3β-(Benzoyloxy)-5α-cholest-8(14)-en-7α-ol (7a) prepared above: mp 103 °C, clearing at 120 °C; IR (KBr) 3400, 3060, 3000–2820, 1720, 1600, 1580, 1110, 710 cm^{-1}; ^1H and ^{13}C NMR, Tables III and II; MS, m/z (rel intensity) 506 (2, M^+), 488 (M $-H_2O$, 1), 393 (1), 384 (1), 375 (7), 366 (3), 361 (3), 351 (5), 298 (4), 290 (6), 253 (24), 199 (13), 177 (17), 145 (21), 107 (28), 105 (100), 55 (51), 43 (73); HPLC (methanol, 1.2 mL/min) single peak (detection limit 1%) at 8.7 mL.

Hydrolysis of 7a to 7b. A solution of 26.6 mg (0.05 mmol) of **7a** in 0.9 M KOH in absolute ethanol was stirred at 20 °C for 1 h. Standard workup gave a pale yellow solid (19 mg). The ^1H and ^{13}C NMR spectra (Tables III and II) were identical within experimental error with those reported previously.[13]

3β-(Benzoyloxy)-5β-cholesta-8,14-diene (5b). A diene isomerization reaction was carried out on a 500-g scale as described for **3a**. The filtrate from the first crop of crystals (353.6 g, 71% yield of 92% pure **3a**) was evaporated to 2 L and crystallized at 4 °C, giving a product (40 g) consisting of 94% **5b** and 6% **3a** (^1H NMR analysis). Three recrystallizations from $CHCl_3$–acetone yielded an analytical sample (13.2 g) having no ^1H NMR vinyl impurity peaks (detection limit 0.3%): mp 157.5–158.5 °C; $[\alpha]^{24}_D$ −17.5° (*c* 1.2, $CHCl_3$); IR (KBr) 3040, 3000–2820, 1720, 1600, 1580, 1110, 710 cm^{-1}; UV (EtOH) λ_{max} (ε) 237 (26 000); ^1H and ^{13}C NMR, Tables III and II; MS, m/z (rel intensity) 488 (4, M^+), 366 (4), 351 (10), 312 (2), 253 (5), 238 (37), 105 (100); exact mass calcd for $C_{34}H_{48}O_2$ 488.3654, obsd 488.3646. Anal. Calcd for $C_{34}H_{48}O_2$: C, 83.55; H, 9.90. Found: C, 83.48; H, 10.06.

5β-Cholesta-8,14-dien-3β-ol (5e). To a solution of 2 g (4.1 mmol) of **5b** in 200 mL of absolute EtOH was added 13.2 g (200 mmol) of KOH. The reaction mixture was stirred vigorously at 40 °C for 1 h; after 40 min, the sterol had completely dissolved, and TLC analysis showed disappearance of **5b**. Standard workup conditions afforded 1.7 g of white solid, which was recrystallized from hot acetone (5 mL) to give an analytical sample (1.35 g, 86%): mp 93–94 °C (lit.[12a] mp 75 °C); $[\alpha]^{24}_D$ −53.4° (*c* 1, $CHCl_3$) (lit.[12a] $[\alpha]^{20}_D$ −48°); IR (KBr) 3300, 3060, 3000–2820, 1630, 1030 cm^{-1}; UV (EtOH) λ_{max} (ε) 249 (20 600); ^1H and ^{13}C NMR, Tables III and II; MS, m/z (rel intensity) 384 (100, M^+), 369 (82), 351 (82), 325 (23), 312 (11), 238 (71), 57 (60), 55 (65); exact mass calcd for $C_{27}H_{44}O$ 384.3392, obsd 384.3401; TLC, R_f 0.63 (silica gel, EtOAc/hexanes 1:1) and R_f 0.72 (silica gel/$AgNO_3$, EtOAc/hexanes 1:1); GC (3% OV-17 packed column, 250 °C, TMS derivative) single peak at 16.8 min. Anal. Calcd for $C_{27}H_{44}O$: C, 84.31; H, 11.53. Found: C, 84.16; H, 11.23.

3β-Acetoxy-5β-cholesta-8,14-diene (5f). Acetylation of 1.0 g (2.6 mmol) of **5e** in 9.0 g of dry pyridine and 9.0 g of acetic anhydride at 20 °C for 23 h gave a crude product of 0.87 g (95% pure). Chromatography (silica gel, eluted with toluene/hexane 4:6) followed by recrystallization from acetone gave an analytical sample (0.50 g, 45%): mp 81.5–83 °C (lit.[12a] mp 80–81 °C); $[\alpha]^{24}_D$ −46.5° (*c* 2, $CHCl_3$) (lit.[12a] $[\alpha]^{19}_D$ −49.3° (*c* 1.3, $CHCl_3$)); IR (KBr) 3060, 3000–2820, 1745, 1240, 1120, 800 cm^{-1}; UV (EtOH) λ_{max} (ε) 249 (20 300) (lit.[12a] UV 248 (22 000)); ^1H and ^{13}C NMR, Tables III and II; MS, m/z (rel intensity) 426 (67, M^+), 411 (12), 366 (54), 352 (80), 351 (100), 313 (37), 253 (56), 238 (100), 105 (70), 55 (88); exact mass calcd for $C_{29}H_{46}O_2$ 426.3498, obsd 426.3507; TLC, R_f 0.47 (EtOAc/hexane 1:19) and R_f 0.78 (EtOAc/hexane 1:3); HPLC (2-propanol/methanol 1:4) 3.2 mL (0.3%), 7.6 mL (0.3%), 9.5 mL (99.4%). Anal. Calcd for $C_{29}H_{46}O_2$: C, 81.63; H, 10.87. Found: C, 81.68; H, 10.90.

5α-Cholesta-8,14-dien-3β-ol (5c). The synthesis was carried out as described by Fieser[4d] using 10 g of 7-dehydrocholesterol. A crude product of 5.24 g was obtained and shown by ^{13}C NMR, GC (3% OV-17 packed column), and HPLC to contain 93% **5c**, 5% **5e**, and 2% other compounds. A 99% pure sample was obtained by fractional crystallization from methanol: MS, m/z (rel intensity) 384 (100, M^+), 369 (93), 351 (46), 271 (35), 257 (20), 253 (19), 238 (42), 159 (40); HPLC (methanol, 1.2 mL/min) 7.6 mL (99%), 8.4 mL (1%); GC (3% OV-17, 248 °C) 21.0 min (99%), 19.4 min (1%).

3β-(Benzoyloxy)-5α-cholesta-8,14-diene (5a). A mixture of 0.35 g (0.91 mmol) of **5c**, 2.5 g of pyridine, and 0.55 g (3.9 mmol) of benzoyl chloride was heated at 90 °C for 1 h. To the cooled solution was added 10 mL of water; the precipitated material was filtered, washed (water, saturated Na_2CO_3, acetone), and dried in vacuo, giving 0.39 g (88%) of colorless crystals: mp 146–147 °C (lit.[26] mp 147–148 °C); $[\alpha]^{24}_D$ +2° (*c* 0.5, $CHCl_3$) (lit.[26] $[\alpha]_D$ −6.9° (*c* 0.6, $CHCl_3$)); ^1H and ^{13}C NMR, Tables III and II; MS, m/z (rel intensity) 488 (74, M^+), 473 (6), 375 (10), 366 (9), 351 (100), 253 (14), 239 (24), 105 (50); HPLC (2-propanol/methanol 1:1, 1.1 mL/min) single peak at 7.6 mL (>99%).

3β-Acetoxy-5α-cholesta-8,14-diene (5d). A sample was prepared from 7-dehydrocholesterol using the Fieser procedure.[4d] Repeated recrystallization from ether/methanol to remove **5f** gave a 99% pure sample: mp 101–101.5 °C (lit.[4e] mp 101–102 °C); $[\alpha]^{24}_D$ −26° (*c* 1.5, $CHCl_3$) (lit.[26] $[\alpha]_D$ −22.9° (*c* 0.6, $CHCl_3$)); ^1H and ^{13}C NMR, Tables III and II; MS, m/z (rel intensity) 426 (67, M^+), 411 (21), 366 (8), 351 (100), 313 (18), 253 (15), 238 (32), 159 (20); HPLC (methanol) 14.2 mL (**5f**, 0.5%), 16.3 mL (99%), 18.0 mL (0.5%); GC (3% OV-17, 268 °C) 15.0 min (0.7%, **5f**) 18.6 min (99.3%).

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Registry No. **2**, 1182-06-5; **3a**, 34227-12-8; **3b**, 113349-57-8; **4a**, 57565-84-1; **4b**, 113274-90-1; **5a**, 74524-23-5; **5b**, 113349-58-9; **5c**, 19431-20-0; **5d**, 5226-33-5; **5e**, 113349-59-0; **5f**, 113301-80-7; **6**, 113274-91-2; **7a**, 113274-92-3; **7b**, 69140-06-3.

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Highly Selective Photoinduced Dimerization of Alkyl Pyruvates Catalyzed by Cobaloxime

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Alkyl pyruvates with an electron-withdrawing group, an α-methyl group, and a group that can react with hydridocobaloxime were dimerized selectively to dialkyl 4-hydroxy-4-methyl-2-oxopentanedioates in the presence of a catalytic amount of benzyl(pyridine)cobaloxime under irradiation by a tungsten lamp. Hydridocobaloxime is the active species produced by the reaction of photoactivated benzylcobaloxime and alkyl pyruvate in the initiation step. The hydridocobaloxime induced the dimerization reaction catalytically via the insertion of enol pyruvate into the Co–H bond of the hydridocobaloxime to give an intermediate alkylcobaloxime, which, in the catalytic cycle, reacted with the second alkyl pyruvate.

Currently, considerable interest is directed toward alkylcobaloximes as models for vitamin B_{12}[1] and organocobalt reagents.[2] However, their usefulness as catalysts has been little explored.[3] On irradiation, an alkylcobal-

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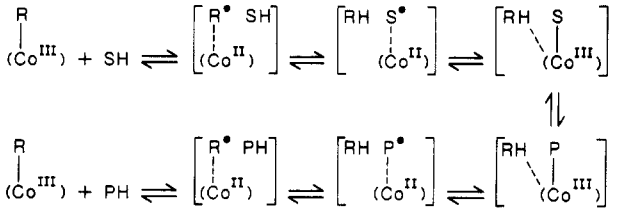
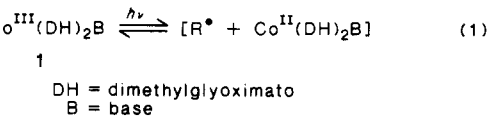
Scheme I[a]



[a] R = adenosyl, (Co) = cobalamin, SH = substrate, PH = product.

oxime is known to undergo homolytic Co–C bond cleavage to generate an alkyl radical and a cobaloxime (eq 1).[4]

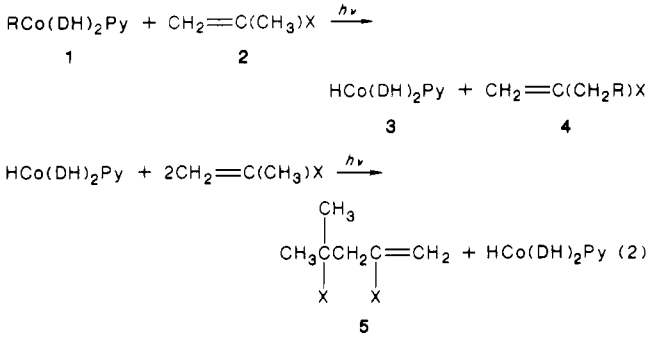


(1)

DH = dimethylglyoximato
B = base

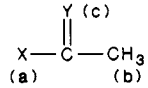
A similar Co–C bond cleavage is believed to occur as the key step in the enzyme-catalyzed rearrangements using adenosylcobalamin as a coenzyme. Generally accepted features[5] of these enzymic rearrangements involve the homolytic cleavage of the Co–C bond of the coenzyme and the abstraction of a hydrogen atom from substrate by the C-5′ methylene radical to give a C-5′ methyl group and a substrate radical. Combination of the Co(II) and the substrate radical generates a new alkylcobalamin involving the substrate as the sixth ligand. Rearrangement of the substrate ligand and reverse transalkylation give the product and the regenerating coenzyme (Scheme I). These features, the rearrangement, the hydrogen atom abstraction reaction, transalkylation of the cobalt, and the catalytic action, with cobalamin or related model complexes are interesting from the viewpoint of synthetic as well as bioorganic chemistry.

We have recently reported[6] the selective photoinduced dimerization of olefins catalyzed by an alkylcobaloxime as shown in eq 2. The reaction proceeded by using olefins



(2)

2 which were characterized by (a) an electron-withdrawing group, X, (b) an α-methyl group, and (c) a group that can react with hydridocobaloxime, Y.



In order to investigate the scope of alkylcobaloxime-catalyzed reactions under irradiation, we examined pyruvates and related compounds as substrates for the dimerization reactions, and more detailed mechanistic interpretations are stated in this article.

Table I. Dimerization of Ethyl Pyruvate Catalyzed by Cobaloxime[a]

run	1/substrate	temp, °C	dimer, %	turnover no.[e]
1	0.002	30	42	21 000
2	0	30	0	
3[b]	0.002	30	0	0
4[c]	0.002	30	0	0
5[c]	0.002	70	17[d]	47 500

[a] Conditions: tungsten lamp (400 W); distance from lamp to reaction vessel, 20 cm; 72 h; under Ar. [b] Presence of *p*-benzoquinone or an aerobic condition. [c] Dark reaction. [d] Other product (82%). [e] Division of conversion by 0.002.

Table II. Photoinduced Dimerization of 2-Keto Acid Derivatives Catalyzed by Cobaloxime[a]

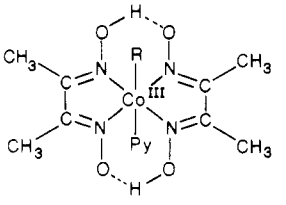
run	substrate	dimer, %	turnover no.[b]
1	methyl pyruvate	35	17 500
2	ethyl pyruvate	42	21 000
3	isopropyl pyruvate	41	20 500
4	*tert*-butyl pyruvate	45	22 500
5	benzyl pyruvate	22	11 000
6	pyruvic acid	0	0
7	ethyl 2-oxobutyrate	0	0

[a] Conditions: benzylcobaloxime 1/substrate = 0.002; tungsten lamp (400 W); 72 h; 30 °C; under Ar. [b] Division of conversion by 0.002.

Results and Discussion

We chose carbonyl compounds possessing the three structural features previously described. Both olefins and carbonyl compounds have been shown to react with hydridocobaloxime to give alkanes and alcohols respectively.[7]

Ethyl pyruvate was irradiated by a tungsten lamp (400 W) in the presence of a catalytic amount of benzyl(pyridine)cobaloxime (1) for 72 h at 30 °C under an argon atmosphere. The product was purified by column chromatography and was identified by ^{1}H NMR, GC–MS, IR, and elemental analysis to be an aldol-type dimer, diethyl 4-hydroxy-4-methyl-2-oxopentanedioate (6). The reaction proceeds selectively as in eq 3 to give dimer 6 in good yield (Table I, run 1).



R = benzyl
Py = pyridine
benzyl(pyridine)cobaloxime (1)

The reaction did not proceed in the absence of alkylcobaloxime 1 (run 2) or in the dark (run 4). Thus, the photoactivated alkylcobaloxime is needed for the reaction. Since *p*-benzoquinone or aerobic conditions inhibited the

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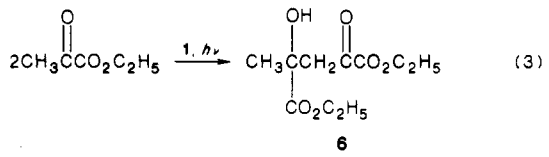


(3)

6

reaction (run 3), the reaction might involve radical steps. In the case of the thermally induced reaction, a considerable amount of byproducts with high molecular weight were obtained (run 5). Alkylcobaloximes are activated by irradiation with visible light or by heating, but the thermally induced reaction is less selective than the photoinduced reaction.

Several alkyl pyruvates gave the corresponding dimers selectively in good yields (Table II, runs 1–5). Various ester groups did not affect the reactivity. Pyruvic acid (run 6) and ethyl 2-oxobutyrate (run 7) gave no dimeric products.

Other carbonyl compounds, benzaldehyde, propanal, acetone, acetylacetone, ethyl acetoacetate, benzil, acetyl chloride, pyruvonitrile, and acetophenone, were recovered unchanged on irradiation under similar conditions[8] as in Table I. In the cases of acetyl chloride and pyruvonitrile, the alkylcobaloxime decomposed during the reaction. An unidentifiable mixture was obtained when biacetyl was used as a substrate.

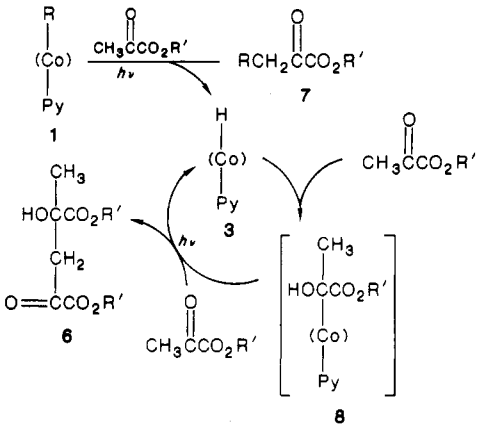
Hydridocobaloxime prepared according to the reported method[9] was used as a catalyst in an ethyl pyruvate dimerization reaction. Dimer (14%), polymeric products (16%), and other products (69%) were obtained. The formation of large amounts of byproducts is due to the presence of hydrogen. These results indicate that hydridocobaloxime is the active catalyst of the dimerization reaction.

Dimer **6** was assumed to be produced via the reaction of the enol form of ethyl pyruvate with the hydridocobaloxime. Methyl 2-acetoxyacrylate, equivalent to the enol pyruvate, has been reported[10] to react with hydridocobaloxime to give an organocobaloxime containing an acetoxy-substituted tertiary α-carbon supporting the above assumption. If the C=O double bond of ethyl pyruvate is inserted into Co–H as in the case of catalytic hydrogenation,[11] the course of the reaction would become a different one.

The dimerization of pyruvates proceeds as in Scheme II analogously with the dimerization of olefins.[6] In the initiation step, alkyl pyruvate reacts with photoactivated benzylcobaloxime to give the α-keto ester **7** and hydridocobaloxime **3**. α-Keto ester **7** is produced only in a small amount, but its formation can be detected by the GC–MS analysis (see Experimental Section). In the catalytic cycle, the dimer **6** is produced by the reaction of alkyl pyruvate and intermediate alkyl cobaloxime **8** made by the insertion of enol pyruvate into the Co–H bond of hydridocobaloxime **3**, which works as the catalyst in the dimerization.

The catalytic effect of metal ions on pyruvate aldolization is well-known,[12] and the effect is interesting with respect to the enzymic action of pyruvate aldolase.[13] However, the present dimerization of alkyl pyruvates

Scheme II. Reaction Pathway of the Dimerization of Alkyl Pyruvate



catalyzed by cobaloxime is quite different from the conventional metal-catalyzed aldolization. The present method offers a useful synthetic method for pyruvate dimers, since this highly selective dimerization can be carried out under mild conditions in high efficiency.

Experimental Section

General Procedures. ^{1}H NMR spectra were measured with Hitachi R-600 and Varian XL-300 NMR spectrometers in $CDCl_3$ with Me_4Si as an internal standard. IR spectra were recorded on a Hitachi 260-10 infrared spectrophotometer. GLC analyses were carried out on a Hitachi 163 gas chromatograph (10% SE-30, stainless steel column, N_2 carrier gas). GC–MS were measured with a JEOL DX-300 mass spectrometer.

Materials. Benzylcobaloxime **1** was prepared by the procedure of Schrauzer.[14] Isopropyl pyruvate, *tert*-butyl pyruvate, and benzyl pyruvate were prepared from pyruvic acid and the corresponding alcohol in the presence of *p*-toluenesulfonic acid as a catalyst by refluxing in benzene with an azeotropic dehydrating apparatus. Other chemicals used in this study were reagent grade.

Dimerization of Alkyl Pyruvates Catalyzed by Photoactivated Benzylcobaloxime. Ethyl pyruvate (5.806 g, 50 mmol) and benzylcobaloxime (0.046 g, 0.1 mmol) were put into a Pyrex Schlenk tube. The mixture was degassed and replaced with an argon gas. The reaction mixture was irradiated with tungsten lamp (400 W) at a distance of 20 cm with stirring for 72 h at 30 °C. The NMR spectra of the reaction mixture showed that ethyl pyruvate converted to another compound. The reaction mixture was purified by silica gel column chromatography with an eluent of $CHCl_3$. The second elution (R_f 0.2) was collected, and the solvent was evaporated to isolate a pure dimer, diethyl 4-hydroxy-4-methyl-2-oxopentanedioate (44%).

Diethyl 4-hydroxy-4-methyl-2-oxopentanedioate: NMR ($CDCl_3$) δ 1.28 (t, 3 H, $CCO_2CH_2CH_3$), 1.37 (t, 3 H, $COCO_2CH_2CH_3$), 1.46 (s, 3 H, CCH_3), 3.36 (s, 2 H, CH_2), 4.25 (q, 2 H, $CCO_2CH_2CH_3$), 4.37 (q, 2 H, $COCO_2CH_2CH_3$); IR (neat) 3500 (OH), 1720 (C=O) cm^{-1}; GC–MS 233 (M + 1). Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.94. Found: C, 51.61; H, 6.97.

The dimer yield from the reaction mixture could be determined (44%) from the ^{1}H NMR peak ratio of the methyl group on ethyl pyruvate (δ 2.45) and the methylene group on the product (δ 3.36). The isolated yields coincided with the NMR yields.

Other substrates were treated with benzylcobaloxime according to the procedure already described.

Dimethyl 4-hydroxy-4-methyl-2-oxopentanedioate: NMR ($CDCl_3$) δ 1.46 (s, 3 H, CCH_3), 3.33 (s, 2 H, CH_2), 3.76 (s, 3 H, CCO_2CH_3), 3.84 (s, 3 H), $COCO_2CH_3$); IR (neat) 3480 (OH), 1715 (C=O) cm^{-1}. Anal. Calcd for $C_8H_{12}O_6$: C, 47.06; H, 5.92. Found: C, 46.04; H, 5.65.

Diisopropyl 4-hydroxy-4-methyl-2-oxopentanedioate: mp 48–49 °C; NMR ($CDCl_3$) δ 1.26 (dd, 6 H, $CCO_2CH(CH_3)_2$), 1.34 (d, 6 H, $COCO_2CH(CH_3)_2$), 1.44 (s, 3 H, CCH_3), 3.32 (s, 2 H, CH_2),

(8) Irradiation by a tungsten lamp (200 W) in the presence of a catalytic amount of benzyl(pyridine)cobaloxime (1) for 72 h at 40 °C under an argon atmosphere.

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4.85–5.35 (m, 2 H, $CCO_2CH(CH_3)_2$, $COCO_2CH(CH_3)_2$); IR (KBr) 3480 (OH), 1710 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.14; H, 7.59.

Dibenzyl 4-hydroxy-4-methyl-2-oxopentanedioate: NMR ($CDCl_3$) δ 1.42 (s, 3 H, CCH_3), 3.31 (s, 2 H, CH_2), 5.11 (s, 2 H, CCO_2CH_2Ph), 5.17 (s, 2 H, $COCO_2CH_2Ph$), 7.24 (s, 5 H, $CCO_2CH_2C_6H_5$), 7.28 (s, 5 H, $COCO_2CH_2C_6H_5$); IR (neat) 3500 (OH), 1730 (C=O) cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.31; H, 5.81.

Di-*tert*-butyl 4-hydroxy-4-methyl-2-oxopentanedioate: NMR ($CDCl_3$) δ 1.40 (s, 3 H, CCH_3), 1.48 (s, 9 H, $CCO_2C(CH_3)_3$), 1.58 (s, 9 H, $COCO_2C(CH_3)_3$, 3.20 (s, 2 H, CH_2); IR (KBr) 3520 (OH), 1740 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.52; H, 8.21.

Photoinduced Dimerization of Ethyl Pyruvate Catalyzed by Hydridocobaloxime 3. $Co(OAc)_2 \cdot 4H_2O$ (49.8 mg, 0.2 mmol) and dimethylglyoxime (46.4 mg, 0.4 mmol) were dissolved in MeOH (2 mL), and the solvent was evaporated after the addition of pyridine (0.016 mL, 0.2 mmol). Ethyl pyruvate (2.2 mL, 20 mmol) was added to the Co(II) complex, and the mixture was degassed by a freeze-thaw-pumping cycle and replaced with hydrogen. The reaction was carried out by irradiation with a tungsten lamp (200 W) at a distance of 10 cm from the reaction vessel at 15 °C for 72 h to give a mixture of dimer (14%), polymeric products (16%), and other products (69%).

Detection of Ethyl 4-Phenyl-2-oxobutanoate (7). Benzyl(pyridine)cobaloxime (1.378 g, 3 mmol), ethyl pyruvate (3.484 g, 30 mmol), and CH_2Cl_2 (30 mL) were added into a Schlenk tube, and the mixture was degassed by a freeze-thaw-pumping cycle and replaced with an argon gas. The reaction was carried out by irradiation with a tungsten lamp (400 W) for 6 days at 35 °C. After the reaction, the solvent was evaporated, and the organic compounds were separated from the reaction mixture by column chromatography (silica gel). The mixture was investigated by GC–MS. The molecular ion peak at m/e 207 (M + 1) of the α-keto ester 7 was found. There are main fragment peaks at m/e 116 ($CH_3CH_2OCOCH_2^+$) and m/e 91 ($PhCH_2^+$).

Registry No. 1, 27860-79-3; 6 (R′ = CH_3), 113548-35-9; 6 (R′ = C_2H_5), 113548-36-0; 6 (R′ = i-C_3H_7), 113548-37-1; 6 (R′ = t-C_4H_9), 113548-38-2; 6 (R′ = $CH_2C_6H_5$), 113548-39-3; 7 (R = $C_6H_5CH_2$, R′ = Cx_2H_5), 64920-29-2; CH_3COCO_2H, 127-17-3; $CH_3COCO_2CH_3$, 600-22-6; $CH_3COCO_2C_2H_5$, 617-35-6; $CH_3COCO_2C_3H_7$-i, 923-11-5; $CH_3COCO_2C_4H_9$-t, 76849-54-2; $CH_3COCO_2CH_2C_6H_5$, 18854-19-8.

Synthesis and NMR Spectral Properties of Phosphines in the 2-Phosphabicyclo[2.2.2]oct-5-ene and 2-Phosphabicyclo[2.2.2]octa-5,7-diene Systems[1]

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1,6-Dihydrophosphorin 1-oxides were synthesized by dehydration of 3-hydroxy-1,2,3,6-tetrahydrophosphorin 1-oxides; Diels–Alder reactions with maleic acid derivatives gave the 2-phosphabicyclo[2.2.2]oct-5-ene ring system, while reaction with dimethyl acetylenedicarboxylate gave the corresponding octa-5,7-diene system. The latter system was also approached by lead tetraacetate oxidation of a dicarboxylic acid in the oct-5-ene system. Removal of the phosphoryl oxygen required very gentle conditions with the dienes to prevent fragmentation. This was accomplished with trichlorosilane at −8 to 0 °C. The dienic phosphines were stable at 0–25 °C but lost the P-containing bridge at 30–50 °C. The ^{31}P NMR shifts of all compounds were normal and resembled monocyclic phosphorin models. This ring structure, either with one or two double bonds, therefore does not cause the strong deshielding so characteristic of the related 7-phosphanorbornene system. To interpret the ^1H and ^{13}C NMR spectra of the dienic phosphines, 2-D techniques were used.

Phosphines with the 7-phosphanorbornene framework were first synthesized in 1980 and immediately became of interest because they displayed unusual spectral and chemical properties. To illustrate, such compounds give the most downfield ^{31}P NMR shifts ever recorded for a tertiary phosphine[2] and tend to form P(V) adducts with various reagents, leading to fragmentation by retrocycloaddition.[3] Even the synthesis of the phosphines is made complicated by the tendency to form P(V) adducts; the phosphines are synthesized by deoxygenation of the corresponding phosphine oxides with silanes, but for success a procedure is required that avoids the possibility of P(V) intermediates. The combination of a highly contracted bond angle at P and forced proximity of P to a double bond appears to be responsible for these and other effects.

It is not known if homologous phosphines, having the 2-phosphabicyclo[2.2.2]octene framework, possess any of these or other special properties; a *P*-(trifluoromethyl)-3,3-difluoro derivative (^{31}P NMR δ +5.8) is the only known[4] phosphine with this ring system, but it is not a good model for NMR considerations. We have devised a procedure that provides less specialized derivatives, and we have synthesized the first phosphines in the 2-phosphabicyclo[2.2.2]octa-2,5-diene series as well. This work, as well as some properties of the new compounds, is reported in this paper.

Our synthetic approach makes use of the unsaturated 3-phosphorinone derivatives that were reported earlier[5] as being easily formed in a two-step sequence from readily

(1) Some of this work was conducted at Duke University. Taken in part from the doctoral dissertation for J.C.K., Duke University, Durham, NC, 1985.

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