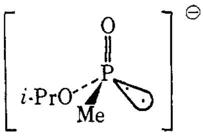
anol) (58% optically pure), to heptene[11] gave (+)-isopropyl heptylmethylphosphinate (**3**), bp 119° (1.8 mm), [α]D +2.21° (ethanol), presumably with the (*S*) configuration, as shown. At least two possibilities exist for the configurationally stable radical intermediate in the former reaction [Me(*i*-PrO)$\dot{P}$(OH)SC_6H_5 by $C_6H_5S\cdot$ addition to **2a**,[12] and **6** by $C_6H_5S\cdot$ abstraction of H· from **2** or **2a**]. Only the phosphinyl radical (**6**) appears possible as an intermediate in the heptene addition reaction, however, if one assumes a radical chain process is involved. It follows, then, that the phosphinyl radical must be configurationally stable, at least as a transient intermediate.

Unlike the radical systems, reactions of the corresponding anion (**7**) lead to racemic products (however, see below). Here, the intermediate, as customarily prepared, is rapidly (possibly instantaneously) racemized. Thus, when (−)-**2** was treated with sodium or potassium in ether or benzene to form the Michaelis–Becker intermediate,[13] the resulting solutions had zero rotation, and the products of the reactions of these solutions with alkyl halides were optically inactive. Similarly, treatment of (+)-**2** with butyllithium and then benzyl bromide gave the racemic product.



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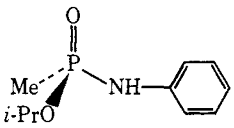

(*R*)-(−)-**8**

The (*R*)-(−)-**2**, [α]D −0.90° (CCl_4) (4.6% optically pure), reacted rapidly and probably stereospecifically with *N*-chlorosuccinimide[14] in carbon tetrachloride to give the (*S*)-(+)-**5**. The product was identified by ir, then converted with inversion of configuration to the anilide, (*R*)-(−)-**8**, mp 91–95°, [α]D −9.2° (benzene) (8% optically pure).[15] Also (*R*)-(−)-**2** slowly reacted with carbon tetrachloride containing tributylamine[16] at 25° in the presence of added aniline to form (*S*)-(+)-**5**, which was converted *in situ* and isolated as the (*R*)-(−)-**8** anilide. In the absence of the added aniline, a racemized product mixture was obtained. Both the *N*-chlorosuccinimide and the amine–CCl_4 reactions must take place with predominant if not complete retention of configuration (though not necessarily *via* similar mechanisms), based on the known[15] relationship of (*R*)-(−)-**5** to (*S*)-(+)-**1**, as indicated in Chart I. The stereoselectivity of the amine–CCl_4 reaction indicates that either the suggested[16b] mechanism is incorrect, or else the postulated anion (**7**), like the phosphinyl radical, does maintain its configuration, if present only as a transient reaction intermediate. Other stereochemical studies of the reactions of **2** will be reported at a later date.

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[11] Compare, for example, A. N. Pudovik and I. V. Konovalova, *Zh. Obshch. Khim.*, **29**, 3342 (1959).

[12] Compare, for example, W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Jr., *Chem. Commun.*, 296 (1969).

[13] A. Michaelis and T. Becker, *Chem. Ber.*, 30, 1003 (1897).

[14] G. W. Kenner, A. R. Todd, and F. J. Weymouth, *J. Chem. Soc.*, 3675 (1952).

[15] H. S. Aaron, R. T. Uyeda, H. F. Frack, and J. I. Miller, *J. Amer. Chem. Soc.*, **84**, 617 (1962). The apparent increase in optical purity in going from (−)-**2** *via* (+)-**5** to (−)-**8** is due to the fact that the (−)-**8** is more insoluble than the racemic compound.

[16] (a) F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 660 (1945); (b) G. M. Steinberg, *J. Org. Chem.*, **15**, 637 (1950).

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Received May 11, 1970

Reaction of Oxime *O*-Acetates with Chromous Acetate. A Method for the Conversion of Ketoximes to Ketones under Mild Conditions

Sir:

Despite the ready availability of ketoximes as synthetic intermediates and as derivatives for carbonyl protection, the utilization of oximes as precursors of ketones which are sensitive to acid and/or base has not been satisfactory.[1] In two instances recently encountered in these laboratories, none of the conventional or recently described procedures have shown promise.[2–4] This note describes a new reductive deoximation reaction which is highly effective even in the presence of acid- and base-sensitive functional groups such as ketal, hemithioketal, ester, and epoxide. The method involves the conversion of an oxime to the *O*-acetate derivative followed by reaction with >2 mol equiv of chromous acetate in 9:1 tetrahydrofuran–water (by weight) at temperatures between 25 and 65°. The selection of the reagent chromous acetate was based on the premise that it would cause reductive fission of the oxime N–O linkage to give an imine which then would suffer rapid hydrolysis to ketone at the pH (*ca.* 5) of the acetate ion buffered solution. The following procedure is illustrative of the new reaction.

Propiophenone. Propiophenone oxime *O*-acetate[5] (193 mg, 1.0 mmol) and excess chromous acetate (*ca.* 1 g)[6,7] were stirred in 10 ml of 9:1 tetrahydrofuran–

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[1] For a recent example see N. Finch and J. J. Fitt, *Tetrahedron Lett.*, 4639 (1969).

[2] Hydrolytic methods: (a) E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948); (b) M. P. Cava, R. L. Little, and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2260 (1958); (c) C. H. De Puy and B. W. Ponder, *ibid.*, **81**, 4629 (1959); (d) S. H. Pines, J. M. Chemerda, and M. A. Kozlowski, *J. Org. Chem.*, **31**, 3446 (1966).

[3] Oxidative methods: (a) (nitrosating agents) D. T. Manning and H. A. Stansbury, Jr., *J. Amer. Chem. Soc.*, **81**, 4885 (1959), and references cited therein; (b) (lead tetraacetate) G. Just and K. Dahl, *Can. J. Chem.*, **48**, 966 (1970); (c) (Ce(IV)–HNO_3) J. W. Bird and D. G. M. Diaper, *ibid.*, **47**, 145 (1969); (d) (ozone) R. E. Erickson, P. J. Andrulis, Jr., J. C. Collins, M. L. Lungle, and G. D. Mercer, *J. Org. Chem.*, **34**, 2961 (1969).

[4] Reductive methods: (a) (zinc–acetic acid, 100°) M. S. Ahmad and A. H. Siddiqui, *J. Indian Chem. Soc.*, **46**, 44 (1969); (b) (iron carbonyl–boron trifluoride) H. Alper and J. T. Edward, *J. Org. Chem.*, **32**, 2938 (1967).

[5] Oxime *O*-acetates were prepared by brief treatment of the ketoximes with acetic anhydride at 20°; see H. Metzger in "Methoden der Organischen Chemie," Vol. 10, No. 4, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1968, p 182.

[6] An aqueous solution of Cr(II), prepared by reduction of chromic chloride by zinc–hydrochloric acid [J. H. Balthis, Jr., and J. C. Bailar, Jr., *Inorg. Syn.*, **1**, 122 (1939)], was transferred by syringe into a filtering apparatus [L. R. Ocone and B. P. Block, *ibid.*, **8**, 125 (1966)] containing air-free sodium acetate solution. The precipitate of chromous acetate was collected, washed sequentially with air-free water, ethanol, and ether, and dried *in vacuo* to afford the dihydrate as a pink powder. The dried powder can be transferred with brief exposure to air with only slight oxidation.

[7] Most of the hydrolytic experiments which have been carried out in this work have been conducted on a 0.5–2-mmol scale using a substantial excess of chromous acetate. For larger scale work, where air oxidation of the reagent would be insignificant using approximately anaerobic techniques, a modest excess (*ca.* 20%) over the theoretical 2 mol equiv is preferred.

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.

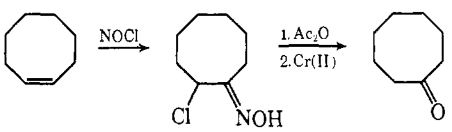
Table I. Conversion of Oxime *O*-Acetates to Ketones with Chromous Acetate in 9:1 Tetrahydrofuran–Water

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

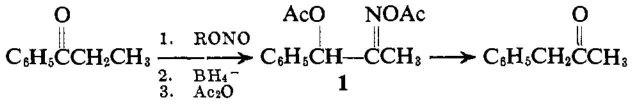
[a] Conditions for complete disappearance of starting oxime *O*-acetate. [b] Yield of product after isolation by distillation or tlc. [c] Starting material, progesterone 3,20-bis-*O*-acetoxime.

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.



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

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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Received June 23, 1970

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.