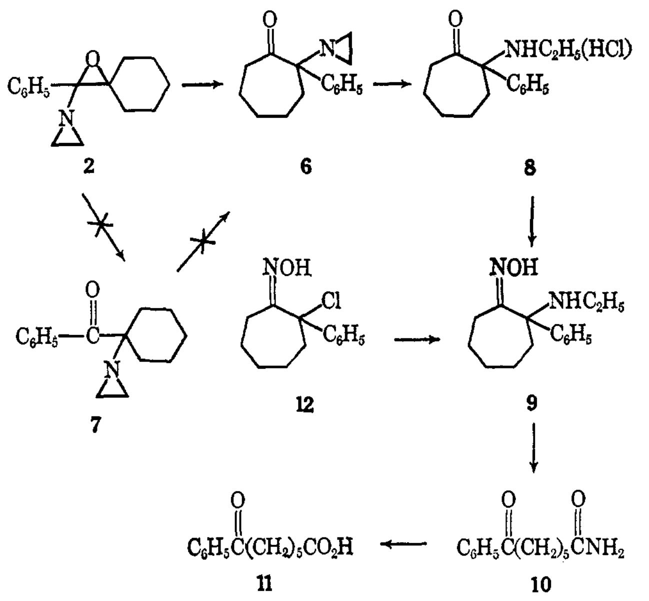
(4) M. Mousseron, J. Jullien, and Y. Jolchine, *Bull. Soc. Chim. France*, 757 (1952), reported the formation of an epoxyamine as a by-product in the reaction of 2-chlorocyclohexanone with aqueous dimethylamine, but they did not fully characterize or establish the structure of the material.

(5) The fact that ethylenimine forms stable addition products with aldehydes and ketones suggested that it might impart stability to this class of compounds. *Cf.* A. Dornow and W. Schacht, *Chem. Ber.*, **82**, 464 (1949).

(6) C. L. Stevens and E. Farkas, *J. Am. Chem. Soc.*, **74**, 618 (1952).

(7) A. Kirmann, R. Muths, and J-J Riehl, *Bull. Soc. Chim France*, 1469 (1958).

(8) C. L. Stevens and C. H. Chang, *J. Org. Chem.*, **27**, 4392 (1962).



enimine on an epoxy ether, 2-methoxy-2-phenyl-1-oxaspiro[2.5]octane,[6] in 84% yield (bp 102–105° (0.01 mm), $n^{25}\text{D}$, 1.5502). After **7** was subjected to the same rearrangement conditions, most of the starting material (55%) was recovered unchanged and an examination of the infrared spectrum of the crude reaction mixture provided evidence that no detectable amount of **6** was formed.

Upon hydrogenation in ethyl acetate at atmospheric pressure in the presence of 10% palladium on carbon, **6** was selectively reduced to 2-N-ethylamino-2-phenylcycloheptanone (**8**), characterized as its hydrochloride (85%), mp 233–235° dec, $\text{p}K_a' = 7.70$ (50% methanol). Ketone **8** was converted to the corresponding oxime **9** (64%), mp 105–106°, $\text{p}K_a' = 8.75$ (50% methanol). Synthesis of **9** was also achieved by the action of ethylamine on the known 2-chloro-2-phenylcycloheptanone oxime[9] (**12**). Structure **9** was further confirmed by the formation of 6-benzoylhexanamide (**10**) (60%), mp 107–108°, when the oxime was subjected to Beckmann degradation conditions using polyphosphoric acid. On treatment with aqueous alcoholic sodium hydroxide **10** was hydrolyzed to the known 6-benzoylhexanoic acid (**11**) (90%), mp 82–83°. The identity of **11** was established by mixture melting point determination with an authentic sample.

All new numbered compounds have analyses and spectral data consistent with their structures.

Acknowledgment. The authors are grateful to Dr. K. Grant Taylor for helpful suggestions.

---

[9] D. Ginsberg and R. Pappo, *J. Am. Chem. Soc.*, 75, 1098 (1953).

Calvin L. Stevens, P. Madhavan Pillai
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received May 8, 1967

Additions and Corrections

Catalysis of α-Hydrogen Exchange. I. The Reaction of Isobutyraldehyde-2-*d* with Tertiary Amines and Oxygen Bases [*J. Am. Chem. Soc.*, **87**, 5050 (1965)]. By JACK HINE, JAMES G. HOUSTON, JAMES H. JENSEN, and JULIEN MULDERS, School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia.

In this paper an incorrect value for the van der Waals radius of argon was used. The distance 2.45 A, at which the energy of repulsion is 11.2 kcal/mole, is 64% of 2 times 1.91 A, the atomic radius for argon listed by G. Pannetier, "Noveau Traité de Chimie Minérale," P. Pascal, Ed., Vol. 1, Masson et Cie., Paris, 1956, p 941. With this change, eq 2 becomes

$$E_r = 0.112\left(\frac{d_0}{d}\right)^{11} - 0.175\left(\frac{d_0}{d}\right)^{7} + 0.06 \qquad (2)$$

The energies of repulsion (calculated without allowance for molecular distortion) are only 32% as large as those calculated originally, but they are still considerably larger than the experimental values. None of the qualitative conclusions is affected by this change.

A Molecular Orbital Theory of Optical Rotatory Strengths of Molecules [*J. Am. Chem. Soc.*, **88**, 4157 (1966)]. By YOH-Han PAO and D. P. SANTRY, Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, and Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

On page 4158, eq 1.2 should read

$$\psi_i = \sum_{\mu} \chi_\mu C_{\mu i} \qquad (1.2)$$

On page 4159, line 10 of column 1 should read *M* is the magnetic moment operator. Equation 2.9 should read