A mixture of **9** (0.25 g, 1.1 mmol) and P_2O_5 (0.50 g) in xylene (20 mL) was refluxed for 2 h to give 0.22 g (95%) of **2**, which was identical in all respects with an authentic specimen.

By the same method, **3** was converted into 4-methylpyrene (**5**) in 82% yield, mp 147.5–148.5 °C.

4,5-Dimethylpyrene (**6**) was produced from **4** in 85% yield, mp 215–216 °C.

Beckmann Rearrangement of 4-Hydroxyiminocyclopenta[*def*]phenanthrene (21). A mixture of **21**[5] (1.095 g, 5 mmol, prepared from **20**[1] in 96% yield) and PPA (80%, 30 g) was stirred at 175–180 °C for 5 min to yield 0.62 g (57%) of 4,5-dihydro-4-azapyren-5-one (**17**): mp 348–350 °C (dec); IR 3160 and 1661 cm^{-1}.

Reaction of 4-Oxocyclopenta[*def*]phenanthrene (20) with Hydrogen Peroxide. To a solution of **20** (0.51 g, 2.5 mmol) in HOAc (30 mL) were added dropwise concentrated H_2SO_4 (7 mL) and then H_2O_2 (28%, 2.5 mL). The mixture was stirred at room temperature for 2 h to afford 0.45 g (82%) of 4-oxapyren-5-one (**18**): mp 200.5–201.5 °C; IR 1727 cm^{-1}.

4-Azapyrene (19). Concentrated H_2SO_4 (2 mL) was added to a suspension of NaN_3 (0.57 g, 8.8 mmol) in $CHCl_3$ (5 mL) at −10 °C with stirring for 30 min; then a suspension of 4-hydroxycyclopenta[*def*]-phenanthrene (**22**)[12] (1.03 g, 5 mmol, prepared from **20** in 86% yield) in $CHCl_3$ (50 mL) was added to the first mixture at 25 °C during a period of 20 min. After stirring at room temperature for an additional 1 h, ice (20 g) was added and the resulting mixture was allowed to stand overnight; **19** (0.43 g, 43%), mp 157.5–159.0 °C, was isolated.

Di(4,5-phenanthrylene)-1,2-ethanediol (23). Ketone **20** (2.04 g, 10 mmol) was treated with $TiCl_4$ (3.0 g, 15.8 mmol) and Zn dust (1.96 g, 0.03 g-atom) in THF (140 mL) according to the method described elsewhere[9] to give 1.73 g (84%) of **23:** mp 230.5–232.0 °C (dec); IR 3525 cm^{-1}; NMR (Me_2SO-d_6) δ 3.40 (2 H, s) and 6.25–8.05 (16 H, m).

Pinacol–Pinacolone Rearrangement of 23. A solution of 0.30 g (0.73 mmol) of **23** in 15 mL of HOAc was refluxed for 1 h with a few drops of concentrated H_2SO_4 to yield 0.25 g (87%) of **24:** mp 230.–230.5 °C; IR 1667 cm^{-1}; mass spectrum *m/e* 392 (M^+) and 364.

Retro-pinacol Rearrangement of 4,5-Dihydro-4-oxo-5-(4,5-phenanthrylene)pyrene (24). A solution of 0.45 g (1.1 mmol) of **24** in 45 mL of HOAc was refluxed for 18 h with HI (57%, 1 mL) and red P_4 (1.0 g) to give 0.39 g (91%) of tetrabenzo[*de,hi,mn,qr*]naphthacene (**25**): mp 296–297 °C; mass spectrum *m/e* 376 (M^+) and 202; NMR (C_5D_5N) δ 8.00–8.52 (16 H, m).

4,5-Dihydro-4-hydroxy-5-(4,5-phenanthrylene)pyrene (26). A solution of **24** (0.5 g, 1.3 mmol) in THF (60 mL) was refluxed with $LiAlH_4$ (0.12 g, 3.2 mmol) for 3 h to afford 0.42 g (84%) of **26:** mp 151–152 °C (dec); IR 3570 and 3460 cm^{-1}; NMR (C_6D_6) δ 1.50 (1 H, d, J = 6.3 Hz), 5.08 (1 H, d), and 6.75–7.85 (16 H, m).

Alcohol **26** (0.37 g, 74%) was also isolated by the reaction of **24** (0.5 g, 1.3 mmol) with hydrazine hydrate (90%, 0.2 g, 4 mmol) and KOH (0.1 g, 1.8 mmol) in diethylene glycol (60 mL) at 100–110 °C for 1 h and then at 200–210 °C for additional 3 h.

Wagner–Meerwein Rearrangement of 26. A mixture of **26** (0.25 g, 0.63 mmol), HI (57%, 0.14 mL), and red P_4 (0.07 g) in HOAc (20 mL) was refluxed for 30 min; 0.21 g (88%) of **25** was obtained.

Registry No.—**1**, 203-64-5; **2**, 129-00-0; **3**, 64884-30-6; **4**, 64884-31-7; **5**, 3353-12-6; **6**, 15679-25-1; **7**, 5660-87-7; **8**, 64884-32-8; **9**, 64884-33-9; **10**, 64900-53-4; **11**, 64884-34-0; **12**, 64884-35-1; **13**, 64884-36-2; **14**, 64884-37-3; **15**, **64884-38-4**; **16**, 64884-39-5; **17**, 64884-40-8; **18**, 23702-49-0; **19**, 194-03-6; **20**, 5737-13-3; **21**, 64884-41-9; **22**, 64884-42-0; **23**, 64884-43-1; **24**, 64913-41-3; **25**, 385-13-7; **26**, 64884-44-2; BuBr, 109-65-9; EtOAc, 141-78-6.

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A New Preparative Method for α,β-Unsaturated δ-Lactones from the Reaction of 3-Hydroxy Acids with 1,3,5-Trioxane

Tsutomu Fujita, Shoji Watanabe,* Kyoichi Suga, Ryuichi Yanagi, and Fusao Tsukagoshi

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan 280

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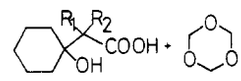
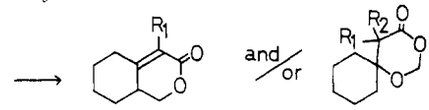
Various methods for the preparation of lactones are well known; for example, saturated lactones are prepared by oxidation of cyclobutanones,[1] reduction of cyclic carboxylic acid anhydrides,[2] cyclization of 4-hydroxy acids,[3] and so on. Synthetic methods for unsaturated lactones[4] and α-methylene lactones[5] are also well known. However, a synthesis of α,β-unsaturated δ-lactones from 3-hydroxy acids has not been known. We now wish to report a synthesis of α,β-unsaturated δ-lactones **2** from the reaction of 3-hydroxy acids **1** with



1

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = C_2H_5$; $R_2 = H$
d, $R_1 = n\text{-}C_3H_7$; $R_2 = H$
e, $R_1 = i\text{-}C_3H_7$; $R_2 = H$
f, $R_1 = n\text{-}C_4H_9$; $R_2 = H$
g, $R_1 = R_2 = CH_3$



2

a, $R_1 = H$
b, $R_1 = CH_3$
c, $R_1 = C_2H_5$
d, $R_1 = n\text{-}C_3H_7$
e, $R_1 = i\text{-}C_3H_7$
f, $R_1 = n\text{-}C_4H_9$

3

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = C_2H_5$; $R_2 = H$
d, $R_1 = n\text{-}C_3H_7$; $R_2 = H$
e, $R_1 = i\text{-}C_3H_7$; $R_2 = H$
f, $R_1 = n\text{-}C_4H_9$; $R_2 = H$
g, $R_1 = R_2 = CH_3$

1,3,5-trioxane or paraformaldehyde. When a mixture of 2-(1′-hydroxycyclohexan-1′-yl)propionic acid (**1b**), 1,3,5-trioxane, and sulfuric acid was refluxed in acetic acid for 0.5

Table I. Reaction of 2-(1′-Hydroxycyclohexan-1′-yl)propionic Acid (1b) with 1,3,5-Trioxane or Paraformaldehyde in the Presence of Acidic Materials[a]

Acidic materials	Yield (%)[b] of **3b**[f]	Yield (%)[b] of **2b**[g]	Yield (%)[b] of **3b**[g]
H_2SO_4	71	88[d]	
	(55)[c]	(80)	*c,e*
H_3PO_4	33	61	
	(33)[c]	(1)	(55)[c]
$ZnCl_2$	19	61	23
	(19)[c]	(5)	(48)[c]
$AlCl_3$	96	97	
	(78)[c]	(52)	(25)[c]
BF_3–ether complex	99	66	
	(59)[c]	(56)	*e*
Polyphosphoric acid	99	50	
	(48)[c]	(51)	*c*

[a] 3-Hydroxy acid **1b** (8.6 g, 50 mmol), 1,3,5-trioxane (2.7 g, 30 mmol), acidic materials (25 mmol), and acetic acid (50 mL) were used. [b] The yield are based on 3-hydroxy acid used. [c] In these cases, paraformaldehyde was used. [d] Reaction time was 0.5 h. [e] Reaction time was 2 h. [f] At 25 °C for 8 h. [g] At 118 °C for 8 h.

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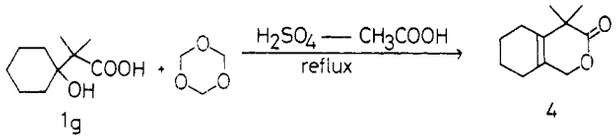
Table II. Reaction of 3-Hydroxy Acids 1 with 1,3,5-Trioxane or Paraformaldehyde in the Presence of 97% Sulfuric Acid[a]

Compd	Registry no.	Temp, °C	Product	Registry no.	Yield,[b,f] (%)	Bp, °C (mm)	IR (film), cm^{-1}, $\nu_{C=O}$	UV (CH_3OH) λ_{max}, nm (ϵ)	^1H NMR spectra (CCl_4 soln), δ (ppm)
1a	14399-63-4	118	**2a**	6051-18-9	59 (20)[c]	115–118 (5)	1695, 1720	223 (10 000)	1.2–2.1 [m, 6 H, $-(CH_2)_3-$], 2.2–2.7 (m, 2 H, $-CH_2C{=}C$), 2.6 (m, 1 H, $-CHC{=}C$), 3.4–4.5 (m, 2 H, $-COOCH_2$), 5.6 (s, 1 H, $-CH{=}C$)
1b	34239-39-9	118	**2b**	64884-47-5	88[d] (80)[c,e]				
1c	512-16-3	118	**2c**	64884-48-6	64 (44)[c]	130–132 (4)	1710	234 (9500)	1.0 (t, J = 7 Hz, 3 H, CH_3CH_2), 1.5–1.9 [m, 6 H, $-(CH_2)_3-$], 2.0 (t, J = 7 Hz, 2 H, $-CH_2{=}C$), 2.3 (q, J = 7 Hz, 2 H, CH_3CH_2), 2.6 (m, 1 H, $-CH{=}C$), 3.6–4.4 (m, 2 H, $-COOCH_2-$)
1d	58888-86-1	118	**2d**	64884-49-7	88 (31)[c]	135–138 (4)	1710	234 (7500)	0.9 (t, J = 6 Hz, 3 H, CH_3CH_2), 1.2–1.8 [m, 8 H, $-(CH_2)_3-$, CH_3CH_2], 2.0 (t, J = 7 Hz, 2 H, $-CH_2C{=}C$), 2.3 (t, J = 6 Hz, 2 H, $CH_3CH_2CH_2$), 2.7 (m, 1 H, $-CHC{=}C$), 3.6–4.4 (m, 2 H, $-COOCH_2-$)
1e	64884-45-3	118	**2e**	64884-50-0	59 (16)[c]	130–134 (4)	1710	232 (7000)	1.0 [d, J = 7 Hz, 6 H, $(CH_3)_2CH$], 1.4–2.1 [m, 8 H, $-(CH_2)_4-$], 2.9 [m, 2 H, $(CH_3)_2CH$, $CHC{=}C$], 3.6–4.3 (m, 2 H, $-COOCH_2-$)
1f	27925-40-2	118	**2f**	64884-51-1	64 (37)[c]	132–136 (3)	1710	235 (6900)	0.95 (t, J = 6 Hz, 3 H, CH_3CH_2), 1.1–1.5 [m, 10 H, $-(CH_2)_3-$, $CH_3CH_2CH_2$)], 2.0 (t, J = 7 Hz, 2 H, $-CH_2C{=}C$), 2.25 (t, J = 7 Hz, 2 H, $-CH_2C{=}C$), 2.8 (m, 1 H, $-CHC{=}C$), 3.6–4.4 (m, 2 H, $-COOCH_2-$)
1a		25	**3a**	64884-52-2	25 (23)[c]	86–88 (6)	1760		1.4–1.8 [m, 10 H, $-(CH_2)_5-$], 2.5 (s, 2 H, $-CH_2COO-$), 5.25 (s, 2 H, $-OCH_2O-$)
1b		25	**3b**	64884-53-3	71 (55)[c]				
1c		25	**3c**	64884-54-4	43 (22)[c]	110–113 (4)	1755		1.0 (t, J = 6 Hz, 3 H, CH_3CH_2), 1.3–1.8 [m, 12 H, $-(CH_2)_5-$, CH_3CH_2], 2.4 (d, J = 9 Hz, 1 H, $-CHCOO-$), 5.35 (q, J_{AB} = 6 Hz, 2 H, $-OCH_2O-$)
1d		25	**3d**	64884-55-5	67 (20)[c]	112–115 (3)	1755		1.0 (t, J = 6 Hz, 3 H, CH_3CH_2), 1.3–1.8 [m, 14 H, $-(CH_2)_5-$, $-(CH_2)_2-$], 2.45 (d, J = 9 Hz, 1 H, $-CHCOO-$), 5.35 (q, J_{AB} = 6 Hz, 2 H, $-OCH_2O-$)
1e		25	**3e**	64884-56-6	60 (36)[c]	110–113 (3)	1745		1.05 and 1.1 (d, J = 6 Hz, 6 H, CH_3CH 2×), 1.4–1.85 [m, 10 H, $-(CH_2)_5-$]. 2.0 (m, 1 H, $(CH_3)_2CH-$), 2.2 (d, J = 9 Hz, 1 H, $-CHCOO-$), 5.3 (q, J_{AB} = 6 Hz, 2 H, $-OCH_2O-$)
1f		25	**3f**	64884-57-7	51 (30)[c]	126–129 (4)	1755		0.95 (t, J = 6 Hz, 3 H, CH_3CH_2), 1.2–1.9 [m, 16 H, $-(CH_2)_5-$, $-(CH_2)_3-$], 2.45 (d, J = 9 Hz, 1 H, $-CHCOO-$), 5.3 (q, J_{AB} = 6 Hz, 2 H, $-OCH_2O-$)
1g	27925-40-2	25	**3g**	64884-58-8	80 (34)[c]	126–128 (3)	1740		1.15 [s, 6 H, $(CH_3)_2$], 1.3–1.8 [m, 10 H, $-(CH_2)_5-$], 5.3 (s, 2 H, $-OCH_2O-$)

[a] 3-Hydroxy acid 1 (50 mmol), 1,3,5-trioxane (30 mmol), 97% sulfuric acid (2.5 g), and acetic acid (50 mmol) were used; reaction time, 8 h. [b] The yields are based on 3-hydroxy acid. [c] Paraformaldehyde was used instead of 1,3,5-trioxane. [d] Reaction time, 0.5 h. [e] Reaction time, 2 h. [f] Satisfactory analytical data (±0.3% for C, H) were reported for all compounds.

h, α,β-unsaturated δ-lactone **2b** was obtained in 88% yield; interestingly, at 25 °C for 8 h only spirolactone **3b** was obtained in 71% yield. The structures of compounds **2b** and **3b** were confirmed by spectral and elemental analyses. The same technique was used for the synthesis of **2b** and **3b** using several acidic materials. The results are listed in Table I. The reaction has also been extended to other 3-hydroxy acids. As shown in Table II, α,β-unsaturated δ-lactones **2** and spirolactones **3** are obtained in good yield. In the case of 2-(1′-hydroxycyclohexan-1′-yl)isobutyric acid (**1g**), β,γ-unsaturated δ-lactone **4** was obtained. These observations indicate that the reaction at lower temperature gives spirolactones **3**, but at higher temperature gives unsaturated δ-lactones **2**, respectively.



1g 4

Experimental Section

The reaction products were analyzed by GLC on a Shimadzu Model GC-3BF chromatograph using a 3 m × 3 mm column of 15% silicone DC 200 on 60–80 mesh Celite 545. NMR spectra were obtained using carbon tetrachloride as a solvent on a Hitachi Model R-24 spectrometer. The chemical-shift values are expressed in δ values (parts per million) relative to a tetramethylsilane internal standard. IR spectra were obtained on a Jasco Model IR-G infrared spectrophotometer. UV spectra were obtained on a Hitachi Model EPS-3T spectrophotometer. Mass spectra were obtained on a Hitachi Model RMU-7M mass spectrometer.

Synthesis of Starting Materials. 3-Hydroxy acids **1** were prepared from carboxylic acids and cyclohexanone as reported previously.[6]

α,β-Unsaturated δ-Lactone 2b. A mixture of 2-(1′-hydroxycyclohexan-1′-yl)propionic acid (**1b**) (8.6 g, 50 mmol), 1,3,5-trioxane (2.7 g, 30 mmol), and 97% sulfuric acid (2.5 g) in 50 mL of acetic acid was refluxed for 0.5 h. To the reaction mixture, 200 mL of water was slowly added. It was then extracted with diisopropyl ether. The organic extract was washed with water and dried over sodium sulfate, the solvent was removed, and the residue was distilled in vacuo to give 7.3 g of **2b** (yield 88%): bp 124–125 °C (4 mm); IR (film) ν_{max} 1710 cm^{-1}; UV (CH_3OH) λ_{max} 232 nm (ϵ 10 000); NMR δ 1.1–1.7 [m, 6 H, $-(CH_2)_3-$], 1.8 (s, 3 H, CH_3C=C), 2.0 (m, 2 H, $-CH_2C$=C), 2.7 (m, 1 H, CHC=C), 3.2–4.4 (m, 2 H, $-COOCH_2-$); MS (*m/e*) M$^+$ 166.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.08; H, 8.50.

Spirolactone 3b. A mixture of 3-hydroxy acid **1b** (8.6 g, 50 mmol), 1,3,5-trioxane (2.7 g, 30 mmol), and 97% sulfuric acid (2.5 g) in 50 mL of acetic acid was stirred for 8 h at 25 °C. Workup in the usual fashion gave 6.5 g of **3b** (yield 71%): bp 117–119 °C (4 mm); IR (film) ν_{max} 1745 cm^{-1}; NMR δ 1.0 (d, J = 6 Hz, CH_3CH), 1.3–2.1 [m, 10 H, $-(CH_2)_5-$], 2.65 (q, J = 6 Hz, 1 H, CH_3CH), 5.3 (q, J = 6 Hz, $-OCH_2O-$); MS (m/e): M$^+$ = 184.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.21; H, 8.80.

β,γ-Unsaturated δ-Lactone 4. A mixture of 3-hydroxy acid **1g** (9.3 g, 50 mmol), 1,3,5-trioxane (2.7 g, 30 mmol), 97% sulfuric acid (2.5 g), and 50 mL of acetic acid was refluxed for 0.5 h. The mixture was treated in the usual way to give 7.5 g of β,γ-unsaturated δ-lactone **4** (yield 83%): bp 118–120 °C (5 mm); IR (film) ν_{max} 1735 cm^{-1}; NMR δ 1.2 [s, 6 H, $(CH_3)_2$], 1.65 (m, 4 H, $-CH_2CH_2-$), 1.9 (m, 4 H, $-CH_2C$=CCH_2-), 4.5 (s, 2 H, $-C$=CCH_2O-); MS (*m/e*) M$^+$ 180.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.19; H, 8.99.

When paraformaldehyde was used instead of 1,3,5-trioxane, 3.0 g of **4** was obtained (yield 33%).

Registry No.—**4**, 64884-59-9; 1,3,5-trioxane, 110-88-3; paraformaldehyde, 30525-89-4.

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Phosphorus Nuclear Magnetic Resonance Spectra of Complexes of Aluminum Chloride with Phosphorus(III) Chlorides: Structure of the Reaction Product from the Phenylphosphonous Dichloride Complex with Tetramethylethylene[1]

Courtland Symmes, Jr., and Louis D. Quin*

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

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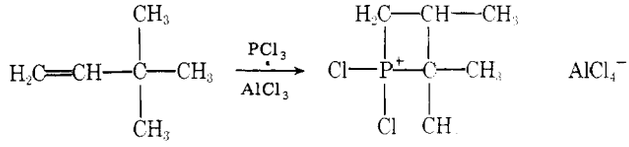
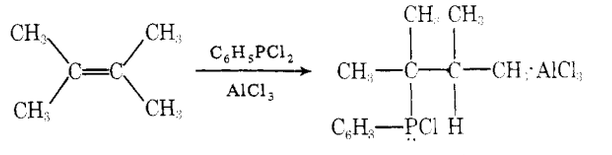
The use of aluminum chloride to activate phosphorus trichloride toward reaction with aromatic compounds dates back nearly one hundred years and has provided a standard method for the preparation of arylphosphonous dichlorides.[2] More recently, carbon–phosphorus bonds have been established by the reaction of olefins and mixtures of $AlCl_3$ and phosphorus(III) halides; the products are diverse and controlled by the structure of the olefin. The best known reaction of this type involves an olefin having a branched carbon attached to the double bond, which leads to the phosphetane system[3,4] via a skeletal rearrangement. A number of olefins have been used



in this process,[3,4] and other phosphorus halides that participate include $C_6H_5PCl_2$,[4] CH_3PCl_2,[4] and PBr_3.[5] Another course is followed with tetramethylethylene[6] and $C_6H_5PCl_2$; the product is noncyclic and alleged to have trivalent phosphorus in a complex with $AlCl_3$ (**1**). A reaction also occurs between



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ethylene and PCl_3[7] or PBr_3[8] in the presence of the corresponding aluminum halide; the products are more complex but depend in part on addition of a PX_2 fragment and halogen to the double bond. Phenylphosphonous dichloride gives the product $C_6H_5P(Cl)CH_2CH_2Cl$ in this reaction.[9] Extension of the reaction to dienes[10,11] has provided novel heterocyclic systems from participation of the second double bond.

In some of the reports on these reactions,[3-6,10,11] it has been assumed that the $AlCl_3$–PCl_3 interaction forms an ionic complex ($Cl_2\ddot{P}^+$ $AlCl_4^-$) and that the cation is the species attacking the olefin. Similar structures are also sometimes assumed to be formed from phosphonous dichlorides. While formation of such ionic complexes seems reasonable, there is actually no experimental evidence in the literature that points to their existence. Indeed, there is evidence to the contrary in the case of PCl_3; it is explicitly stated[12,13] that no complex, ionic or molecular, is formed in detectable amount from $AlCl_3$ and PCl_3, and recent reviews[2,14] of the reaction of such mixtures with aromatics are careful to point out that the attacking

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