furan at −70° gave a mixture of substances separable by thin-layer chromatography. Acetylation of the slower moving diol in excess acetic anhydride containing sodium acetate at room temperature yielded a monoacetate (60%), mp 182–185°, whose ir ($CHCl_3$) and mass spectra were indistinguishable from those of natural vindorosine (**1**). Identity was confirmed by thin-layer chromatography using two different solvent combinations.

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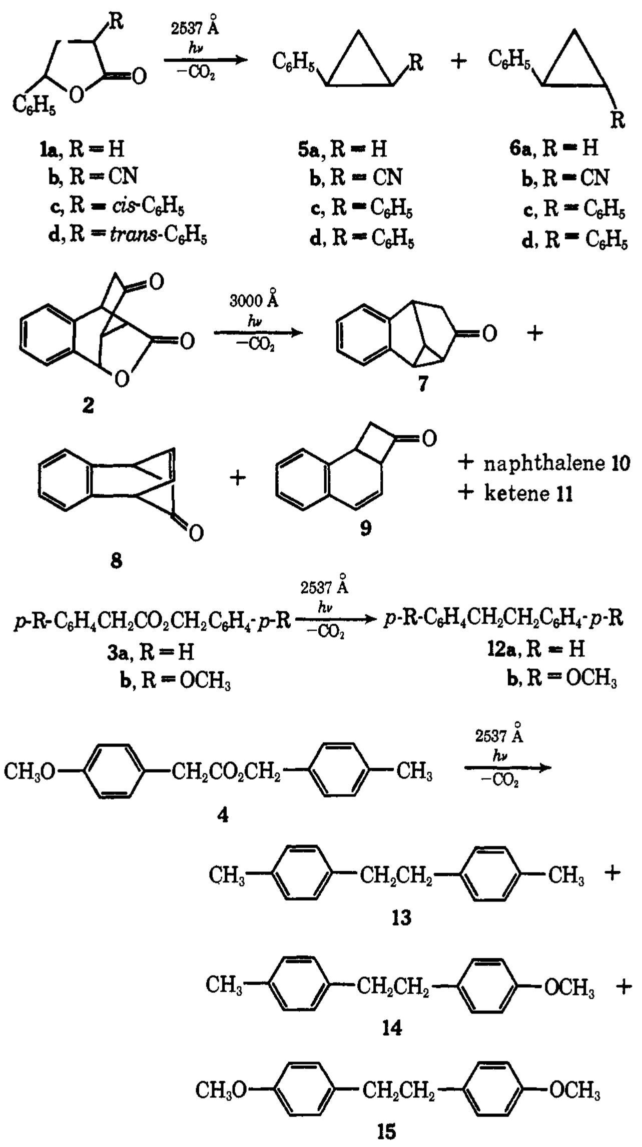
Photodecarboxylation of Benzyl Esters[1,2]

Sir:

Recent reports[3–6] on the photoelimination of carbon dioxide from lactones and esters have prompted us to report our results that carbon dioxide extrusion is a general photochemical process for γ-phenyl-γ-butyrolactones (*e.g.*, **1** and **2**, Scheme I) and for their acyclic analogs (*e.g.*, benzyl esters **3** and **4**). In previous communications,[7,8] we reported an efficient photodecarboxylation of lactone **2**. Although efficient loss of carbon dioxide has been observed for a dihydrosantonin[3] and for simple γ-butyrolactones in the vapor phase,[4] carbon dioxide loss is ordinarily a minor pathway in the solution photochemistry of lactones[5] and esters.[6]

The model compounds chosen for study are shown in Scheme I.[9] Qualitative and quantitative results of photolysis of the model compounds are shown in Table I and Scheme I.[10] For all γ-phenyl-γ-butyrolactones studied, the efficiency of carbon dioxide loss is good, with Φ_{dis} = 0.03–0.18. However, in contrast to γ-phenyl-γ-butyrolactone (**1a**) (Φ_{CO_2} = 0.020), the α- and β-phenyl isomers decarboxylate very inefficiently ($\Phi_{CO_2} \leq 0.001$) indicating that efficient carbon dioxide loss requires phenyl substitution at the γ position.

Scheme I. Products from Photolysis of Benzyl Esters



A priori either stepwise or unsymmetrical concerted mechanisms for the transformation are possible. To study the mechanistic pathway further, the *cis*- and *trans*-α,γ-diphenyl-γ-butyrolactones (**1c** and **d**) were prepared and photolyzed. The results are clearly inconsistent with a completely concerted loss of carbon dioxide with cyclopropane formation, since the zero-time quantum yields for appearance of *cis*- and *trans*-

Table I. Quantum Yields[a] for Photolysis of Esters

Ester	λ, Å	Φ_{dis}[b,c]	Φ_{CO_2}[c,d]	% yield[e]
1a	2537	0.026	0.020	
1b	2537	0.092	0.100	77
1c	2537	0.045	0.026	51
1d	2537	0.051	0.027	51
2	3000	0.18	0.15	38
3a	2537	0.033	0.031	57
3b	2537	0.25	0.19	

[a] Direct irradiation, dioxane solvent. [b] Obtained by quantitative vpc. [c] Quantum yields at 20–30% conversion. [d] Trapped with tared Ascarite–Anhydrone scrubber. [e] Yield of radical coupling products based on the disappearance of ester at *ca.* 50% conversion.

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(2) Presented in part at the Midwest Regional Meeting of the American Chemical Society, Lincoln, Neb., 1970.

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(10) Products **5–8**, **10**, and **12–15** were identified by comparison of spectral and physical properties with known samples; **9** was identified by analysis of the nmr, ir, and mass spectra, by nmr double irradiation studies, and by elemental analysis. Ketene **11** was trapped as ethyl acetate (R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, in press).

1,2-diphenylcyclopropane[11] show that both are primary products of each lactone. Solvent effects[12] on the composition of the zero-time mixtures are consistent with a discrete intermediate 1,3 diradical, since these are similar to the solvent effect on the photostationary state of 1,2-diphenylcyclopropane. In addition, photolysis of *p*-methylbenzyl *p*-methoxyphenylacetate (**4**) affords a nearly statistical mixture of the three possible bibenzyls, again indicative of discrete radical intermediates. These results are consistent with the radical cleavage products found in the photolysis of *p*-methoxybenzyl acetate by Zimmerman and Sandel.[13]

Our results suggest that the triplet excited state is responsible for the reaction, since the photolysis of **2** could be quenched by 1,3-cyclohexadiene with appearance of the characteristic photodimers resulting from triplet sensitization of 1,3-cyclohexadiene.[14] Although the photolysis of **2** can be sensitized quite efficiently with triplet sensitizers such as acetone or acetophenone, lactones **1a–d** show sensitization quantum yields an order of magnitude smaller than those for direct irradiation. The observed reaction in these runs does result from sensitization, however, since uv spectra indicate $\geq 98\%$ light absorption by the sensitizers.

Thus, photodecarboxylation has been shown to be a general process for benzyl esters (including γ-phenyl-γ-butyrolactones), occurring from the triplet state *via* discrete radical intermediates. We are currently extending our studies on the scope of this process.

(11) For the *trans*-lactone, $\Phi_{\mathrm{cis,lim}} = 0.022$ and $\Phi_{\mathrm{trans,lim}} = 0.037$; *cis*-lactone, $\Phi_{\mathrm{cis,lim}} = 0.040$ and $\Phi_{\mathrm{trans,lim}} = 0.044$ (acetonitrile solvent). These values were obtained by extrapolating several runs to zero time.

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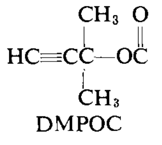
A New Amino Blocking Group Removable from Sulfur-Containing Peptides by Catalytic Hydrogenolysis

Sir:

Hydrogenolysis of tertiary acetylenic alcohols has been observed with partially poisoned catalysts, *e.g.*, Lindlar catalyst.[1] This led us to believe that hydrogenolysis of tertiary acetylenic urethanes of sulfur-containing peptides might also proceed and that these derivatives could therefore be useful nitrogen-blocking groups during peptide synthesis.

Tertiary acetylenic urethanes of several amino acids were prepared and converted to peptides in order to study their hydrogenolysis. The simplest acetylenic urethane, namely, the 1,1-dimethyl-2-propynyloxycarbonyl (DMPOC), was chosen for investigation.



$$\mathrm{HC{\equiv}C\text{–}C(CH_3)_2\text{–}OC(=O)}$$

DMPOC

Amino acids were converted to the DMPOC derivatives, I and II, *via* the 2,4,5-trichlorophenylcarbonate procedure employed by Morley[2] for introducing the *tert*-butyloxycarbonyl (BOC) group. Alternatively, the DMPOC group could be introduced by the chloroformate procedure. Isolation as the *N,N*-dicyclohexylammonium (DCHA) salts was necessary to obtain crystalline derivatives (Table I).

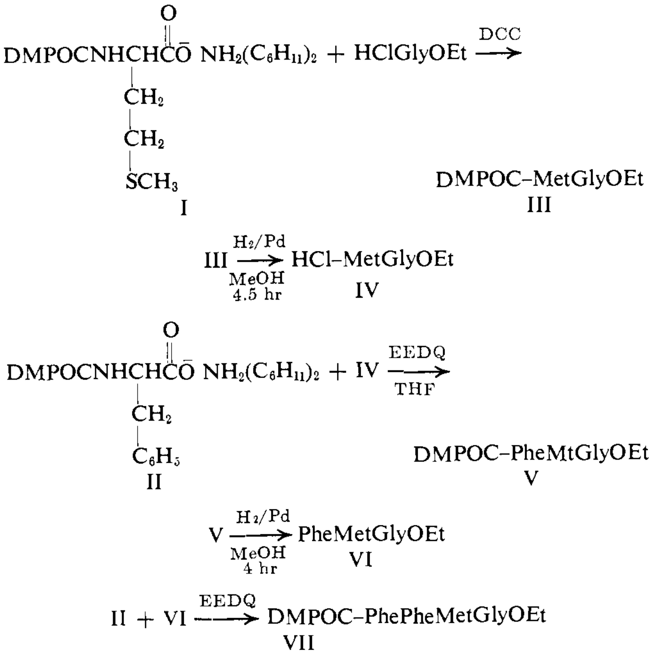
Table I[a]

No.	Derivatives	Yield, %	Mp, °C
I	DMPOC-Met-DCHA	79	117–119
II	DMPOC-Phe-DCHA	88	204–206
III	DMPOC-MetGlyOEt	63	78–79
V	DMPOC-PheMetGlyOEt	53	120–122
VII	DMPOC-PhePheMetGlyOEt	50	169–171
VIII	DMPOC-Cys(*S*-Bzl)GlyPheOMe	50	Oil
IX	HCl-Cys(*S*-Bzl)GlyPheOMe	51	166–169

[a] All melting points are uncorrected. Satisfactory analyses were obtained for all elements in these compounds.

The tetrapeptide sequence DMPOC–PhePheMetGly-OEt (VII) was then synthesized stepwise using the DMPOC as the amino protecting group and catalytic hydrogenolysis for its removal at each synthetic step. Hydrogenolyses were conducted in methanol over 0.1 g of palladized carbon (5%)/mmol of III and V. In the case of III, an equimolar amount of 1 *N* aqueous HCl was used to prevent diketopiperazine formation. Both IV and VI were coupled without purification using *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ)[3] to give V and VII, respectively. The hydrogenolyses were monitored by means of a $Ba(OH)_2$ trap and were judged to be complete when the $BaCO_3$ ceased to form.

Scheme I



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