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Synthesis of α-Ylidene-γ-butyrolactones Using an α-Phosphono-γ-butyrolactone Carbanion

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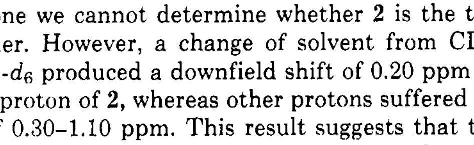
Reactions of an α-phosphono-γ-butyrolactone carbanion with aldehydes, ketones, heterocumulenes, and nitrosobenzene gave α-ylidene-γ-butyrolactones and α-anilino-γ-crotonolactone in good yields.

Phosphono carbanions bearing an electron-withdrawing substituent on the carbon α to the phosphorus function are useful reagents for olefin synthesis.[1] As an extension of this phosphonate olefin synthesis, we have investigated the reactions of an α-(*O,O*-diethylphosphono)-γ-butyrolactone carbanion (**1**)[2] with aldehydes, ketones, heterocumulenes, and nitrosobenzene.

The phosphonate carbanion **1** easily reacted with benzaldehyde to give only α-*trans*-benzylidene-γ-butyrolactone (**2**) in almost quantitative yield, regardless of the reaction temperatures employed. The structure of **2** was determined as follows. The nmr spectrum ($CDCl_3$) of **2** shows β-methylene (d–t, 2 H), γ-methylene (t, 2 H), phenyl (s, 5 H), and olefinic protons (t, 1 H) at δ 3.10, 4.45, 7.30, and 7.40, respectively. Although it is anticipated that the olefinic proton of the trans isomer would be observed downfield from the corresponding proton of the cis isomer, with the above data alone we cannot determine whether **2** is the trans or cis isomer. However, a change of solvent from $CDCl_3$ to benzene-d_6 produced a downfield shift of 0.20 ppm for the olefinic proton of **2**, whereas other protons suffered upfield shifts of 0.30–1.10 ppm. This result suggests that the olefinic proton is situated at the cis position to the carbonyl group.[3] Therefore, the structure was determined to be α-*trans*-benzylidene-γ-butyrolactone.

Reactions of **1** with *p*-nitrobenz-, cinnam-, and trichloroacetaldehyde similarly gave α-*trans*-(*p*-nitrobenzylidene)- (**3**), α-cinnamylidene- (**4**), and α-*trans*-(2,2,2-trichloroethylidene)-γ-butyrolactone (**5**) in 71, 55, and 100% yields, respectively.

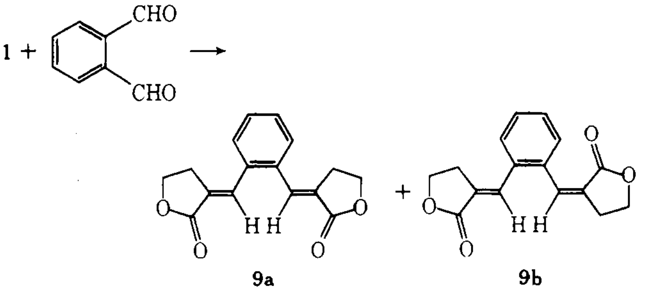


2, R = Ph
3, R = *p*-$NO_2C_6H_4$
4, R = PhCH=CH
5, R = CCl_3
6a, R = *i*-Pr
7a, R = Et
6b, R = *i*-Pr
7b, R = Et

In contrast, the reactions with isobutyr- and propionaldehyde resulted in the formation of the mixtures of the corresponding α-*trans*- (**6a** and **7a**) and α-*cis*- (substituted ylidene)-γ-butyrolactones (**6b** and **7b**), ratios of which were approximately 1:1 and 3:2 by nmr, in good yields. Although separation of individual α-*trans*- (**6a**) and α-*cis*-(isobutylidene)-γ-butyrolactone (**6b**) was unsuccessful, their structural assignments rested upon nmr data and hydrogenation of the mixture over a platinum/carbon catalyst to α-isobutyl-γ-butyrolactone (**8**).

Thus, in the cases using aldehydes containing bulky substituents such as the phenyl, styryl, and trichloromethyl groups, only trans olefins were obtained, but use of aldehydes having rather small substituents such as the isopropyl and ethyl groups yielded mixtures of trans and cis olefins.

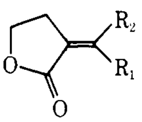
Interestingly, the reaction with *o*-phthalaldehyde gave a mixture of α,α′-bis(*trans,trans-o*-xylidene)- (**9a**, 47%) and α,α′-bis(*cis,trans-o*-xylidene)-γ-butyrolactone (**9b**, 7.3%).

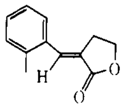
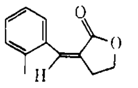
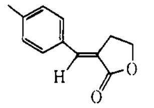
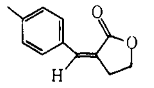


9a **9b**

In the reaction with *p*-phthalaldehyde, α,α′-bis(*trans,trans-p*-xylidene)- (**10a**) and α,α′-bis(*cis,trans-p*-xylidene)-γ-butyrolactone (**10b**) were likewise obtained in 67 and 4.4% yields. No corresponding α,α′-bis(*cis,cis*-xylidene)-γ-butyrolactones could be detected in either reaction. Although the formation of the trans,trans isomers, **9a** and **10a**, in both reactions is in accord with the results ob-

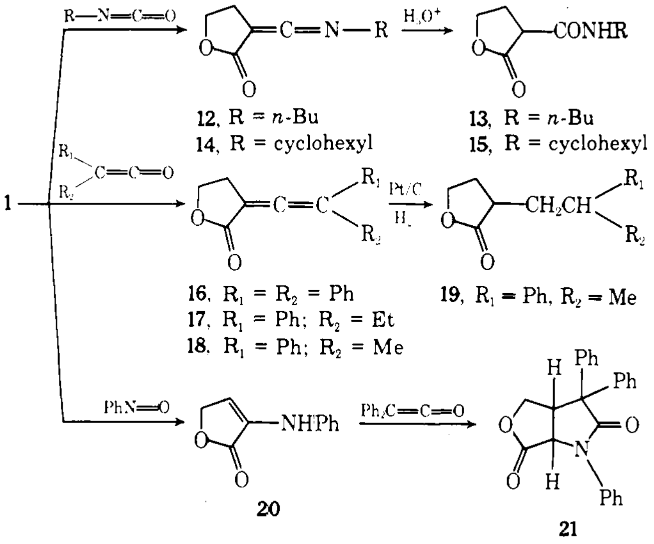
Table I
α-Ylidene-γ-butyrolactones



Compd	Substituents R1	R2	Yield, %	Mp [bp (mm)], °C	Ir (Nujol), cm^{-1} $\nu_{C=C}$	$\nu_{C=C=N}$ or $\nu_{C=C=C}$	Empirical formula[a]
2	H	Ph	100	118.5	1640		$C_{11}H_{10}O_2$
3	H	p-$NO_2C_6H_4$	71	189–190	1640		$C_{11}H_9NO_4$
4	H	PhCH═CH	55	135–136	1630		$C_{13}H_{12}O_2$
5	H	CCl_3	100	76.0	1650		$C_6H_5O_2Cl_3$
6a + **6b**	H or *i*-Pr	*i*-Pr or H	89	[55–57 (0.5)]	1650		$C_8H_{12}O_2$
7a + **7b**	H or Et	Et or H	100	[60 (0.5)]	1670		$C_7H_{10}O_2$
9a	H		47	255–259	1640		$C_{16}H_{14}O_4$
9b	H		7.3	152–153	1645		$C_{16}H_{14}O_4$
10a	H		67	283–284	1640		$C_{16}H_{14}O_4$
10b	H		4.4	208–210	1630		$C_{16}H_{14}O_4$
11	–$(CH_2)_5$–		92	[106 (0.5)]	1670		$C_{10}H_{14}O_2$
12	═N–*n*-Bu		91	[110–115 (0.5)]		2050	$C_9H_{13}NO_2$
14	═N–C_6H_{11}		95			2050	$C_{11}H_{15}NO_2$
16	═CPh_2		100	132–133		1945	$C_{18}H_{14}O_2$
17	═C(Ph)Et		100	60–61		1940	$C_{14}H_{14}O_2$
18	═C(Ph)Me		81	Viscous liquid		1950	$C_{13}H_{12}O_2$

[a] Satisfactory analytical data (±0.4% for C, H, N) were found for all new compounds except for compounds 12, 14, and 18 in the table.

Scheme I



tained above with bulky monoaldehydes, the formation of the cis,trans isomers, **9b** and **10b,** is difficult to explain.

The reaction with cyclohexanone similarly gave α-cyclohexylidene-γ-butyrolactone (**11**) in 92% yield but the reaction with benzophenone afforded no olefin.

Reactions with isocyanates and ketenes under mild conditions yielded ketenimines **12** and **14** and allenes **16, 17,** and **18** in almost quantitative yields (Scheme I). The acid-catalyzed hydrolysis of the ketenimines readily led to α-carbamoyl-γ-butyrolactones **13** and **15.**[6] Hydrogenation of the allene **18** over a platinum/carbon catalyst gave α-(2-phenylpropyl)-γ-butyrolactone (**19**)[6] in quantitative yield.

The reaction with nitrosobenzene gave α-anilino-γ-crotonolactone (**20,** 94%), which was heated together with diphenylketene in a sealed tube to yield 2,3,3a,4,6,6a-hexahydro-2,6-dioxo-1,3,3-triphenyl-1*H*-furo[3,4-*b*]pyrrole (**21,** 35%) as the only isolable product.

These results are summarized in Table I.

Experimental Section[4]

General Procedure. To sodium hydride (50%, 0.50 g, 0.01 mol) in 40 ml of dry benzene was added dropwise α-diethylphosphono-γ-butyrolactone[5] (2.22 g, 0.01 mol) in 10 ml of dry benzene with stirring. After the addition, the solution was stirred at 50–60° for 30 min until gas evolution had ceased. To the resulting yellowish-orange solution were added 0.01 mol of aldehydes (or ketones, heterocumulenes, or nitrosobenzene) in 10 ml of benzene. The reactions were run under dry N_2.

***α-trans*-Benzylidene-γ-butyrolactone (2).** To a benzene solution containing the phosphonate carbanion 1 prepared above was added freshly distilled benzaldehyde (1.06 g, 0.01 mol) in 10 ml of benzene with stirring and then the reaction mixture was refluxed for 2.5 hr. After removal of insoluble sodium diethyl phosphate by filtration, the filtrate was concentrated *in vacuo* to give 3.90 g (100%) of **2**. The crude product **2** was recrystallized from benzene–hexane to afford the pure sample as white needles: nmr (CDCl$_3$) δ 3.10 (d-t, J = 7.5, 3 Hz, 2 H, OCH$_2$CH$_2$–), 4.45 (t, J = 7.5 Hz, 2 H, OCH$_2$CH$_2$–), 7.30 (s, 5 H, phenyl protons), and 7.40 (t, J = 3 Hz, 1 H, olefinic proton); nmr (C$_6$D$_6$) δ 2.00 (d-t, 2 H), 3.80 (t, 2 H), 7.10 (s, 5 H), and 7.60 (t, 1 H); mass spectrum (70 eV) *m/e* 174 (M$^+$), 146 (M$^+$ – CO), and 129 (M$^+$ – CO$_2$ – H).

In the reaction at ambient temperature for 2.5 hr, an only trans isomer **2** was similarly obtained in 98% yield.

Reduction of α-(Isobutylidene)-γ-butyrolactone (6a and 6b). A solution of 1.00 g (7.14 mmol) of a mixture of **6a** and **6b** dissolved in ethanol was shaken in a hydrogen atmosphere over PtO$_2$. After the theoretical amount of hydrogen was consumed (50 hr), the reaction was stopped. The catalyst was removed and the solution was concentrated. The residue was vacuum distilled to give 1.01 g of **α-isobutyl-γ-butyrolactone (8):** bp 56° (0.4 mm); $n^{20}\mathrm{D}$ 1.4446; ir (neat) 1760 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 142 (M$^+$); nmr (CCl$_4$) δ 0.95 (d, J = 6 Hz, 6 H, methyl protons), 1.10–2.50 (m, 6 H, methylene and methine protons), and 4.20 (split t, 2 H, O CH$_2$CH$_2$–).

Anal. Calcd for C$_8$H$_{14}$O$_2$: C, 67.57; H, 9.93. Found: C, 67.45, H, 10.32.

α,α′-Bis(*o*-xylidene)-γ-butyrolactone (9a and 9b). The reaction was carried out using the procedure described above with **1** and *o*-phthalaldehyde. After removal of insoluble sodium diethyl phosphate by filtration while hot, the filtrate was allowed to stand at room temperature overnight. The resulting solid was filtered and recrystallized from a large quantity of ethanol–benzene to give pure **α,α′-bis(*trans,trans-o*-xylidene)-γ-butyrolactone (9a,** 47%): nmr (DMSO-d_6) δ 3.20 (d-t, J = 7.5, 3 Hz, 4 H, OCH$_2$CH$_2$–), 4.40 (t, J = 7.5 Hz, 4 H, OCH$_2$CH$_2$–), 7.55–7.67 (4 H, phenyl protons) and 7.70 (t, J = 3 Hz, 2 H, olefinic proton); mass spectrum (70 eV) *m/e* 270 (M$^+$), 241 (M$^+$ – CO – H), 226 (M$^+$ – 2CO$_2$).

The filtrate was concentrated and the resulting solid was recrystallized from benzene–hexane to afford pure **α,α′-bis(*cis,trans-o*-xylidene)-γ-butyrolactone (9b,** 7.3%): nmr (CDCl$_3$) δ 3.20 (d-t, J = 7.5, 2 Hz, 4 H, OCH$_2$CH$_2$–), 4.40 (t, J = 7.5 Hz, 4 H, OCH$_2$CH$_2$–), 7.20 [t, J = 2 Hz, 1 H, trans H of –HC=C(CO)–], 7.30–7.45 (s, 4 H, phenyl protons), and 7.60 [t, J = 3 Hz, 1 H, cis H of –HC=C(CO)–]; nmr (C$_6$D$_6$) δ 1.90–2.40 (2 d-t, J = 7.5, 3, 2 Hz, 4 H, OCH$_2$CH$_2$–), 3.35–3.70 (2 t, J = 7.5 Hz, 4 H, OCH$_2$CH$_2$–), 6.67 [t, J = 2 Hz, 1 H, trans H of –HC=C(CO)–], 7.12 (d, 4 H, phenyl protons), and 7.80 [t, J = 3 Hz, cis H of –HC=C(CO)–]; mass spectrum (70 eV) *m/e* 270 (M$^+$), 241 (M$^+$ – CO – H), 226 (M$^+$ – CO$_2$), and 182 (M$^+$ – 2CO$_2$).

2,3,4,5-Tetrahydro-2-oxo-3-[(butylimino)methylene]furan (12). To 200 ml of a benzene solution of **1** (0.04 mol), butyl isocyanate (3.96 g, 0.04 mol) in 50 ml of benzene was added at 0° with stirring. Then the reaction temperature was generally raised to 60° and held at that temperature for 1 hr. After similar work-up, distillation of the residue gave 6.10 g (91%) of **12:** bp 110–115° (0.5 mm); nmr (CCl$_4$) δ 0.90–2.00 (m, 7 H, NCH$_2$CH$_2$CH$_2$CH$_3$), 3.00 (t, J = 7.5 Hz, OCH$_2$CH$_2$–), 3.60 (t, J = 6 Hz, NCH$_2$–), and 4.20 (t, J = 7.5 Hz, OCH$_2$CH$_2$–); mass spectrum (70 eV) *m/e* 167 (M$^+$) and 110 (M$^+$ – Bu).

The satisfactory analytical data for **12** were not reported because of its instability.

α-(*n*-Butylcarbamoyl)-γ-butyrolactone (13). A solution of **12** (3.0 g, 0.018 mol) in ethanol (50 ml) containing 0.5 *N* hydrochloric acid (2 ml) was refluxed for 48 hr. After removal of solvent *in vacuo*, the residue was extracted with chloroform, followed by washing with water and drying over sodium sulfate. The chloroform layer gave 3.04 g (92%) of **13**. Recrystallization of crude **13** from benzene–hexane (1:1) afforded the pure sample: mp 49°; ir (Nujol) 3210 (NH), 1770 (lactone C=O), and 1630 cm^{-1} (amide C=O); nmr (CCl$_4$) δ 0.70–1.55 (m, 7 H, NCH$_2$CH$_2$CH$_2$CH$_3$), 2.15–2.80 (m, 2 H, OCH$_2$CH$_2$–), 3.00–3.75 (m, 3 H, methine and NCH$_2$-protons), 4.15–4.50 (split t, 2 H, OCH$_2$CH$_2$–) and 7.40 (t, J = 6 Hz, NH); mass spectrum (70 eV) *m/e* 185 (M$^+$) and 141 (M$^+$ – CO).

Anal. Calcd for C$_9$H$_{15}$NO$_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.05; H, 8.21; N, 7.59.

α-Anilino-γ-crotonolactone (20). To 100 ml of a benzene solution of **1** (0.02 mol) was added nitrosobenzene (2.14 g, 0.02 mol) in benzene (20 ml) at 0° with stirring. Then the solution was stirred at ambient temperature for 2 hr. After similar work-up, **20** was obtained (3.28 g, 94% yield). Recrystallization of crude **20** from benzene–hexane gave the pure sample as white needles: mp 152–153°; ir (Nujol) 3300 (NH), 1745 (C=O), and 1654 cm^{-1} (C=C); nmr (DMSO-d_6) δ 4.95 (d, J = 2 Hz, 2 H, OCH$_2$CH=), 6.70 (t, J = 2 Hz, 1 H, olefinic proton), 6.75–7.30 (m, 5 H, phenyl protons), and 8.20 (broad, 1 H, NH); mass spectrum (70 eV) *m/e* 175 (M$^+$) and 147 (M$^+$ – CO).

Anal. Calcd for C$_{10}$H$_9$NO$_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.21; H, 5.19; N, 8.02.

Reaction of 20 with Diphenylketene. A solution of **20** (0.84 g, 4.8 mmol) and diphenylketene (1.86 g, 9.6 mmol) in 20 ml of dry benzene was heated at 160° for 2.5 hr in a sealed tube. Then the reaction mixture was chromatographed on alumina to give 0.60 g (35%) of **2,3,3a,4,6,6a-hexahydro-2,6-dioxo-1,3,3-triphenyl-1*H*-furo[3,4-*b*]pyrrole (21)** and 0.30 g of unidentified brown, polymeric liquid. Recrystallization of crude **21** from benzene–hexane gave the pure sample: mp 142–143.5°; ir (Nujol) 1780 (lactone C=O) and 1745 cm^{-1} (lactam C=O); nmr (CDCl$_3$) δ 2.00 (t-d, J = 6, 15 Hz, 1 H, methine proton), 2.75 (d-t, J = 15, 10.5 Hz, 1 H, methine proton), 4.30 (d-d, J = 10.5, 6 Hz, 2 H, methylene protons), and 7.30 (broad s, 15 H, phenyl protons); mass spectrum (70 eV) *m/e* 369 (M$^+$), 250 (M$^+$ – PhNCO), 248 (M$^+$ – Ph – CO$_2$), and 194 (Ph$_2$CCO$^+$).

Anal. Calcd for C$_{24}$H$_{19}$NO$_3$: C, 78.03; H, 5.18; N, 3.79. Found: C, 78.03; H, 5.23; N, 3.96.

α-Ylidene-γ-butyrolactones[6] 3–7, 10, 11, 14, 16–18. These derivatives were similarly obtained from **1** and *p*-nitrobenz-, cinnam-, trichloroacet-, isobutyr-, propion- and *p*-phthalaldehydes, cyclohexanone, cyclohexyl isocyanate, and diphenyl-, phenylethyl, and phenylmethylketenes. Yields and some physical data of the products are shown in Table I.

Registry No.—1, 52217-10-4; **2,** 30959-91-2; **3,** 52216-84-9; **4,** 52216-85-0; **5,** 52216-88-3; **6a,** 52216-86-1; **6b,** 52216-87-2; **7a,** 52216-89-4; **7b,** 52216-90-7; **8,** 13888-02-3; **9a,** 52216-91-8; **9b,** 52216-92-9; **10a,** 52216-93-0; **10b,** 52278-84-9; **11,** 21681-63-0; **12,** 52217-13-7; **13,** 52217-14-8; **14,** 52217-15-9; **15,** 52217-16-0; **16,** 52217-17-1; **17,** 52217-18-2; **18,** 52217-19-3; **19,** 52217-20-6; **20,** 52217-21-7; **21,** 52217-22-8; α-diethylphosphono-γ-butyrolactone, 2907-85-9; benzaldehyde, 100-52-7; *o*-phthalaldehyde, 643-79-8; butyl isocyanate, 111-36-4; nitrosobenzene, 586-96-9; diphenylketene, 525-06-4; *p*-nitrobenzaldehyde, 555-16-8; cinnamaldehyde, 104-55-2; trichloroacetaldehyde, 75-87-6; isobutyraldehyde, 78-84-2; propionaldehyde, 123-38-6; *p*-phthalaldehyde, 623-27-8; cyclohexanone, 108-94-1; cyclohexyl isocyanate, 3173-53-3; phenylethylketene, 20452-67-9; phenylmethylketene, 3156-07-8.

Supplementary Material Available. Nmr data of **3–7, 10, 11,** and 14–19 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3236.

References and Notes

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(4) All melting points of products were determined with a Yanagimoto micromelting apparatus and uncorrected. The nmr spectra were obtained on a JEOL LNM 3H-60 spectrometer with tetramethylsilane as an internal standard. The ir spectra were recorded with a Jasco IR-E spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer.

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(6) See paragraph at end of paper regarding supplementary material.