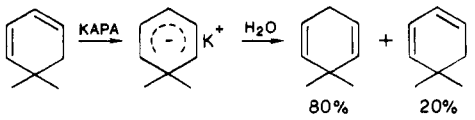
equilibrium distribution,[12] which indicates that only a very small fraction of the diene is present as the carbanionic salt. The result is like the report that in the presence of the macrobicyclic diamino polyether[2.2.2], a cation encapsulating agent,[13] allylic carbanions exhibit increased reactivity toward the solvent, which results in the recovery of some unreacted starting material in addition to the expected reaction products.[14]

Addition of 18-crown-6 seems to have an effect on the apparent acidity of cyclohexadiene. The deep red color of the carbanion is rapidly generated upon addition of the diene to KAPA in DAP; however, the color did not develop in solutions of KAPA/DAP containing an equivalent of 18-crown-6 though the latter solutions were found to convert both triphenylmethane (pK_a = 31.4)[15] and diphenylmethane (pK_a = 33.4)[15] to their colored conjugate bases when the amide solutions were titrated with neopentyl alcohol in xylene (see the Experimental Section). The apparent decrease in acidity may indicate that the crown ether lowers the interaction between the potassiusm cation and the cyclohexadienyl anion more than it affects the interaction between the cation and the amide ion. Such an effect could be due to the ability of the localized charge of the latter to penetrate the molecular framework of the crown ether that surrounds the cation.[16] Olmstead and Bordwell have discussed the effect of added [2.2.2]-cryptand[13] and the anion's structure on ion pair dissocation constants in dimethyl sulfoxide.[17]

The reaction of 5,5-dimethyl-1,3-cyclohexadiene with excess KAPA (0.05 M diene, 0.13 M KAPA) at 25 °C yields a deep red solution. Water-quenched samples contain a mixture of 1,4- and 1,3-dienes in the ratio of nearly 4:1, which indicates that the excess KAPA has deprotonated the diene,[9,10] the reprotonation of the U-shaped pentadienyl carbanion resulting in the formation of the 1,4-diene as the principal isomer.[10] 6,6-Dimethylcyclohexadienyl anion, which has been reported to be stable even at room temperature,[18] was found to undergo protonation preferentially at the central carbon atom by Bates, Gosselink, and Kaczynski.[19] In our experiment, toluene was not detected in the GC analysis, which indicates the absence of aromatization.



Experimental Section

Reagents. 1,3- and 1,4-Cyclohexadienes were purified by distillation from calcium hydride under nitrogen. Cyclooctane was distilled prior to use. 1,3-Diaminopropane (DAP) was distilled from calcium oxide and stored over 3A molecular sieves. 18-Crown-6 was purified by means of its acetonitrile complex,[20] mp 37–38.5 °C. 5,5-Dimethyl-1,3-cyclohexadiene was synthesized according to the literature.[21] *n*-Pentane was distilled from sodium under nitrogen. Neopentyl alcohol was distilled over calcium hydride under nitrogen, and the white crystalline solid (mp 52 °C) was dissolved in dry xylene to titrate the base. Xylene was purified by distillation from sodium benzophenone ketyl and stored over $LiAlH_4$ under nitrogen. Triphenylmethane was recrystallized from absolute ethanol and dried in air.

Reactions of Cyclohexadienes with KAPA. KAPA in DAP was prepared from potassium hydride and DAP in a cylindrical tube (50 mL) fitted with two stopcocks, a connector to permit the attachment of a solids addition tube, and a male ST 24/40 joint, which could be closed with a rubber septum. The transfer to the reaction vessel of 4–5 drops of a 35 wt % potassium hydride suspension in mineral oil (Aldrich Chemical Co.) was done in a dry nitrogen swept glovebag. The reaction tube was then closed with a tight-fitting septum and connected to the source of dry nitrogen and to an automatic gas burette. The mineral oil was removed under a stream of nitrogen by washing with several portions of dry pentane introduced and removed by syringe. The excess pentane was removed in the nitrogen stream. Dry 1,3-diaminopropane (10 mL) was added to the dry powder, and the volume of evolved hydrogen was noted. The concentration of the amide formed was calculated from the volume of gas generated. The solution remaining after the removal of samples for GC analysis was titrated with a solution of neopentyl alcohol in xylene (triphenylmethane indicator) to determine the concentration of strong base present.[2] After equilibrating the base solution at a selected temperature, 1,3- or 1,4-cyclohexadiene was introduced via a gas-tight syringe. Cyclooctane was added as internal standard in amounts half that of the total diene concentration. At selected intervals, 0.30-mL aliquots of the reaction mixture were withdrawn by means of a gas-tight syringe, quenched in 1 mL of ice-cold water, and after extracting with 0.20 mL of *n*-pentane, the organic layer was analyzed by using a Varian Model 940 GC connected to a Laboratory Data Control Model 308 computing integrator. A 25 ft × $^1/_8$ in. column containing 10% Carbowax 750 on 60–80 mesh Chromosorb P was operated at 55 °C with nitrogen as carrier gas.

Experiments Using 18-Crown-6. When desired, 18-crown-6 was added to the KAPA solution before the introduction of the diene by using the solid-addition tube. A solution of KAPA, which was calculated to be 0.103 M from the measurement of the gas evolved in its preparation from potassium hydride and 1,3-diaminopropane, was found to be 0.095 M by titration with neopentyl alcohol in xylene after the addition of 1 equiv of 18-crown-6 ether. This solution converted both triphenylmethane and diphenylmethane to their conjugate bases as judged by the immediate generation of the color of these carbanions. The addition of 1,3-cyclohexadiene to solutions of KAPA generates a deep red color; however, this does not occur in solutions that contain the crown ether.

Registry No. 1, 592-57-4; 2, 628-41-1; 3, 110-83-8; KAPA, 56038-00-7; benzene, 71-43-2; 5,5-dimethyl-1,3-cyclohexadiene, 33482-80-3; 3,3-dimethyl-1,4-cyclohexadiene, 35934-83-9.

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Ph_4SbI-Catalyzed Selective Formation of γ- and δ-Lactones from Oxiranes or Oxetanes with Ketenes

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Five- and six-membered lactones are very common in nature and are important targets in organic synthesis.[1] As

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Table I. Cycloaddition of Oxiranes with Ketenes[a]

run	R^1	R^2	R^3	R^4	solvent	temp, °C	yield, %	ratio 2:3
1	Me	H	Ph	Ph	PhH	40	90	0:100
2	Me	H	Ph	Ph	CH_3CN	40	79	0:100
3	Et	H	Ph	Ph	CH_2Cl_2	40	100	0:100
4[b]	Me	Me	Ph	Ph	CH_3CN	40	65	0:100
5	Ph	H	Ph	Ph	PhH	45	91[g]	100:0
6	Ph	H	Ph	Ph	CH_3CN	45	80[g]	0:100
7	Ph	H	Ph	Ph	HMPA	45	63[g]	0:100
8[c]	Ph	H	Ph	Ph	PhH	45	74[g]	37:63
9[d]	Ph	H	Ph	Ph	PhH	45	29[g]	23:73
10[e]	Ph	H	Ph	Ph	PhH	45	23[g]	0:100
11	Ph	H	Ph	Ph	PhH	0	69[g]	22:78
12	Ph	H	Ph	Et	PhH	80	63	100:0
13	CH_2=CH	H	Ph	Ph	PhH	45	95	100:0
14[f]	CH_2=CH	H	Ph	Ph	CH_3CN	45	85	0:100
15	CH_2=CH	H	Ph	Et	PhH	45	50	100:0
16[f]	CH_2=CH	Me	Ph	Ph	PhH	45	0	
17	CH_2=CH	Me	Ph	Ph	CH_3CN	45	42	0:100

[a] Oxirane/ketene/1 = 3/3/0.3 mmol, solvent 5 mL, 2 h, yields were determined by GLC. [b] 4 h. [c] Catalyzed by Ph_4SbBr. [d] Catalyzed by Ph_4SbCl. [e] Catalyzed by Ph_3SbI_2. [f] 1 h. [g] Yields and selectivities were determined by ^1H NMR.

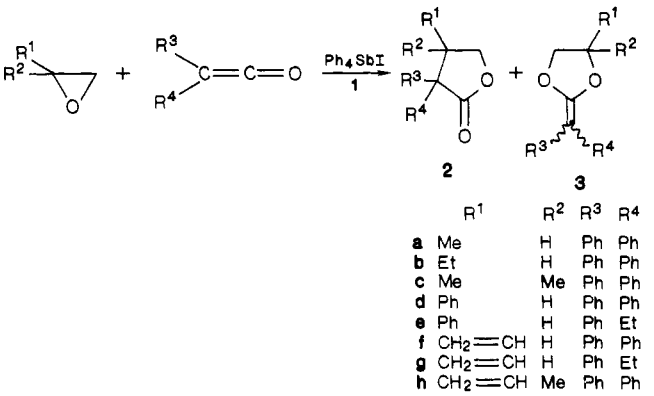
Table II. Cycloaddition of Oxetanes with Ketenes[a]

run	R^1	R^2	R^3	cat.	solvent	temp, °C	time, h	yield, %	ratio 4:5
1	H	Ph	Ph	Ph_4SbI	PhH	45	4	67	100:0
2	H	Ph	Ph	Ph_4SbI	CH_3CN	45	12	50	100:0
3	H	Ph	Ph	Ph_4SbI	CH_2Cl_2	40	8	80	100:0
4	H	Ph	Ph	Ph_4SbBr	PhH	45	24	tr	
5	H	Ph	Ph	Ph_3SbI_2	PhH	45	60	0	
6	H	Ph	Ph	Bu_2SnI_2–HMPA		40	2	24	50:50
7	H	Ph	Ph	LiBr–HMPA[b]		45	2	0	
8	H	Ph	Ph	Bu_4NI	PhH	45	9	tr	
9	H	Ph	Et	Ph_4SbI	CH_2Cl_2	40	18	48	100:0
10	Ph	Ph	Ph	Ph_4SbI	PhH	80	45	91	100[c]:0
11	Ph	Ph	Ph	Ph_4SbI	CH_2Br_2	80	45	81	100[d]:0

[a] Oxetane/ketene/cat. = 3/3/0.3 mmol, solvent 5 mL, yields were determined by GLC. [b] LiBr/HMPA = 0.3/0.6 mmol. [c] Mixture of 4-phenyl derivative **4c–1** and 6-phenyl one **4c–2** (53:47). [d] Only 4-phenyl derivative was obtained.

the cycloaddition of cyclic ethers with heterocumulenes is essentially a fine method for preparing heterocycles in comparison with a condensation reaction because of producing no co-product,[2] it is expected that the cycloaddition of oxiranes or oxetanes with ketenes provides one of the simplest pathways for γ- or δ-lactone formation. However, these types of cycloadditions are scarcely known.[3] Oxetanes, because of their low reactivity in ring opening reactions,[4] are not predicted to react with ketenes. In addition, the cycloaddition of oxiranes with ketenes has been reported to produce isomeric cyclic ketene acetals when conventional catalysts such as lithium halide are used.[5,6] Recently, a Pd(0) catalyst was used in the cycloaddition of vinyloxiranes with heterocumulenes, where π-allyl complexes were key intermediates,[7-9] but lactones were not obtained even in this system.[9] Thus, the selective lactone

Scheme I



	R^1	R^2	R^3	R^4
a	Me	H	Ph	Ph
b	Et	H	Ph	Ph
c	Me	Me	Ph	Ph
d	Ph	H	Ph	Ph
e	Ph	H	Ph	Et
f	CH_2=CH	H	Ph	Ph
g	CH_2=CH	H	Ph	Et
h	CH_2=CH	Me	Ph	Ph

formation seems to be very difficult in the reaction of cyclic ethers with ordinary ketenes such as diphenylketene and phenylethylketene. On the other hand, we have already revealed that Ph_4SbI (1) was a unique catalyst, promoting both the α-cleavage cycloaddition of oxiranes and the cycloaddition of oxetanes.[10] Now, we report the first examples of the lactone formation from the cycloaddition of oxiranes or oxetanes with diphenyl- or phenylethylketene

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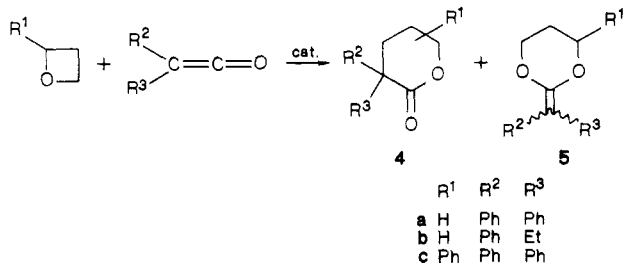
Scheme II



in the presence of a catalytic amount of **1**.

First, we examined the cycloaddition of oxiranes with ketenes (Scheme I). The results are summarized in Table I. Although alkyl-substituted oxiranes gave only cyclic ketene acetals **3**, oxiranes bearing phenyl or vinyl groups reacted with diphenylketene and phenylethylketene to produce the corresponding γ-lactones **2** exclusively in good yields (runs 5, 12, 13, and 15).[11] Noteworthy is the fact that 4-substituted lactones **2** were exclusively obtained without the formation of 5-substituted ones, indicating that the selective α-cleavage of oxiranes occurs. The choice of solvent was critical in this cycloaddition. Benzene solvent gave lactones selectively, whereas when CH_3CN or HMPA were used, no lactone was produced (runs 5–7). Meanwhile, it is interesting that 2-methyl-2-vinyloxirane gave no cycloadduct in benzene (run 16), whereas in the case using CH_3CN as solvent the ketene acetal **3** was obtained in a moderate yield (run 17). Temperature control was also important; the desired lactone was obtained cleanly at 40 °C, but the considerable amount of **3** was accompanied with **2** at 0 °C (runs 5 and 11). Other antimony halide catalysts such as Ph_4SbBr and Ph_4SbCl had no ability to selectively form **2** (runs 8 and 9).

In general, oxetanes have not been extensively used in organic synthesis because of their poor reactivity. Only one patent[12] to our knowledge was reported on the cycloaddition of oxetanes with carbodiimides besides ours.[10b,d,e] In fact, addition of diphenylketene to oxetanes was not promoted by a reported talent catalyst, LiBr–HMPA, for the reaction of oxiranes (Table II, run 7).[13] On the contrary, Ph_4SbI catalyst gave δ-lactones **4** (Scheme II) exclusively as shown in Table II. Neither phenyl or vinyl substituents nor benzene solvent was essential for selective generation of δ-lactones different from those formed in the case of oxiranes. However, **1** was still the indispensable catalyst. Other antimony halides, organotin halide–Lewis base systems such as n-Bu_2SnI_2–HMPA,[14] and conventional catalysts such as n-Bu_4NI[15] had little activity (runs 4–8). In addition, the regioselective fission (substituted site fission) of 2-phenyloxetane was achieved when dibromomethane was employed as solvent (run 11), a solvent most suitable for the α-cleavage cycloaddition of oxiranes as recently reported.[10c]

A plausible reaction mechanism of the cycloaddition of oxiranes is illustrated in Figure 1. As reported in our previous papers,[10c] the catalyst **1** promotes the cycloaddition via α-cleavage of oxiranes with heterocumulenes, and only 4-substituted γ-lactones were obtained in this

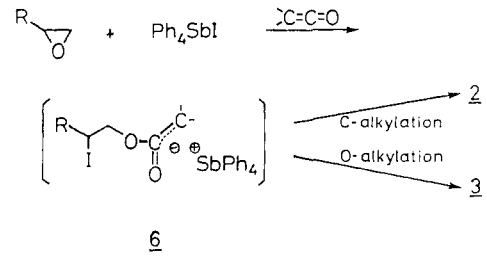


Figure 1.

reaction with ketenes. At first, an oxirane is cleaved at α-position, and then the addition of a ketene is followed by the formation of intermediate **6**.[16] When R^1 is a phenyl or vinyl group, the resulting **6** has an extremely soft alkyl halide (benzyl iodide or allyl iodide) moiety[17] and the antimony enolate attacks at the C-site, giving cycloadduct **2**. In other cases nucleophilic substitution at the more reactive and harder O-site occurs preferentially to yield **3** exclusively.[18] When CH_3CN or HMPA is employed as solvent, the alkyl halide moiety is solvated extensively to be harder and the antimony enolate is also polarized by the solvent to be harder, so selective O-alkylation takes place.[19] As either Ph_4SbBr or Ph_4SbCl forms a harder alkyl halide in the intermediate **6**, ketene acetals **3** were obtained preferentially to lactones **2**.[20] In the reaction of 2-methyl-2-vinyloxirane, the corresponding γ-lactone was not produced perhaps because of its steric hindrance. Although the palladium–π-allyl complex is thought to be a very soft electrophile,[17,21] vinyloxiranes gave no lactone by Pd(0).[9] The use of other metal halide catalysts such as LiCl[5] and Sn–base complexes[6] also did not produce γ-lactones. In conclusion, both the antimony iodide and the substituents such as phenyl and vinyl groups in oxiranes are required to produce γ-lactones from oxiranes with diphenylketene or phenylethylketene.

On the other hand, in the case of oxetanes, the lactone formation was achieved irrespective of the substituents. Even the Sn–base complex, a catalyst for the selective formation of **3** in the reaction of oxiranes gave a considerable amount of δ-lactones **4** (Table II, run 6). In addition, as previously reported, **4** was exclusively obtained by the reaction of diphenylketene and tributyltin γ-bromopropoxide in the absence of base, which was thought to be equivalent to the adduct of oxetane and tributyltin bromide.[6] Thus, δ-lactones **4** seem to be formed more readily than cyclic ketene acetals **5** in constract to the case of oxiranes, although a reasonable mechanism cannot be proposed here. Finally, as well as the case of oxiranes, **1** was the best catalyst in forming δ-lactones from oxetanes with ketenes.

Experimental Section

Melting points were obtained by using a Yanaco micromelting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260-30 spectrometer using KBr pellets or KRS-5 cells. Mass spectra were obtained on a Hatachi RUM-6 spectrometer

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operating at 70 eV. ^1H NMR and ^{13}C NMR spectra were run on a Hitachi R-90H spectrometer. Analytical GLC was performed on a Shimadzu GC-8A chromatograph with an FID (OV-1) column. Elemental analyses were performed by the section on elemental analysis in our department.

Methyloxirane, ethyloxirane, 2,2-dimethyloxirane, and phenyloxirane were purchased and freshly distilled from CaH_2. Diphenylketene, phenylethylketene,[22] oxetane,[23] 2-phenyloxetane,[24] Ph_4SbI, Ph_4SbBr, Ph_4SbCl,[25] and Ph_3SbI_2[26] were prepared according to published procedures. Vinyloxirane was obtained from the reaction of NaOH with 1-bromo-3-buten-2-ol,[27] which was prepared from butadiene by a reported procedure.[28] 2-Methyl-2-vinyloxirane was obtained in a similar manner to that of vinyloxirane.

General Procedure. To a solution of the oxirane or oxetane (3 mmol) and Ph_4SbI (1) (0.17 g, 0.3 mmol) in dry benzene (5 mL) was added the ketene (3 mmol) with stirring under dry nitrogen. The resulting mixture was heated at 45 °C. The end of reaction was monitored by the disappearance of the infrared absorption band due to ketene (2100 cm^{-1}). Yields of products were monitored by GLC or ^1H NMR (internal standard was 1,1,2,2-tetrachloroethane). Isolation of **2** and **4** was carried out in the following manner: The solvent was removed under reduced pressure, and the residue was chromatographed over silica gel (benzene), yielding nearly pure product. Recrystallization using benzene/hexane or distillation gave a pure product. Products **3** and **5** were isolated as already reported.[6]

3,3,4-Triphenyloxolan-2-one (2d): mp 114–115 °C; IR (KBr) 1760 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 4.40–4.80 (m, 3 H), 6.60–7.75 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 50.66 (d), 62.12 (s), 69.81 (t), 127.03 (d), 127.52 (d), 127.74 (d), 128.28 (d), 128.41 (d), 128.56 (d), 128.89 (d), 129.20 (d), 129.54 (d), 136.55 (s), 139.75 (s), 139.99 (s), 177.22 (s). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.73; H, 5.70.

3-Ethyl-3,4-diphenyloxolan-2-one (2e): mp 63 °C; IR (KBr) 1770 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.70 (t, 3 H, J = 7.0 Hz), 1.40–1.90 (m, 2 H), 3.86 (t, 1 H, J = 5.8 Hz), 4.20–4.75 (m, 2 H), 6.60–7.70 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 8.15 (q), 25.60 (t), 53.52 (d), 55.84 (s), 69.62 (t), 126.85 (d), 127.07 (d), 127.49 (d), 127.77 (d), 128.04 (d), 128.41 (d), 136.64 (s), 138.56 (s), 178.17 (s). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.95, H, 6.80.

3,3-Diphenyl-4-vinyloxolan-2-one (2f): mp 148 °C; IR (KBr) 1770 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.85–4.20 (m, 2 H), 4.25–4.50 (m, 1 H), 5.00–5.45 (m, 3 H), 6.85–7.70 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 48.55 (d), 59.65 (s), 68.31 (t), 119.56 (t), 125.63 (d), 125.91 (d), 127.52 (d), 128.22 (d), 128.89 (d), 133.01 (d), 138.19 (s), 140.08 (s), 177.31 (s). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.80; H 6.10. Found: C, 81.74; H, 6.06.

3-Ethyl-3-phenyl-4-vinyloxolan-2-one (2g): bp 63 °C (0.01 mmHg); IR (neat) 1770 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.65–1.20 (m, 3 H), 1.80–2.20 (m, 2 H), 3.15–3.50 (m, 1 H), 3.95–4.50 (m, 2 H), 5.05–5.45 (m, 2 H), 5.70–6.15 (m, 1 H), 7.05–7.65 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 8.55 (q), 25.69 (t), 51.85 (d), 54.71 (s), 69.07 (t), 119.44 (t), 126.82 (d), 127.71 (d), 128.59 (d), 132.61 (d), 138.93 (s), 178.26 (s). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.99; H, 7.27.

3,3-Diphenyloxan-2-one (4a):[6] mp 116 °C; IR (KBr) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.88 (m, 2 H), 2.62 (t, 2 H, J = 7.5 Hz), 4.22 (t, 2 H, J = 7.5 Hz), 7.22 (m, 10 H).

3-Ethyl-3-phenyloxan-2-one (4b): bp 77 °C (0.01 mmHg); IR (neat) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 8.5 Hz), 1.70–2.20 (m, 6 H), 3.70–4.40 (m, 2 H), 7.15–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.00 (q), 19.62 (t), 27.79 (t), 34.30 (t), 51.86 (s), 67.71 (t), 126.17 (d), 128.82 (d), 140.76 (s), 174.81 (s). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.00; H, 7.92.

3,3,4-Triphenyloxan-2-one (4c-1): mp 161 °C; IR (KBr) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.39 (dd, 2 H, J = 10.5 and 15.5 Hz), 3.92–4.55 (m, 3 H), 6.40–7.85 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 27.88 (t), 46.63 (d), 61.97 (s), 66.45 (t), 126.33 (d), 126.79 (d), 127.64 (d), 128.16 (d), 129.02 (d), 130.30 (d), 140.21 (s), 140.91 (s), 141.88 (s), 172.59 (s). Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.08; H, 6.16.

3,3,6-Triphenyloxan-2-one (4c-2): mp 162 °C; IR (KBr) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.51–1.55 (m, 2 H), 2.69–2.93 (m, 2 H), 5.40 (dd, 1 H, J = 6.5 and 11.0 Hz), 7.19–7.50 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 28.49 (t), 32.79 (t), 57.37 (s), 82.06 (d), 125.78 (d), 127.28 (d), 127.43 (d), 128.35 (d), 128.47 (d), 140.08 (s), 142.28 (s), 142.68 (s), 171.96 (s). Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.42; H, 6.21.

2-(Diphenylmethylene)-4-methyl-1,3-dioxolane (3a):[6] mp 88–89 °C; IR (KBr) 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.42 (d, 3 H, J = 7.5 Hz), 3.82 (t, 1 H, J = 6.0 Hz), 4.38 (dd, 1 H, J = 6.0 Hz), 4.70 (m, 1 H), 7.00–7.40 (m, 10 H).

2-(Diphenylmethylene)-4-ethyl-1,3-dioxolane (3b):[6] mp 57–58 °C; IR (KBr) 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.5 Hz), 1.50–1.90 (m, 2 H), 3.90 (t, 1 H, J = 6.5 Hz), 4.30 (t, 1 H, J = 6.5 Hz), 4.30–4.60 (m, 1 H), 7.00–7.40 (m, 10 H).

2-(Diphenylmethylene)-3,3-dimethyl-1,3-dioxolane (3c):[6] mp 98–100 °C; IR (KBr) 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.15 (s, 3 H), 1.45 (s, 3 H), 4.00 (d, 2 H, J = 5.5 Hz), 7.00–7.40 (m, 10 H).

2-(Diphenylmethylene)-3-phenyl-1,3-dioxolane (3d):[6] bp 132 °C (0.01 mmHg); IR (KBr) 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 4.10 (t, 1 H, J = 7.5 Hz), 4.60 (t, 1 H, J = 7.5 Hz), 5.50 (t, 1 H, J = 7.5 Hz), 7.00–7.40 (m, 15 H).

2-(Diphenylmethylene)-1,3-dioxane (5a):[6] mp 80–81 °C; IR (KBr) 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.95–2.25 (m, 2 H), 4.15 (t, 4 H, J = 6.5 Hz), 7.10–7.40 (m, 10 H).

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Registry No. **1**, 13903-91-8; **2d**, 117040-43-4; **2e**, 117040-44-5; **2f**, 117040-45-6; **2g**, 117040-46-7; **3a**, 109911-27-5; **3b**, 109911-28-6; **3c**, 109911-29-7; **3d**, 95025-62-0; **3f**, 117040-47-8; **3h**, 117040-50-3; **4a**, 68319-09-5; **4b**, 68319-11-9; **4c-1**, 117040-48-9; **4c-2**, 117040-49-0; **5a**, 94029-61-5; HMPA, 680-31-9; Ph_4SbBr, 21450-52-2; Ph_4SbCl, 19638-17-6; Ph_3SbI_2, 1538-60-9; Bu_2SnI_2, 2865-19-2; $BrCH_2CH(OH)CH{=}CH_2$, 64341-49-7; $Ph_2C{=}C{=}O$, 525-06-4; $PhEtC{=}C{=}O$, 20452-67-9; 2-methyloxirane, 75-56-9; 2-ethyloxirane, 106-88-7; 2,2-dimethyloxirane, 558-30-5; 2-phenyloxirane, 96-09-3; 2-vinyloxirane, 930-22-3; 2-methyl-2-vinyloxirane, 1838-94-4; oxetane, 503-30-0; 2-phenyloxetane, 4436-23-1.

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On the Condensation of 2,4-Dioxocarboxylates (β-Acylpyruvates) with Urea. An Example of the Utility of Selective Heteronuclear $^{13}C(^1H)$ NOE Difference Spectroscopy in Structure Elucidation†

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In the course of exploring the chemistry of 2,4-dioxocarboxylic esters[1] (β-acylpyruvates, $ROC(O)C(O)CH_2C(O)R'$, **1**), we investigated some condensation reactions with two- and three-atom units to form heterocycles. The utility

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