50 °C. The remaining white solid was partly dissolved in 30 mL of water. The undissolved material (0.070 g) was identical with an authentic sample of **1a** and did not contain excess ^{18}O as indicated by mass spectrometry.[23] The aqueous filtrate was acidified with 2 N H_2SO_4 (10 mL) and extracted with ether (2 × 20 mL). The combined ethereal extracts were washed with 2 N H_2SO_4 (10 mL) and dried over $MgSO_4$. Removal of the solvent in vacuo afforded *p*-toluenesulfinic acid (0.150 g), identical with an authentic sample. The aqueous layer was made alkaline with 10 N NaOH and the water was removed in vacuo. The resulting white material was extracted in a Soxhlet apparatus with 100 mL of anhydrous ethanol for 4 h. After removal of the ethanol in vacuo, sodium *p*-toluenesulfonate was obtained, which was crystallized from anhydrous ethanol. The corresponding *S*-benzylisothiouronium salt was prepared according to a standard procedure[4] and exhibited mp 180.3–181.8 °C (lit. 182 °C)[4] after crystallization from 33% (v/v) ethanol–water. The same salt (mp 180.5–181.5 °C) was also prepared from a sample of sodium *p*-toluenesulfonate obtained from the reaction of 0.310 g (0.91 mmol) of **1a** in 33% (v/v) ethanol–^{18}O-enriched water (30 mL) containing 0.130 g (3.25 mmol) of sodium hydroxide (45 min at 80 °C). The mass spectrum of *S*-benzylisothiouronium *p*-toluenesulfonate shows a peak at *m/e* 172 for a $C_7H_7SO_3H^+$ fragment and a peak at *m/e* 174 for the same fragment enriched in ^{18}O. The ratio of the intensities of both fragments (I^{174}/I^{172}; estimated accuracy $\pm 0.1 \times 10^{-2}$) was determined on the monitor of the instrument. Comparison of this ratio ($I^{174}/I^{172} = 6.5 \times 10^{-2}$ in dioxane–^{18}O-enriched water) with that produced by using the *S*-benzylisothiouronium salt of natural *p*-toluenesulfonic acid ($I^{174}/I^{172} = 5.2 \times 10^{-2}$) indicated that exclusive S–O bond fission had occurred upon reaction of **1a** with hydroxide ion.[24]

A test reaction for oxygen exchange by the *p*-toluenesulfonate anion was run on a solution of 0.350 g (1.80 mmol) of sodium *p*-toluenesulfonate, 0.315 g (1.77 mmol) of sodium *p*-toluenesulfinate, and 0.120 g (3 mmol) of sodium hydroxide in 30 mL of 50% (v/v) dioxane–^{18}O-enriched water. After keeping this mixture at 67 ± 1 °C for 19 h, the *S*-benzylisothiouronium *p*-toluenesulfonate (mp 180.3–181.7 °C) was prepared as described above. Mass spectrometric analysis showed that no ^{18}O had been incorporated in the *p*-toluenesulfonate anion during the treatment in the alkaline medium.

Product Composition. Sulfonate **1a** (0.300 g, 0.88 mmol) was dissolved in 20 mL of 50% (v/v) ethanol–*n*-butylamine containing 0.180 g (2.6 mmol) of sodium ethoxide and kept at room temperature for 90 h. Gas chromatographic analysis of 2 mL of the reaction mixture unequivocally established the presence of considerable amounts of diethyl ether and formaldehyde as indicated by careful comparison with gas chromatographic data of reference solutions. The other 18 mL of the reaction mixture was evaporated to dryness and the resulting solid was dissolved in 15 mL of water. After acidification with 2 N H_2SO_4 no *N*-*n*-butyl-*p*-toluenesulfonamide could be detected.

Registry No.—*p*-Toluenesulfonic acid, 104-15-4; methanesulfonic acid, 75-75-2; *tert*-butanesulfonic acid, 16794-13-1; *p*-tolylsulfonylphenyldiazomethane, 52629-22-8; *p*-tolylsulfonyldiazomethane, 1538-98-3; hydroxide ion, 14280-30-9; *p*-toluenesulfinic acid, 536-57-2; *S*-benzylisothiouronium *p*-toluenesulfonate, 35469-22-8.

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(11) (a) $k_{HO_2^-}/k_{OH^-} = 72$ for the reaction of phenyl α-disulfone in 60% (v/v) dioxane–H_2O at 25 °C; see J. L. Kice and L. F. Mullan, *J. Am. Chem. Soc.*, **98**, 4259 (1976). (b) The rate enhancement found for **1c** excludes the possibility of a mechanism involving a sulfene intermediate. For the latter type of mechanism see J. F. King and T. W. S. Lee, *J. Am. Chem. Soc.*, **91**, 6524 (1969).

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Localized Photochemical Isomerization in a 1,4-Bichromophore. Photochemistry of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone Anil

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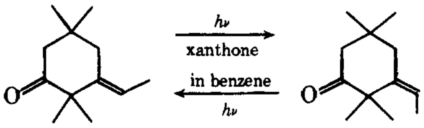
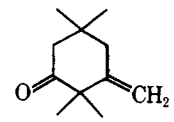
We wish to report an interesting case of an apparently localized rotational deactivation[1] in β,γ-unsaturated imine bichromophores. There is already considerable evidence that excited-state rotation (geometric isomerization) is an important governing factor in the photochemistry of the related 1,4-bichromophores, the di-π-[2] and oxa-di-π-methanes.[3,4] A germane illustration is the contrasting behavior of β,γ-unsaturated ketones **1** and **2** on photosensitized irradiation. Unconstrained ketone **1** undergoes only cis–trans isomerization,[3] whereas the structurally similar steroid **2**, for which geometric isomerization (rotational deactivation) would cause



1-(*E*) 1-(*Z*)



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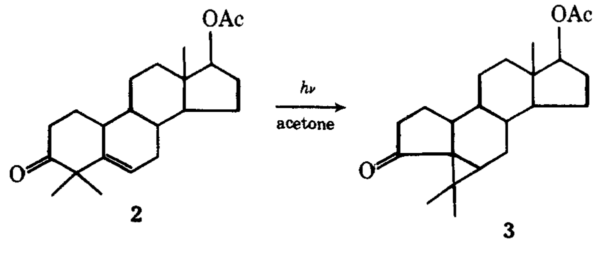
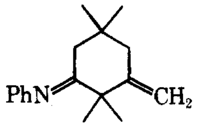


2 3

intolerable strain, follows an alternative reaction course—the 1,2-acyl shift.[5] Methylene ketone **4**, in which cis–trans isomerization is degenerate, shows no apparent triplet reactivity.[3b]

Our interest in the excited-state chemistry of bichromophores prompted exploration of the photochemistry of the β,γ-unsaturated imine analogues of **1** and **4**, viz., 3-methylene- and 3-ethylidene-2,2,5,5-tetramethylcyclohexanone anil (**5** and **6**, respectively), in which triplet-state isomerizational[6] deactivation could occur, in principle, in either one or both of the olefin and imine chromophores.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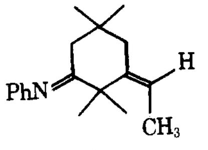
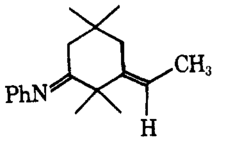
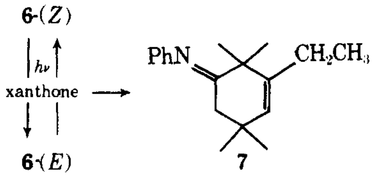

6-(*Z*)


6-(*E*)

Results and Discussion

The anil **6** was prepared from an 81:19 *Z*:*E* isomer mixture of β,γ-unsaturated ketone **1**[3] by reaction with a twofold excess of aniline over 4A molecular sieves in refluxing cyclohexane.[10] After two successive treatments, product **6** (>95%), unreacted **1**, and aniline were separated by preparative GLC (10% butanediol succinate on Chrom P-DMCS, 12 ft × ⅜ in., 163 °C). Analysis of the anil by NMR (Figure 1) indicated it was an 81:19 mixture of two isomers, **6**-(*Z*) and **6**-(*E*), differing in their stereochemical configuration at the C=C bond, and having a common stereochemistry (presumably *E*) at the C=N bond. As expected from previous studies on similar compounds,[3,11] the *Z* isomer showed pronounced allylic and $-H_2CC{=}CCH_3$ coupling which was absent in **6**-(*E*), and both isomers exhibited NMR deshielding effects of proximal methyls. The high stereoselectivity during anil formation was to be anticipated in view of the observations of Curtin,[7a] Iwamura,[10b] and others. Anil **5** was prepared in the same manner from methylene ketone **4**.

Prolonged direct irradiation of ethylidene anil **6** (λ_{max} of isomer mixture 266 nm) in benzene solution (0.2 M, Corex or unfiltered, medium-pressure mercury lamp) caused only inefficient reaction (<5% conversion in several days) to a complex mixture of trace products not identified. Methylene anil **5** was singularly unreactive on both direct and photosensitized irradiation. In contrast, photosensitization of ethylidene anil **6** with xanthone (0.19 M, 350 nm) caused the *Z*:*E* isomer ratio to change rapidly. On prolonged sensitized irradiation the **6**-(*Z*):**6**-(*E*) ratio reached a stationary value of 23:77, according to NMR analysis. The only other change noted was a gradual buildup of one other photoproduct (**7**, 6% by GLC when the **6**-(*Z*):**6**-(*E*) photoequilibrium had been established). On the basis of IR, NMR, and mass-spectral parameters, **7** was identified as 3-ethyl-2,2,5,5-tetramethylcyclohex-3-en-1-one anil, a 1,3-H shift isomer of **6**. Addition of Eu(fod)$_3$ to photolysates caused only a small spread of chemical shifts. No extra resonances attributable to another photoproduct (e.g., a syn isomer of **6**-(*Z*) or **6**-(*E*)) were detected.



Similar results were obtained when samples of **6** in diethyl ether-d_{10} were irradiated at −115 °C. Only slow decomposition on direct irradiation and isomerization of **6**-(*Z*) to **6**-(*E*), accompanied by some **6** → **7** reorganization, on sensitization with xanthone, were observed.[12]

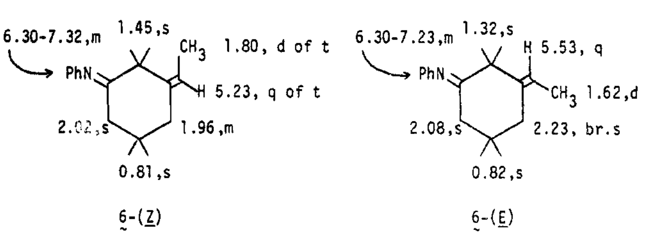
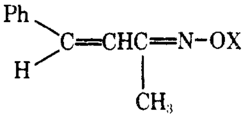


Figure 1. NMR chemical shifts for **6**-(*Z*) and **6**-(*E*), δ scale, 60 MHz, CCl_4.

Although interpretation of the photolysate NMR spectrum as a mixture of **6**-(*Z*) and **6**-(*E*) appeared unequivocal, it seemed important to confirm by chemical means that the binary mixture was a pair of C=C cis–trans isomers and not a pair of C=N syn–anti isomers. Accordingly, a photolysate which had attained **6**-(*Z*):**6**-(*E*) photoequilibrium was hydrolyzed by agitation of the benzene solution with 50% aqueous pyruvic acid.[13] The hydrolysate was partitioned between ether and brine and the ketones **1** were recovered from the concentrated organic phase by preparative GLC (10% BDS, Chrom P, 163 °C). Analysis of the ketone mixture by NMR showed the isomer ratio **1**-(*Z*):**1**-(*E*) to be 21:79, in excellent agreement with the value of the **6**-(*Z*):**6**-(*E*) ratio obtained directly by NMR.

The results clearly indicate that, except for a minor amount of reaction via a 1,3-H shift to **7**, the lone detectable triplet-state reaction of **6** is rotational deactivation via olefin cis–trans isomerization. No product from imine syn–anti isomerization was found. These observations presumably explain the lack of triplet-state reactivity in **5**. Considering that virtually the same olefin isomerization process is involved in the triplets of both β,γ-unsaturated ketone **1** and β,γ-unsaturated anil **6**, it is of interest that the *Z*:*E* isomer ratio is ca. 22:78 in both cases.

The absence of syn–anti isomerization in **5** and **6** is noteworthy, since photochemical interconversion of imine geometric isomers is well established.[8] Padwa and Albrecht showed that isomerization occurred in both the singlet and triplet excited states of acetophenone oxime methyl ether.[8a] Herkstroeter implicated triplet states of surprisingly low energies in the photochemical anti–syn isomerizations of azomethine dyes.[8c–e] However, Sato et al.[14] noted that in benzylideneacetone oxime (**8a**) and oxime ether (**8b**) only olefin cis–trans isomerization, and no imine anti–syn isomerization, was observed, suggesting olefin isomerization is the lower energy reaction in that system.



$$\text{Ph}(\text{H})\text{C}{=}\text{CH}\underset{\underset{\text{CH}_3}{|}}{\text{C}}{=}\text{N}{-}\text{OX}$$

8a, X = H
b, X = CH_3

A priori, the absence of anti–syn photoisomerization in **5** and **6** at 25 °C could have been the artifact of an unexpectedly rapid thermal syn–anti isomerization which efficiently erased any photoisomerization in the contrathermodynamic direction. This explanation seems less likely, however, since no C=N bond isomerization was noted, even when irradiations (both direct and sensitized) were done at −115 °C in (diethyl ether)-d_{10}. Furthermore, similar, though less crowded, anils have been prepared by Iwamura,[10b] lending credence to the notion that the syn isomer should be capable of existence at reasonable temperatures once it is formed. Since C=C isomerization still occurred under photosensitization at −115

°C, it seems clear that, in the triplet state, C=C isomerization is simply of lower energy demand than C=N isomerization in these β,γ-unsaturated anils.[15] The reluctance toward syn-isomer formation is likely connected to the considerable allylic strain[16] which would be present in the syn isomer.

Experimental Section

3-Ethylidene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine (6). According to the method of Taguchi and Westheimer,[9a] the anil was synthesized from 1.25 g (1.34 mmol) of aniline (Mallinckrodt, freshly distilled over zinc dust and potassium hydroxide at 10 Torr, bp 69 °C), 1.65 g (0.915 mmol) of an 81:19 *Z*:*E* isomer mixture of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone[3b] in 10 mL of cyclohexane, and molecular sieves (5 g of Linde Type 4A activated by heating to 230 °C at 2.5 Torr for 24 h) heated at reflux (ca. 96 °C) under nitrogen for 72 h. The solution was filtered and concentrated by rotary evaporation. A second pass was usually necessary to bring the reaction to completion. In that case, approximately 4 additional equiv of aniline was added in 15 mL of dry cyclohexane with 5 g of fresh 4A molecular sieves. The entire solution was refluxed under nitrogen for an additional 72 h. This solution was refiltered and concentrated by rotary evaporation. The concentrate was chromatographed at 190 °C (flow rate 70 mL/min) through a 12 ft × 0.38 in. column of 10% butanediol succinate on Chrom P-DMCS, giving three fractions with retention times of 6.4, 8.4, and 27.3 min. The first (ca. 1%) appeared from NMR comparison to authentic material to be unreacted 3-ethylidene-2,2,5,5-tetramethylcyclohexanone; the second was excess aniline. The third (ca. 98%) yielded 600 mg (2.4 mmol, 36% after chromatography) of clear, colorless, 3-ethylidene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine, as a clear, colorless mixture of *E* and *Z* isomers in a 19:81 ratio. The imine hydrolyzed spontaneously in the presence of atmospheric moisture and was best preserved in a sealed, dry ampule at reduced temperatures: IR (CCl_4) 3060 (w), 2963 (s), 2870 (m), 1648 (s), 1360, 1380 (m), 1140, and 1160 (m) cm^{-1}; mass spectrum (rel intensities) *m/e* 255 (30), 240 (35), 159 (13), 158 (100), 118 (5), 117 (7), 104 (5), 93 (6), 81 (7), 77 (27), 67 (11), 55 (11), 53 (6), 51 (5), 43 (9), 41 (15), and 40 (6); NMR (CCl_4), see Figure 1.

Anal. Calcd for $C_{18}H_{25}N$: M$^+$, 255.1987. Found: M$^+$, 255.1978.

3-Methylene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine (5). The methylene anil was synthesized according to the method of Taguchi and Westheimer[9a] as described above for the ethylidene analogue: NMR (CCl_4) δ 0.78 (6 H, s), 1.35 (6 H, s), 2.09 (2 H, s), 2.22 (2 H, br s), 4.72 (1 H, m), 4.93 (1 H, m), and 6.35–7.33 (5 H, m).

Anal. Calcd for $C_{17}H_{23}N$: M$^+$, 241.1831. Found: M$^+$, 241.1825.

Direct Irradiation of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine. In a quartz 5-mm NMR tube, 96 mg (0.38 mmol) of anil was diluted to a total volume of 1 mL with benzene-d_6, degassed with argon, sealed, and irradiated with a 450-W high-pressure mercury lamp (Hanovia) with Corex filter for 17 h. The progress of the photolysis was monitored by NMR and no changes were observed. The filter was then removed and irradiation was carried out for 150 h at full arc. A deepening yellow color was seen in the tube, but no significant changes in the NMR were seen. Only numerous trace photoproducts were detected by GLC analysis, but these were not identified.

Sensitized Photolysis of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine. In an unpolished, Pyrex 5-mm NMR tube, 100 mg (0.39 mmol) of anil was diluted to a total volume of 1 mL with xanthone-saturated (0.19 M) benzene, degassed with argon, and sealed. Photolysis was carried out with RUL-3500 lamps in a Rayonet reactor to a photostationary time of ca. 200 h and with a 450-W high-pressure mercury lamp (Hanovia) with a Corex filter to a photostationary time of ca. 120 h. The photolysis was monitored by NMR, which indicated olefin cis–trans isomerization was occurring. The concentration of the *Z* isomer steadily decreased from an initial value of 81% to an approximate photostationary value of ca. 23%.

In order to establish the fact that NMR changes were due only to olefin geometrical isomerism and to compare the isomer mixtures in the imine with those found in the ketone, the hydrolysis of the photolyzed imine was effected. In a Pyrex NMR tube, 100 mg (0.39 mmol) of photolyzed imine (isolated by GLC) was diluted to a total volume of 1 mL with benzene. To this tube was injected 25 μL of 50% pyruvic acid in water; the tube was shaken and allowed to sit for 24 h.[13] NMR analysis throughout the procedure indicated quantitative hydrolysis to the ketone. This solution was then partitioned three times between equal volumes of ether and saturated aqueous sodium chloride solution. The ether extracts were dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The 3-ethylidene-2,2,5,5-tetramethylcyclohexanone was isolated by GLC and redissolved in benzene to reveal a *Z*:*E* mixture of 21:79, thus verifying the isomer distribution as determined directly for the anil by NMR.

GLC analysis (12 ft × 0.38 in. column of 10% butanediol succinate on Chrom P-DMCS at 164 °C, flow rate 53 mL/min) of the xanthone-sensitized photolysis gave four fractions with retention times of 8.7, 12.1, 34.5, and 40.0 min. The first and second proved to be 3-ethylidene-2,2,5,5-tetramethylcyclohexanone and aniline, respectively. These products were presumably formed by spontaneous hydrolysis (ca. <1%) caused by trace moisture in the column. The fourth peak was the anil isomer mixture, 23:77::*Z*:*E* by NMR at the steady state.

The third peak (ca. 9% at 170 h of photolysis, Hanovia) was a minor photoproduct which had NMR, IR, and mass spectral data consistent with those expected for 3-ethyl-2,2,5,5-tetramethylcyclohex-3-en-1-one-*N*-phenylimine (7): mass spectrum (rel intensities) *m/e* 255 (60), 240 (21), 226 (6), 212 (71), 199 (55), 196 (7), 184 (15), 158 (4), 139 (12), 138 (100), 124 (7), 123 (53), 118 (14), 117 (50), 110 (10), 109 (62), 107 (10), 105 (7), 95 (19), 93 (14), 91 (13), 82 (8), 81 (22), 79 (13), 78 (6), 77 (55), and 69 (11); NMR (CCl_4) δ 0.91 (6 H, s), 1.06 (3 H, t), 1.30 (6 H, s), 2.04 (2 H, q), 2.11 (2 H, s), 5.19 (1 H, br s), and 6.23–7.43 (5 H, m).

Photolyses of 3-Ethylidene-2,2,5,5-tetramethylcyclohexenone-*N*-phenylimine at −115 °C. Two samples of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine (50 mg, 0.19 mmol) in (diethyl ether)-d_{10} (0.5 mL), one containing 0.02 M xanthone, were prepared in 5-mm quartz tubes, degassed, and sealed. The samples were suspended in a quartz Dewar maintained at −115 °C, and irradiated through an unsilvered window with a 450-W high-pressure mercury lamp (Hanovia). Except for longer irradiation times necessitated by the less efficient optical system, the results of both the direct and photosensitized irradiations were the same as in the photolyses at +25 °C: only extremely slow decomposition to many trace products in direct photolysis and *Z* → *E* olefin isomerization in the sensitized run, with no evidence of imine anti → syn isomerization, were observed in the low-temperature NMR spectra.[12]

Photolyses of 3-Methylene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine. Two samples of 3-methylene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine (90 mg, 0.37 mmol) in 0.50 mL of benzene-d_6 with 20 mg of *p*-dioxane as internal standard in 5-mm quartz tubes were degassed, sealed, and irradiated, the first with a Pyrex-filtered and the second with an unfiltered 450-W high-pressure mercury lamp (Hanovia). Extended irradiation (24 h) caused only darkening and slow decomposition to a multitude of minor, unidentified products in both cases.

A sample of 3-methylene-2,2,5,5-tetramethylcyclohexanone-*N*-phenylimine (90 mg, 0.37 mmol) in 0.50 mL of benzene-d_6 containing 60 mg (0.5 mmol, 1 M) of acetophenone was degassed, sealed in a 5-mm quartz tube, and irradiated with a 450-W high-pressure mercury lamp for up to 5 days. Periodic monitoring by NMR showed the only significant change to be photoreduction of the sensitizer.

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Registry No.—**5**, 62509-56-2; *Z*-**6**, 62509-57-3; *E*-**6**, 62509-58-4; **7**, 62509-59-5.

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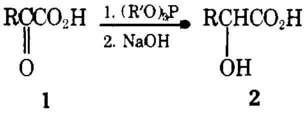
Communications

Selective Reduction of α-Keto Acids to α-Hydroxy Acids by Phosphites

Summary: This paper reports a versatile, selective reduction of α-keto acids to α-hydroxy acids by means of phosphites as reducing agents, which takes place under mild conditions to give products in high yields.

Sir: There are few simple methods for the reduction of α-keto acids to α-hydroxy acids despite their importance in biological as well as organic chemistry.[1,2] We wish to report a versatile, selective reduction method which employs phosphites as reducing agents.

A typical procedure is as follows. In 3 mL of acetonitrile, pyruvic acid (**1a**) (5 mmol) and triethyl phosphite (5 mmol) were dissolved at 0 °C. When the mixture was allowed to warm to room temperature, an exothermic reaction took place. After standing overnight at room temperature, acetonitrile was removed under reduced pressure. The residue was hydrolyzed by stirring with 20 mL of a 2 N NaOH solution at 50 °C for 8 h. Zinc chloride (5 mmol) was added and the mixture was neutralized to precipitate white crystals of the zinc salt. After refrigeration at 0 °C, the salt was filtered, washed two times with cold water, and dried in vacuo to constant weight to give 0.82 g (94%) of $Zn(O_2CCH(OH)CH_3)_2{\cdot}2H_2O$. The salt was identified by comparison of its IR spectrum with that of an authentic sample.[3]

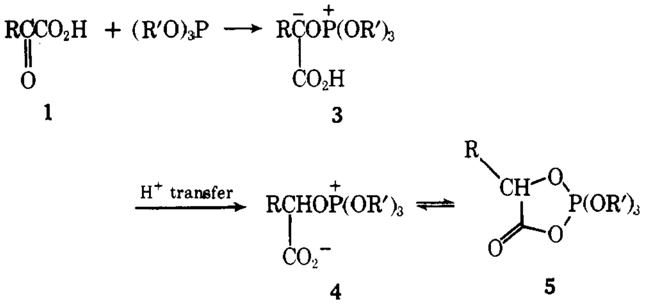


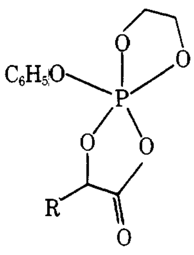
$$\underset{\mathbf{1}}{R\underset{\underset{O}{\|}}{C}CO_2H} \xrightarrow[2.\ NaOH]{1.\ (R'O)_3P} \underset{\mathbf{2}}{R\underset{\underset{OH}{|}}{C}HCO_2H}$$

a, $R = CH_3$; **b,** $R = CH_2CO_2H$; **c,** $R = (CH_2)_2CO_2H$; **d,** $R = C_6H_5$

Similarly, reductions of the other three α-keto acids listed in Table I were carried out by using triethyl phosphite or ethylene phenyl phosphite as reducing agents.

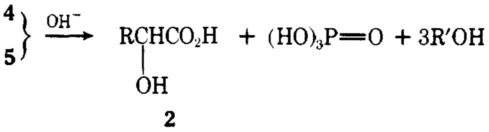
It is known that the phosphorus atom of phosphites reacts with the oxygen atom of carbonyls attached to electron-withdrawing groups.[5] Analogously, reaction of an α-keto acid (**1**) with a phosphite is expected to produce a carbanion (**3**) which rearranges to produce a phosphobetaine **4**. In the case of ethylene phenyl phosphite, the betaine **4** is probably in equilibrium with a pentacovalent phosphorane **5**. Pentacovalent species **6a** and **6b** have actually been isolated.[6] Alkaline hydrolysis of either **4** and/or **5** probably produces the α-hydroxy acids **2**.





6a, $R = CH_3$
b, $R = C_6H_5$

When triethyl phosphite is used, however, the reaction probably proceeds differently after **4** is formed. The betaine species is not stable enough to produce the pentacovalent species **5** ($R' = Et$) but rather undergoes an Arbuzov-type reaction to produce **7**, **8**, and **9**. In the reaction of triethyl phosphite with pyruvic acid ($R = CH_3$), **7** and **9** were formed in 22 and 64% yields, respectively. Alkaline hydrolysis produced lactic acid not only from **7** but also from **8** which must be formed in equimolecular amount with **9**. Previously, Kamai and Kukhtin[7] reported only the isolation of triethyl phosphate **9** with pyruvic acid.



$$\left.\begin{matrix}\mathbf{4}\\ \mathbf{5}\end{matrix}\right\} \xrightarrow{OH^-} \underset{\mathbf{2}}{R\underset{\underset{OH}{|}}{C}HCO_2H} + (HO)_3P{=}O + 3R'OH$$