g, 0.0074 mol) and 1.4 g of potassium hydroxide in 20 ml of 50% aqueous methanol was heated at reflux for 3.5 hr. The solution was cooled and acidified to pH 2 with concentrated hydrochloric acid. The solid material was filtered, washed with water, and dried to give 2.0 g of hydroxy acid V, mp 75–76°. A mixture melting point with the acid obtained from the hydrolysis of polyester II was not depressed and the ir spectra were superimposable.

Registry No.—Ia, 34289-54-8; Ib, 34289-55-9; polymer of Ib, 34287-66-6; II, 34268-90-1; III, 34289-56-0; IV, 34289-57-1; V, 34289-58-2; *N*,*N*-dimethyl-3-hydroxy-4-(*n*-hexadecylthio)butyric acid amide, 34289-59-3.

Hydrogenation of Cinnamic Acids with Iridium(I) Catalysts. Effect of Various Ligands

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Recent communications have described olefin hydrogenations using $Ir(olefin)_2L_n$ based systems as catalysts.[1–3] Green and coworkers have noted ligand and solvent effects on the rate of hydrogenation of 1,5-cyclooctadiene and 1-hexene with these systems.[2] Van der Ent *et al.*, have studied the rate of hydrogenation of 1-hexene in benzene as a function of the ligand-iridium ratio (R).[3] With L = Ph_3P the maximum rate was observed at R = 2 at which point the rate is approximately ten times the rate at R = 1. I now report that *α,β-unsaturated acids can also be reduced* with these iridium catalysts and note some important rate effects based on ligand type, ligand ratio, and the presence or absence of chloride ligand.

Cinnamic acid and α-methylcinnamic acid have been hydrogenated to β-phenylpropionic acid and α-methyl-β-phenylpropionic acid, respectively, with $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ and various phosphines in MeOH solvent at 100° and 75 psig of H_2. Table I records the per cent reduction after 2 hr under these conditions with a substrate–catalyst ratio of 400. It is found that cinnamic acid is reduced faster than α-methylcinnamic acid for all three phosphines (catalyst system A).

The importance of a 2:1 phosphine–iridium ratio as against a 1:1 ratio in the reduction of α-methylcinnamic acid (catalyst system A *vs.* B) manifests itself with the less basic phosphines, Ph_3P and Ph_2PEt, but entirely disappears with $PhPEt_2$. In the latter case the rates of reduction are identical for both systems. Even with Ph_2PEt the rate differences are not nearly so pronounced as with Ph_3P.[4]

Hydrogenation of α-methylcinnamic acid in the absence of chloride ligand (system C) was achieved by use of isolated $[Ir(1,5\text{-cyclooctadiene})L_2]BF_4$ as the catalyst. In this case the reduction proceeds much more rapidly with all three phosphines than the same reduction in the presence of chloride (system A).

TABLE I
PER CENT REDUCTION AT 2 HR[a]

	Cinnamic acid	α-Methylcinnamic Acid		
Catalyst[b]	A	A	B	C
Ph_3P	82	38	1.5	92
Ph_2PEt	55	19	6	39
$PhPEt_2$	64	25	25	78

[a] Reaction cessation at 2 hr was chosen arbitrarily. All catalyst systems were still alive at this point with the possible exception of system B with Ph_3P and Ph_2PEt. In these cases partial loss of catalyst by iridium plate-out was observed early in the reaction. [b] A = PR_3/Ir = 2.0 $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ and PR_3 mixed *in situ;* B = PR_3/Ir = 1.0 $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ and PR_3 mixed *in situ;* C = Used isolated $[Ir(1,5\text{-cyclooctadiene})(PR_3)_2]BF_4$: Prepared by previously published general procedures for analogous rhodium and iridium complexes. *Cf.* ref 1 and 2 and R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc*, **93**, 2397 (1971).

One further observation of note is that the rate of hydrogenation of cinnamic acid with L = Ph_3P was considerably reduced when no effort was made to eliminate the presence of atmospheric oxygen. The inhibitory effect of oxygen with this iridium catalyst is exactly the opposite of the rate-enhancing effect of oxygen in the reduction of maleic acid in DMA catalyzed by $IrX(CO)(Ph_3P)_2$ reported by James and Memon.[5] I have repeated the effect reported by these authors in the reduction of cinnamic acid with $IrCl(CO)(Ph_3P)_2$ in both DMA and MeOH.

Experimental Section

All hydrogenations were conducted in glass Fischer–Porter aerosol compatibility tubes with 20 mmol of substrate and 0.05 mmol of catalyst dissolved in 25 ml of anhydrous MeOH. For systems A and B, $[Ir(1,5\text{-cyclooctadiene})Cl]_2$[6] and the phosphines were premixed in 5 ml of MeOH under N_2 for 15 min prior to the addition of substrate. All reaction mixtures were vigorously sparged with nitrogen prior to being pressured to 75 psig of H_2. Reaction timing commenced upon placement of a 100° oil bath under the reaction vessel and activation of a magnetic stirrer.

Analyses were performed by integrating the $CDCl_3$ nmr spectra of solvent-stripped reaction aliquots. The reported integrals for cinnamic acid are actually corrected from observed figures to allow for integral deviations observed from known values in standard mixtures. In the case of α-methylcinnamic acid and α-methyl-β-phenylpropionic acid, standard mixtures integrated correctly.

Registry No.—Cinnamic acid, 621-82-9; α-methylcinnamic acid, 1199-77-5.

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[1] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969).

[2] M. Green, T. A. Kuc, and S. N. Taylor, *J. Chem. Soc. D*, 1553 (1970).

[3] H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *ibid.*, 1694 (1970).

[4] Van der Ent's work on phosphine–iridium ratios (ref 3) was confined to Ph_3P and the hydrogenation of 1-hexene. It is interesting to speculate whether the rate differences would also disappear in this case with use of $PhPEt_2$ instead of Ph_3P.

(5) B. R. James and N. A. Memon, *Can. J. Chem.*, **46**, 217 (1968).

(6) Strem Chemicals, Inc.

Reduction of α-Substituted Acetoacetate Enolates with Lithium Aluminum Hydride

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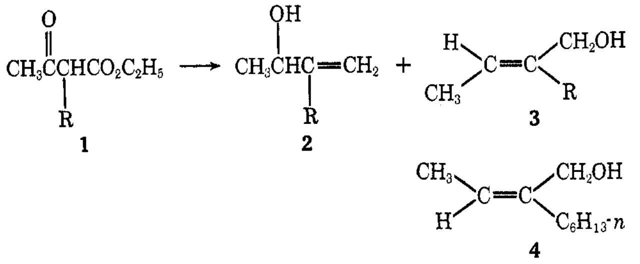
In connection with a current synthesis project we had occasion to examine the reduction of α-substituted ethyl acetoacetate enolates. A recent report concern-

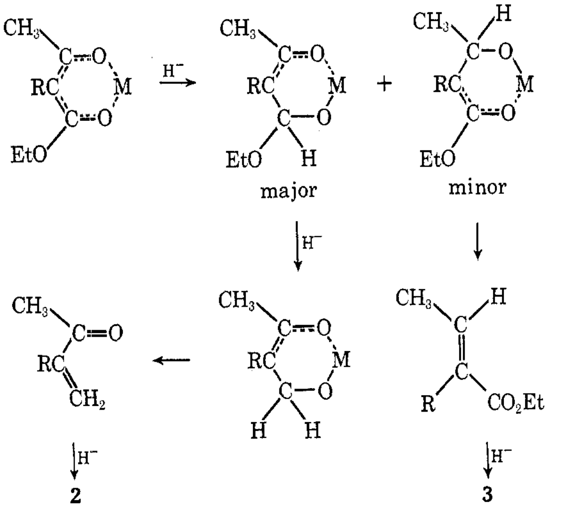


a, series R = n-C_6H_{13}
b, series R = $CH_2C_6H_5$
c, series R = C_6H_{11}

ing related β-diketone reductions prompts this brief disclosure of our findings.[1]

The keto esters **1a-c** were reduced along the lines reported in our earlier studies on malonic esters wherein sodium hydride was employed for enolate formation and ethyl formate was finally added to destroy excess lithium aluminum hydride.[2] The reductions afforded a roughly 80:20 mixture of allylic alcohols **2** and **3** for the three systems examined. This trend can be readily accommodated within the framework of previously postulated pathways for analogous reductions[1-3] as depicted in Scheme I.[4]

SCHEME I



As in the case of β-diketone enolate reductions, the elimination reaction leading to the unsaturated alcohols **3** appears to be highly stereoselective.[1] The stereochemical explanation offered for those systems would seem applicable to the present keto ester enolates as well. As a check on this stereochemical point we employed the method of Corey and Yamamoto[5] to synthesize the stereoisomer **4** of alcohol **3a**. The spectral properties of these two alcohols, while similar, showed distinct differences which left no doubt regarding their nonidentity.

From a synthetic point of view, the β-keto ester enolate reduction offers a simple, direct route to β-methylene alcohols such as **2**.

Experimental Section[6]

General Reduction Procedure.—A solution of 0.1 mol of keto ester **1** in 50 ml of tetrahydrofuran was added dropwise to 2.5 g of sodium hydride (from 5.0 g of 50% oil dispersion) in 200 ml of tetrahydrofuran and the mixture was heated at reflux for 1 hr and treated with 8.00 g of lithium aluminum hydride in portions. The mixture was heated at reflux for 4 hr and cooled, 40 ml of ethyl formate was carefully added, and the mixture was stirred at 40–50° for 1 hr. The product was isolated by through extraction with ether and distillation.

Reduction of Ethyl α-Hexylacetoacetate (1a).[7]—The above procedure afforded an 82:18 mixture of alcohols **2a** and **3a**, bp 49–50° (0.01 mm), in 71% yield. Preparative gas chromatography was used to isolate the pure isomers, which had the following properties.

2-Hexyl-1-buten-2-ol (2a) had $\lambda_{\max}^{\mathrm{film}}$ 6.10 and 11.17 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 4.95, 4.67 ($C{=}CH_2$), 4.0 (H-3 quartet, J = 6 Hz), 1.25 ppm (CH_3 doublet, J = 6 Hz).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.78; H, 12.89. Found: C, 76.54; H, 12.95.

***Z*-2-Hexyl-2-buten-1-ol (3a)** had $\lambda_{\max}^{\mathrm{film}}$ 9.43 and 9.95 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.42 (H-3 quartet, J = 6 Hz), 1.60 (CH_3 doublet, J = 6 Hz), 3.31 ppm (CH_2O–).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.78; H, 12.89. Found: C, 76.71; H, 12.87.

Reduction of Ethyl α-Benzylacetoacetate (1b).[8]—The above procedure afforded an 80:20 mixture of alcohols **2b** and **3b**, bp 55–56° (0.01 mm), in 44% yield. Preparative gas chromatography was used to isolate the pure isomers, which had the following properties.

2-Benzyl-1-buten-3-ol (2b) had $\lambda_{\max}^{\mathrm{film}}$ 6.10 and 11.11 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.00, 4.58 ($C{=}CH_2$), 4.10 (H-3 quartet, J = 6 Hz), 3.26 (benzyl CH_2), 1.20 ppm (CH_3 doublet, J = 6 Hz).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.45; H, 8.70. Found: C, 81.31; H, 8.88.

2-Benzyl-2-buten-1-ol (3b) had $\lambda_{\max}^{\mathrm{film}}$ 6.28 and 11.83 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.58 (H-3 quartet, J = 6 Hz), 1.66 ppm (CH_3 doublet, J = 6 Hz).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.45; H, 8.70. Found: C, 81.33; H, 8.98.

Reduction of Ethyl α-Cyclohexylacetoacetate (1c).[9]—The above procedure afforded an 85:15 mixture of alcohols **2c** and **3c**, bp 47–48° (0.01 mm), in 53% yield. Preparative gas chromatography was used to isolate the pure isomers, which had the following properties.

2-Cyclohexyl-1-buten-3-ol (2c) had $\lambda_{\max}^{\mathrm{film}}$ 6.06, 11.11, 11.28 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.06, 4.84 ($C{=}CH_2$), 4.13 (H-3 quartet, J = 6.5 Hz), 1.20 ppm (CH_3 doublet, J = 6.5 Hz).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.88; H, 11.76. Found: C, 77.67; H, 11.50.

2-Cyclohexyl-2-buten-1-ol (3c) had $\lambda_{\max}^{\mathrm{film}}$ 11.24 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.38 (H-3 quartet, J = 6.5 Hz), 3.90 (–CH_2O–), 1.61 ppm (CH_3 doublet, J = 6.5 Hz).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.88; H, 11.76. Found: C, 77.77; H, 11.71.

***E*-2-Hexyl-2-buten-1-ol (4).**—The procedure of Corey and Yamamoto was employed,[5] affording the title compound: bp 80° (bath temperature) (0.05 mm); $\lambda_{\max}^{\mathrm{film}}$ 6.88 and 9.90 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.27 (H-3 quartet, J = 6.2 Hz), 1.60 ppm (CH_3 doublet, J = 6.2 Hz).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.78; H, 12.89. Found: C, 76.75; H, 12.82.

---

(1) J. W. Frankenfeld and W. E. Tyler, III, *J. Org. Chem.*, **36**, 2110 (1971).

(2) J. A. Marshall, N. H. Andersen, and A. R. Hochstetler, *ibid.*, **32**, 113 (1967).

(3) A. S. Dreiding and J. A. Hartman, *J. Amer. Chem. Soc.*, **75**, 939 (1953).

(4) Our proposed pathway for the reduction of malonic enolater (ref 2) was not intended to replace or discredit the scheme of Dreiding and Hartman (ref 3) as implied by Frankenfeld and Tyler (ref 1). We merely wished to extend the Dreiding and Hartman proposal in somewhat greater detail so as to include the formation of saturated alcohol by-products.

(5) E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226 (1970).

(6) Reactions were conducted under a nitrogen atmosphere using the apparatus described by W. S. Johnson and W. P. Schneider, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 132. Reaction products were isolated by addition of water and extraction with the specified solvent. The combined extracts were washed with saturated brine and dried over anhydrous magnesium sulfate. The solvent was removed from the filtered solutions on a rotary evaporator.

(7) V. H. Wallingford, M. A. Thorpe, and A. H. Homeyer, *J. Amer. Chem. Soc.*, **64**, 580 (1942).

(8) H. R. Snyder, C. W. Smith, and J. M. Stewart, *ibid.*, **66**, 200 (1944).

(9) J. T. Adams, B. Abramovitch, and C. R. Hauser, *ibid.*, **65**, 552 (1943).

Registry No.—**2a**, 34220-09-2; **2b**, 34220-10-5; **2c**, 34220-11-6; **3a**, 34226-07-8; **3b**, 34220-12-7; **3c**, 34220-13-8; **4**, 34226-08-9; lithium aluminum hydride, 16853-85-3.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work.

Preparation of Nitriles from 1,2,5-Oxadiazoles by Reduction with Triphenyl Phosphite[1,2]

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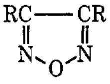
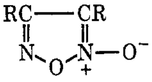
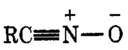
The 1,2,5-oxadiazoles **1** can be made[3a,b] by dehydration of 1,2-dioximes and by deoxygenation[4] of 1,2,5-oxadiazole 2-oxides **2**. The latter are obtained[3] from 1,2-dioximes by oxidation and from nitrile oxides **3** by dimerization.[5]



1



2



$RC\equiv\overset{+}{N}-\overset{-}{O}$

3

The present note reports our results on the conversion of 1,2,5-oxadiazoles (and their 2-oxides) to nitriles. We heated a number of the oxadiazoles with triphenyl phosphite (chosen for cost and convenient boiling point) and were pleased to find that nitriles were produced in preparatively useful amounts. Since the 1,2,5-oxadiazole 2-oxides are reduced to the 1,2,5-oxadiazoles under much milder conditions[4] than ours, we believe that the reactions we report here are all conversions of 1,2,5-oxadiazoles to nitriles.

After the completion of our study a note without experimental details appeared[6] describing the cleavage and reduction to dicyano compounds of the 1,2,5-oxadiazole 2-oxides prepared from acenaphthylenequinone dioxime and camphorquinone dioxime. These workers used trimethyl phosphite and attributed the easy reduction to ring strain because the oxadiazole ring is fused to another 5-ring in each of their examples. We find their argument convincing as a reason for the ease of the reaction in the cases they report, but our findings indicate that under more strenuous conditions this reductive cleavage is general.

The ultimate utility of this sequence in preparative chemistry remains to be worked out. We note, however, that the overall conversion of a ketone with an adjacent CH_2 group to two cyano groups may be a useful alternative to other cleavage schemes.

Our results are too fragmentary to support any speculations about the effects of substituents on yield. Much of the difference in yields reported here can be accounted for by higher losses in isolation and purification of very volatile or very soluble nitriles. The yields are collected in Table I and a typical experiment is described in the Experimental Section.

TABLE I

R in 1 or 2	Ref	RCN, %	Notes
Phenyl 1	*a*	79	*f*
Phenyl 2	*b*	87.4	*f*
4-Methoxyphenyl 2	*c*	31.4	*g, h*
2-Furyl 2	*d*	22.3	*g*
Ethyl 2	*e*	65.2	*g*
Methyl 2	*e*	38.7	*g*

[a] K. Auwers and V. Meyer, *Ber.*, **22**, 714 (1889). [b] J. H. Boyer and U. Toggweiler, *J. Amer. Chem. Soc.*, **79**, 895 (1957). [c] G. Ponzio, *Gazz. Chim. Ital.*, **36**, 596 (1906). [d] H. Rheinboldt, *Justus Liebigs Ann. Chem.*, **451**, 167 (1926). [e] T. Mukaiyama and T. Hoshino, *J. Amer. Chem. Soc.*, **82**, 5339 (1960). [f] Reaction mixture was yellow-orange. [g] Reaction mixture was black. [h] Nitrile mp 57–58° (EtOH) [lit. mp 59°: W. Reinder and W. E. Ringer, *Recl. Trav. Chim. Pays-Bas*, **18**, 328 (1899)].

Experimental Section

It is advisable to use triphenyl phosphite that has been washed with alkali and then water and has been thoroughly dried.

Benzonitrile from 3,4-Diphenyl-1,2,5-oxadiazole 2-Oxide.—To 26.0 g (0.084 mol) of triphenyl phosphite preheated to 270° in a flask equipped with a stirrer, a thermometer in the liquid, and a reflux condenser was added a mixture of 10.00 g (0.042 mol) of 3,4-diphenyl-1,2,5-oxadiazole 2-oxide and 26.0 g of triphenyl phosphite. The reaction mixture, which heated up spontaneously and turned light yellow-orange, was kept under reflux by external heating for 15 min longer and was then fractionated in vacuum to give 7.57 g (87.4%) of benzonitrile identical (infrared) with an authentic sample.

Registry No.—Benzonitrile, 100-47-0; 3,4-diphenyl-1,2,5-oxadiazole-2-oxide, 5585-14-8; triphenyl phosphite, 101-02-0.

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[1] Taken from the Ph.D. Dissertation of Stanley M. Katzman, University of Missouri—Kansas City, January 1967.

[2] Support by the National Science Foundation under Grant No. G10031 is gratefully acknowledged.

[3] (a) J. Doeuvre in "Traité de Chimie Organique," Vol. 21, V. Grignard, G. Dupont, and R. Locquin, Ed., Masson et Cie, Paris, 1953. (b) L. C. Behr in "Heterocyclic Compounds," Vol. 17, A. Weissberger and R. H. Wiley, Ed., Wiley-Interscience, New York, N. Y., 1962. (c) J. V. R. Kaufman and J. P. Picard, *Chem. Rev.*, **59**, 429 (1959).

[4] (a) T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962); (b) Ch. Grundmann, *Chem. Ber.*, **97**, 575 (1964); (c) A. S. Bailey and J. M. Evans, *Chem. Ind. (London)*, 1424 (1964).

[5] Ch. Grundmann and P. Grünanger, "The Nitrile Oxides," Springer Verlag, West Berlin and Heidelberg, 1971.

[6] Altaf-Ur-Rahman and A. J. Boulton, *Chem. Commun.*, 73 (1968).

Nonequivalency of *exo-N*-Methylene Protons of Some 2-Oxazolidones

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Received August 13, 1971

A previous publication[1] reported the preparation of 2-oxazolidones in excellent yields using a hydrocarbon-soluble catalyst composed of lithium bromide and tributylphosphine oxide. The cycloaddition reaction of methoxymethyl isocyanate with phenyl glycidyl ether in benzene gave *N*-methoxymethylene-5-phenoxymethylene-2-oxazolidone (**1**), mp 69.5–70.5°.

Nmr analysis of this compound in *o*-dichlorobenzene and deuteriochloroform indicated that the *exo-N*-methylene protons were nonequivalent. We would like to report some additional nmr studies which further

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[1] J. E. Herweh and W. J. Kauffman, *Tetrahedron Lett.*, 809 (1971).