water at *ca.* 25° for 24 hr, at the end of which time analysis by thin layer chromatography (tlc) indicated the disappearance of all starting oxime acetate. The reaction mixture was then exposed to air to oxidize excess Cr(II). Evaporation of most of the tetrahydrofuran under reduced pressure, addition of water, extraction with ether, washing with dilute acid and base, and concentration afforded after distillation or tlc separation 80–90% of pure propiophenone (by infrared, nmr, tlc, and vpc analysis). No more than trace impurities could be detected in the unpurified ketonic product.

Table I records the results of applying the deoximation procedure to a number of ketoxime *O*-acetates. It is noteworthy that the deoximation occurs readily and smoothly even with hindered cases such as camphor.

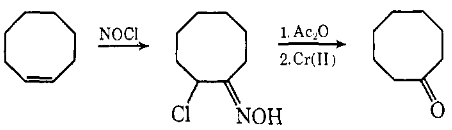
Table I. Conversion of Oxime *O*-Acetates to Ketones with Chromous Acetate in 9:1 Tetrahydrofuran–Water

Ketonic product	Conditions:[a] time, hr; temp, °C	Yield, %[b]
1. Cyclohexanone	4.5; 65	84
2. Phenylacetone	16; 65	74
3. Camphor	11; 65	88
4. Propiophenone	24; 25	80
5. 2-Methyl-2-cyclohexenone	46; 25	80
6. Progesterone 20-monoxime *O*-acetate[c]	24; 25	84
7. 1,4-Cyclohexanedione monohemithioethylene ketal	10; 65	92
8. 4-Benzoyloxycyclohexanone	7; 65	95

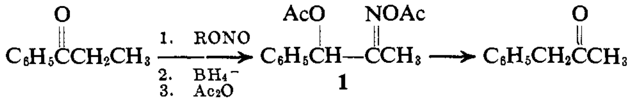
[a] Conditions for complete disappearance of starting oxime *O*-acetate. [b] Yield of product after isolation by distillation or tlc. [c] Starting material, progesterone 3,20-bis-*O*-acetoxime.

Also, the deoximation of acetoximes of *conjugated enones* and *aryl alkyl ketones* occurs much more readily than that of nonconjugated ketones. The reductive cleavage of the conjugated derivatives (items 4 and 5) proceeded readily at 25°, whereas the nonconjugated acetoximes require higher temperatures (*ca.* 65°). This order of reactivity is *opposite* to that for acid-catalyzed hydrolysis, which is known to be especially slow for conjugated oximes.[2c] The differential reactivity is potentially very useful, as indicated, for example, by the efficient and highly selective hydrolysis of the 3-acetoxime function in progesterone 3,20-bis-*O*-acetoxime (item 6). Entries 7 and 8 in Table I demonstrate clearly another important point, *i.e.*, the noninterference of ketal and ester functions.[8]

A three-step conversion of olefins to ketones has been developed on the basis of the reductive hydrolysis process. For example, 2-chlorocyclooctanone oxime, readily available from the addition of nitrosyl chloride to cyclooctene,[9] is acetylated quantitatively by brief treatment with acetic anhydride at 25°, and the acetoxime is further converted to cyclooctanone in 88% yield by treatment with chromous acetate in the usual way at 65° for 16 hr. This process takes advantage of the ability of Cr(II) to effect reductive cleavage of the C–Cl bond in addition to that of the acetoxime function.



A new method for the transposition of a ketonic function has also been devised on the basis of this Cr(II) induced reductive deoximation with α cleavage. Oximation of propiophenone, followed by reduction with sodium borohydride and acetylation, gave the α-acetoxy acetoxime **1**, which upon treatment with excess chromous acetate in tetrahydrofuran–water (10:1) at 65° for 34 hr afforded phenylacetone.



$$C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow[\text{2. } BH_4^- \text{ 3. } Ac_2O]{\text{1. RONO}} C_6H_5\overset{AcO}{\overset{|}{C}H}-\overset{NOAc}{\overset{\|}{C}}CH_3 \longrightarrow C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_3$$

1

A number of general observations with regard to reductive deoximation by Cr(II) deserve mention. Although free oximes are converted to ketones upon treatment with chromous acetate in tetrahydrofuran–water, the reaction is much slower than that of the oxime *O*-acetates and requires higher temperatures. It has also been found that oxime *O*-acetates react more rapidly than the corresponding trifluoroacetates, tosylates, or ethoxyformates. In all cases an intermediate chromium complex (presumably involving coordination of Cr(III) with $-N{=}C{<}$) is produced subsequent to N–O cleavage. The ketonic product can be liberated by hydrolysis at pH 5 and 25° or by reductive cleavage using zinc–acetic acid–water at 25°.

The several applications of the new deoximation reaction reported herein demonstrate its effectiveness in situations beyond the scope of previously known deoximation methods and suggest a significant role in synthetic methodology. Continuing studies are planned on even milder procedures utilizing Cr(II) for deoximation and also on the possible application to the regeneration of ketones from hydrazone derivatives and semicarbazones.[10]

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[8] The following limitations of scope have been noted. Acetoximes derived from diaryl ketones or α-diketones are not deoximated by chromous acetate, but instead undergo C=N reduction to basic products. Acetoximes of aliphatic aldehydes are largely converted to nitriles, at least under the range of conditions employed in this work.

[9] M. Ohno, N. Naruse, S. Torimitsu, and M. Okamoto, *Bull. Chem. Soc. Jap.*, **39**, 1119 (1966), and M. Ohno, N. Naruse, and I. Terasawa, *Org. Syn.*, **49**, 27 (1969).

[10] This research was assisted financially by the National Science Foundation.

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Rearrangement Ions. III.[1] The Tropylium Ion in the Mass Spectrum of Toluene-2,6-$^{13}C_2$

Sir:

One of the most intriguing and important findings in the field of mass spectrometry has been the discovery that the $C_7H_7^+$ ion derived from toluene and related benzyl systems is not the familiar benzyl ion, but rather a more symmetrical species, *viz.*, the tropylium ion.[2] Deuterium labeling studies[2] have shown that the eight hy-

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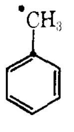
[1] For paper II, see A. S. Siegel, *Org. Mass Spectrom.*, in press.

[2] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10, and references therein.

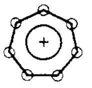
drogen atoms attain almost complete equivalence in the molecular ion of toluene, and that a single ^{13}C atom in position α[2] or 1[3,4]—or 2, as shown in the present work—is lost statistically in the path leading to $C_5H_5^+$ ions. Carbon-13 label retentions in the $C_5H_5^+$ ion (eq 1) derived from toluene-α,1-$^{13}C_2$ (I)[3,4] further indicated that

$$C_7H_8\cdot^+ \xrightarrow{-H\cdot} C_7H_7^+ \xrightarrow[m^* = 46.4]{-C_2H_2} C_5H_5^+ \qquad (1)$$

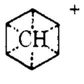
the tropylium ion formed is best represented as one in which the carbon atoms have all lost positional identity related to their toluene origin, *i.e.*, a randomized tropylium ion (II). The latter may arise (a) by a series of rapid benzyl ion–tropylium ion isomerizations, (b) by insertion of the methyl carbon atom randomly between adjacent carbon atoms of the ring (III), or (c) by an even more complex mechanism. Toluene-α,1-$^{13}C_2$, while able to distinguish between a randomized tropylium ion and one formed by insertion of the methyl carbon atom between C_1 and C_2, does not differentiate between processes a and b. It was hoped that the data obtained from a dilabeled toluene, such as IV, in which the labeled carbon atoms were not adjacent, would enhance an understanding of the processes involved.



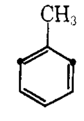
I



II



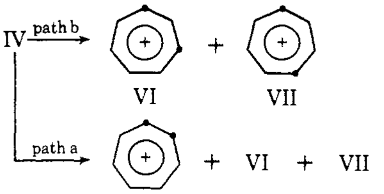
III



IV

Synthesis of IV proceeded from 1,3-dibromopropane and sodium cyanide-^{13}C followed by hydrolysis of the resulting dinitrile[5] to glutaric acid-1, 5-$^{13}C_2$, which was converted successively to the diol with lithium aluminum hydride, and to the dibromide by the action of phosphorus tribromide. The dibromide was converted to toluene by a modification[4] of the procedure of Rieker.[6] Owing to the isotopic impurity in IV, it was necessary to synthesize toluene-2-^{13}C. This was accomplished by treatment of γ-butyrolactone with sodium cyanide-^{13}C followed by hydrolysis to glutaric acid-1-^{13}C.[7] Conversion of the latter to toluene was achieved by the procedure cited above. High-resolution spectra were recorded on an AEIMS-9 mass spectrometer at a resolution of 18,000 (10% valley definition); the data represent averages of 20 readings.

The tropylium ions expected from IV *via* paths a and b are shown in eq 2. Loss of C_2H_2 from path a tropylium ions (V–VII) would give (0.048) $C_5H_5^+$, (0.476) $^{13}CC_4H_5^+$, and (0.476) $^{13}C_2C_3H_5^+$. Loss of C_2H_2 from path b tropylium ions (VI and VII) would give (0.000) $C_5H_5^+$, (0.571) $^{13}CC_4H_5^+$, and (0.429) $^{13}C_2C_3H_5$. No $^{13}C_2H_2$ can be expelled in the latter case since the labeled carbon atoms are always one or two carbon atoms removed from each other. Therefore, no unlabeled $C_5H_5^+$ ions should be formed if path b alone is operative. However, label retentions shown in Table I reveal the presence of unlabeled $C_5H_5^+$ ions, *i.e.*, the data do not agree with the distribution expected for a tropylium ion formed by path b. In fact, the observed retentions compare favorably with those for I,[3] which are close to the values expected for the completely randomized tropylium ion (II).



(2)

Table I. High-Resolution Mass Spectral Peaks

m/e	Composition[a]	Rel abundance[b–d] Toluene-2-^{13}C[e]	 Toluene-2,6-$^{13}C_2$[f]
65	C_5H_5	0.302	0.057
66	$^{13}CC_4H_5$	0.698	0.467
67	$^{13}C_2C_3H_5$		0.476

[a] Other isobaric hydrocarbon ions omitted. [b] Σ = 1.000. [c] Corrected for naturally abundant ^{13}C. [d] Calculated for 100% isotopic enrichment. [e] Sample contained 51.9% labeled toluene. [f] Sample contained 49.9% singly labeled, 23.1% unlabeled, and 27% doubly labeled toluene.

Hence, it may be concluded that the $C_7H_7^+$ ion derived from toluene is not formed by path b, but rather by a mechanism in which all the carbon atoms have lost positional identity with respect to each other. The data do not rule out the occurrence of path b; they simply show that if path b does occur, it must be accompanied by another path, say a, which would result in total scrambling of all the carbon atoms. Further study of these and other ions in the spectrum of IV is under investigation.

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[3] K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

[4] For a comprehensive study on the tropylium ion derived from ^{13}C labeled benzyl-type compounds, see A. S. Siegel and K. L. Rinehart, Jr., 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7-12, 1969, Abstract ORGN 66.

[5] M. Kushner and S. Weinhouse, *J. Amer. Chem. Soc.*, **71**, 3558 (1949).

[6] A. Rieker, K. Scheffler, and E. Mueller, *Justus Liebigs Ann. Chem.*, **260**, 23 (1963).

[7] G. Paris, L. Berlinguet, and R. Gaudry, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 496.

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Intramolecular Nitrone–Allene Cycloadditions[1]

Sir:

The utility of 1,3-dipolar cycloaddition reactions for the synthesis of five-membered ring heterocycles is well documented.[2] Studies reported from this laboratory have revealed examples of the intramolecular cycloaddition of nitrones to olefins.[3] However, few data relate the use of allenes as dipolarophiles in such reactions. We wish to disclose that the intramolecular cyclization of a series of allenic nitrones has been accomplished which results in the formation of several novel bicyclic products.

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[1] Acknowledgment is made to the National Science Foundation for support of this work, under Grant No. GP 14114.

[2] R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).

[3] N. A. LeBel, M. E. Post, and J. J. Whang, *J. Amer. Chem. Soc.*, **86**, 3759 (1964), and earlier references.