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.

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

(12) R. S. Givens and W. F. Oettle, unpublished results.

(13) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).

(14) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **86**, 5202 (1964).

Richard S. Givens,* W. Frederick Oettle
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

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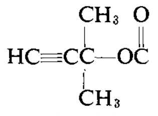
A New Amino Blocking Group Removable from Sulfur-Containing Peptides by Catalytic Hydrogenolysis

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.



$$\mathrm{HC{\equiv}C}\overset{CH_3}{\underset{CH_3}{\mathrm{C}}}\mathrm{{-}O}\overset{O}{\overset{\|}{\mathrm{C}}}$$

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).

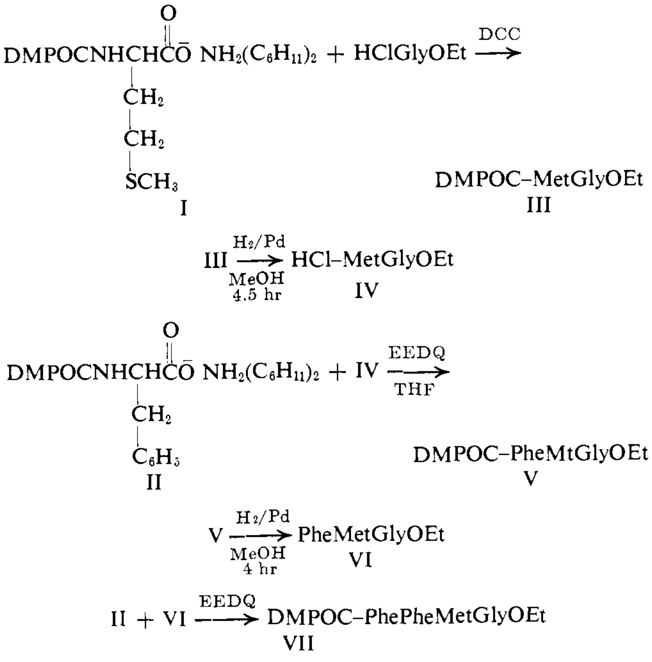
Table I[a]

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



$$\underset{\textbf{I}}{\mathrm{DMPOCNH}\underset{CH_2CH_2SCH_3}{\mathrm{CH}}\overset{O}{\overset{\|}{\mathrm{C}}}\mathrm{O^-}}\ \mathrm{NH_2(C_6H_{11})_2} + \mathrm{HClGlyOEt} \xrightarrow{DCC} \underset{\textbf{III}}{\mathrm{DMPOC{-}MetGlyOEt}}$$

$$\mathrm{III} \xrightarrow[\substack{MeOH\\4.5\ hr}]{H_2/Pd} \underset{\textbf{IV}}{\mathrm{HCl{-}MetGlyOEt}}$$

$$\underset{\textbf{II}}{\mathrm{DMPOCNH}\underset{CH_2C_6H_5}{\mathrm{CH}}\overset{O}{\overset{\|}{\mathrm{C}}}\mathrm{O^-}}\ \mathrm{NH_2(C_6H_{11})_2} + \mathrm{IV} \xrightarrow[THF]{EEDQ} \underset{\textbf{V}}{\mathrm{DMPOC{-}PheMtGlyOEt}}$$

$$\mathrm{V} \xrightarrow[\substack{MeOH\\4\ hr}]{H_2/Pd} \underset{\textbf{VI}}{\mathrm{PheMetGlyOEt}}$$

$$\mathrm{II} + \mathrm{VI} \xrightarrow{EEDQ} \underset{\textbf{VII}}{\mathrm{DMPOC{-}PhePheMetGlyOEt}}$$

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(1) R. J. D. Evans, S. R. Landor, and R. T. Smith, *J. Chem. Soc.*, 1506 (1963).

(2) J. S. Morley, W. Broadbent, and B. E. Stone, *ibid.*, *C*, 2632 (1967).

(3) B. Belleau and G. Malek, *J. Amer. Chem. Soc.*, **90**, 1651 (1968).

For comparing the stability of DMPOC and carbobenzoxy (Z) groups in catalytic hydrogenolysis, the protected dipeptide Z-MetGlyOEt[4] was synthesized and subjected to catalytic hydrogenolysis under the same conditions used in the deblocking of III. A quantitative recovery of starting material was thus obtained.

The DMPOC group was also hydrogenolyzed from S-protected cysteine peptides. Accordingly, DMPOC *S*-benzyl cysteine was coupled *via* carbodiimide to glycine-L-phenylalanine methyl ester hydrochloride to give the DMPOC tripeptide VIII Hydrogenolysis of VIII in methanol over 0.5 g of palladized carbon (5%)/mmol gave the tripeptide IX in 51% yield as the hydrochloride

In summary, the success of catalytic hydrogenolysis of the DMPOC protecting group in the presence of sulfur-containing peptides makes DMPOC useful as a protecting group for general peptide synthesis The application of the DMPOC group and other tertiary acetylenic urethane-protecting groups to the synthesis of known biologically active sulfur-containing peptides is currently under investigation.

Acknowledgment. We are grateful to Dr. E. H. Flynn for his encouragement and helpful discussions.

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(4) Yield 54%; mp 91–92°. *Anal.* Calcd for $C_{17}H_{42}N_2O_5S$: C, 55.42; H, 6.57; N, 7.60; O, 21.70; S, 8.70. Found: C, 55.64; H, 6.54; N, 7.48; O, 21.63; S, 8.69.

G. L. Southard,* B. R. Zaborowsky, J. M. Pettee
The Lilly Research Laboratories, Eli Lilly and Company
Indianapolis, Indiana 46206

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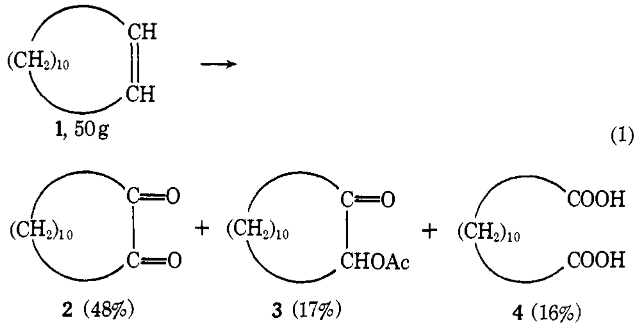
Permanganate in Acetic Anhydride. α-Diketones Directly from Olefins

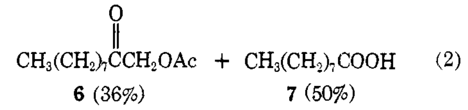
Sir:

We have found that potassium permanganate in acetic anhydride effects the following unique conversions[1] (eq 1 and 2). Further examples of oxidations



$CH_3(CH_2)_7CH{=}CH_2 \longrightarrow$

5, 42.1 g



$$CH_3(CH_2)_7\overset{\overset{\displaystyle O}{\|}}{C}CH_2OAc + CH_3(CH_2)_7COOH \quad (2)$$

6 (36%) **7** (50%)

by this new reagent are illustrated in Table I.

Although reaction 1 should now become the method of choice for preparing α-diketones from acyclic or large ring disubstituted olefins, it fails to produce significant amounts of α-diketones from smaller ring olefins such as cyclohexene and norbornene.[1a] It appears that reaction 1 will succeed only when the carbonyls of the desired α-diketone are not constrained to a cisoid orientation.

Table I. Oxidations by Potassium Permanganate in Acetic Anhydride[a]

Starting material	—Yields, %— α-Diketone	Keto acetate	% DME[b]	Reaction time, hr	Mole equiv of MnO_4^-
trans-Cyclododecene[c,f]	68	10	0	2	4
	50	5	50	3	4
cis-Cyclododecene[d]	20	1	0	2	4
α-Hydroxycyclododecanone (**8**)[e]	69	4	25	3	4
trans-5-Decene[f]	66	15	0	3	3
cis-5-Decene[f]	42	9	0	3	3
trans-Stilbene[g]	46	15	25	3	4
cis-Stilbene[g]	60	12	0	3	4
	50	13	25	3	4
Benzoin (**9**)	73	12	25	3	4
Oleic acid	42		0	1	4
1-Decene		40	0	5	3
Styrene		33	0	1	3

[a] In each experiment the pulverized permanganate was added in one batch to a stirred solution of 6 mmol of starting material in 40 ml of acetic anhydride cooled in an ice bath. Each reaction was stirred in the ice bath for the indicated time; work-ups were performed as described for the large scale reaction of olefin **1**. Yields were determined by glc and/or uv analysis. In the cases of 1-decene and styrene, 2 g of anhydrous potassium acetate was added before the permanganate. [b] The total reaction volume was always 40 ml but in some cases as much as 50% of the acetic anhydride was replaced by dimethoxyethane (DME). [c] This material was only 91% *trans*-cyclododecene (see ref 2). [d] M. Ohno and M. Okamoto, *Org. Syn.*, **49**, 30 (1969). [e] Prepared from the epoxide by the procedure of T. Cohen and T. Tsuji, *J. Org. Chem.*, **26**, 1681 (1961). [f] Obtained from Chemical Samples Co. [g] Benzoin was also produced in *ca.* 20% yield. This contrasts with the oxidations of the cyclododecenes and of the 5-decenes where the α-hydroxy ketones are very minor products.

The following procedure for the conversion of cyclododecene (**1**) to the dione **2** illustrates how the reaction is performed on a large scale. A 6-l. erlenmeyer flask with a 3 in. × ½ in. magnetic stirring bar was charged with 2 l. of acetic anhydride and 50 g (0.30 mol) of cyclododecene.[2] The resulting solution was cooled to 5° by stirring[3] in a large ice–salt bath and 190 g (1.2 mol) of potassium permanganate[4] was added in four portions over a period of 30 min; an exothermic reaction occurs. The permanganate should be added more slowly if necessary to prevent the temperature of the reaction mixture from exceeding 10°. After completion of the addition the mixture was stirred in the cooling bath for 90 min (temperature at this point, 6°). Ice cold hexane–ethyl acetate (1:1; 2 l.) was added, followed by 2 l. of an ice–water (0°) solution containing 250 g of sodium bisulfite. After stirring in the cooling bath for several minutes the mixture was transferred to a 6-l. separatory funnel and the

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(1) The yields indicated are for isolated pure substances.

(1a) Note Added in Proof. *cis*-Cyclooctene, the smallest cyclic olefin to be successfully oxidized, gave a 23% yield of diketone.

(2) Eastman Kodak 99+% acetic anhydride was used as obtained. The cyclododecene was purchased from Chemical Samples Co.; glc analysis revealed 91% trans, 7% cis, and 2% diene.

(3) Efficient stirring was ensured by use of the powerful "9 × 9" Cole Palmer magnetic stirrer.

(4) Fisher reagent grade permanganate was pulverized in a mortar prior to addition.