The triplet lieftime of MK was shown to be quenched by CHD at a rate of $1.8 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, near the maximum rate expected in 2-propanol.[6] Since the addition of CHD establishes a competition between CHD and benzophenone for MK triplets, the quenching of the photoreaction by added CHD allows an estimate of the rate at which benzophenone reacts with the triplet state of MK. This rate is about $8 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. These considerations have led us to postulate Scheme I as the mechanism for the photoreaction of MK with benzophenone.

Scheme I

$$\mathrm{MK} \xrightarrow{h\nu} \mathrm{MK}^1 \longrightarrow \mathrm{MK}^3$$

$$\mathrm{MK}^3 \xrightarrow{k_1} \mathrm{MK}$$

$$\mathrm{MK}^3 + \mathrm{Ph_2CO} \xrightarrow{k_2} [\mathrm{MK}\cdots\mathrm{Ph_2CO}]^3$$

$$\mathrm{MK}^3 + \mathrm{CHD} \xrightarrow{k_3} \mathrm{MK} + \mathrm{CHD}^3$$

$$[\mathrm{MK}\cdots\mathrm{Ph_2CO}]^3 \xrightarrow{k_4} \mathrm{II} + \mathrm{III}$$

$$[\mathrm{MK}\cdots\mathrm{Ph_2CO}]^3 \xrightarrow{k_5} \mathrm{MK} + \mathrm{Ph_2CO}$$

$$\mathrm{II} + \mathrm{III} \xrightarrow{k_6} \mathrm{I}$$

$$\mathrm{II} + \mathrm{III} \xrightarrow{k_7} \mathrm{MK} + \mathrm{Ph_2CO}$$

$$\Phi = \frac{abk_2[\mathrm{Ph_2CO}]}{k_1 + k_2[\mathrm{Ph_2CO}] + k_3[\mathrm{CHD}]}$$

$$a = k_4/(k_4 + k_5) \qquad b = k_6/(k_6 + k_7)$$

$$k_1 = 1.4 \times 10^4\ \text{sec}^{-1}$$

$$k_2 = 8.0 \times 10^6\ M^{-1}\ \text{sec}^{-1}$$

$$k_3 = 1.8 \times 10^9\ M^{-1}\ \text{sec}^{-1}$$

$$k_6 + k_7 = 5.3 \times 10^5 \epsilon_{\mathrm{III}}\ (600\ \text{nm})$$

$$\Phi_{\max} = ab = 0.22$$

There are a number of apparent analogies for this photoreaction, but all are derived from reactions of photoexcited benzophenone. That is, benzophenone in its triplet state interacts with amines to give charge transfer,[7,8] or, in the case of amines with α hydrogens, ultimate hydrogen abstraction.[9,10] Diphenylamine has been found to undergo photochemical electron transfer to the ground state of benzophenone, but this process requires a two-quantum excitation of the amine.[11]

The intermediacy of triplet benzophenone in this photoreaction can be rather rigorously excluded. MK absorbs over 99% of the incident light at 366 nm, and undergoes intersystem crossing with unit efficiency.[12] Thus the energy for the photoreaction initially resides in the triplet state of MK. This energy cannot be transferred to benzophenone in a triplet energy-transfer process, since this process would be more than 7 kcal/mol endothermic,[13] and on these grounds would be expected to occur at a rate about two orders of magnitude less than the observed rate of interaction, $8 \times 10^6\ M^{-1}\ \text{sec}^{-1}$.[3,14] Furthermore, the triplet state of MK is not expected to undergo any photoreactions at all in 2-propanol solution.[15]

Interactions in excimers and exciplexes have been shown to depend upon both excitation resonance and charge-transfer contributions.[16-18]

$$\mathrm{A^*B} \longleftrightarrow \mathrm{AB^*} \longleftrightarrow \mathrm{A^+B^-} \longleftrightarrow \mathrm{A^-B^+}$$

In this case we might expect both excitation resonance and charge transfer from MK to benzophenone to be of importance.

$$\mathrm{MK^3}\cdots\mathrm{Ph_2CO} \longleftrightarrow \mathrm{MK}\cdots\mathrm{Ph_2CO^3} \longleftrightarrow \mathrm{MK^+}\cdots\mathrm{Ph_2CO^-}$$

Even small contributions of the type indicated to the structure of the exciplex could play an important role in directing the internal conversion process so as to give rise to the observed photointermediate.

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Cyclization *via* Solid Phase Synthesis. Unidirectional Dieckmann Products from Solid Phase and Benzyl Triethylcarbinyl Pimelates

Sir:

The Dieckmann cyclization of mixed esters has not been previously reported. In a study of the application of solid phase synthesis[1] to cyclization, we have isolated the products from the essentially unidirectional closure of unsubstituted and 3-ethyl-substituted 1-triethylcarbinyl-7-aralkyl pimelates-*7-*^{14}C (**1**) to triethylcarbinyl 2-oxocyclohexanecarboxylates-*2-*^{14}C (**2**). The preparation of **2b** is particularly significant since the closure of dialkyl 3-alkyladipates, pimelates, and suberates in the opposite direction is well documented.[2-4] We also have observed that replacement of the triethylcarbinyl by ethyl in **1a** and **1b** yields β-keto ester with the label extensively scrambled. This scrambling results from intervention of kinetically competitive transesterification of the original diester prior to cyclization. Use of the triethylcarbinyl moiety as one of the ester groups and as the base minimizes this transesterification, and the extent of transesterification can be mea-

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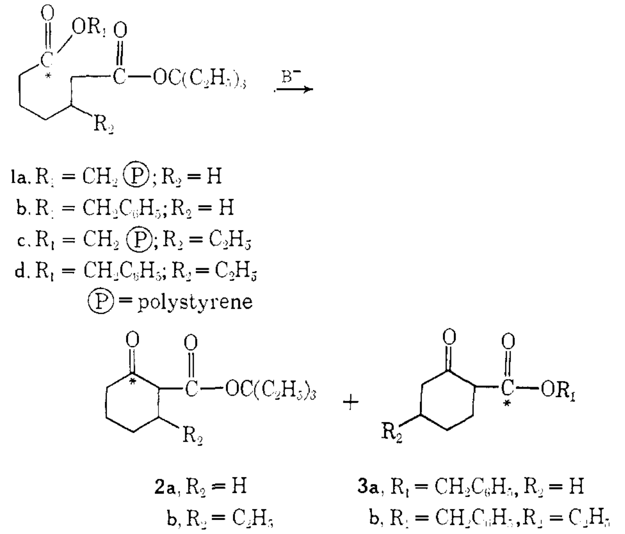

1a, $R_1 = CH_2$Ⓟ; $R_2 = H$
b, $R_1 = CH_2C_6H_5$; $R_2 = H$
c, $R_1 = CH_2$Ⓟ; $R_2 = C_2H_5$
d, $R_1 = CH_2C_6H_5$; $R_2 = C_2H_5$
Ⓟ = polystyrene

2a, $R_2 = H$
b, $R_2 = C_2H_5$

3a, $R_1 = CH_2C_6H_5$, $R_2 = H$
b, $R_1 = CH_2C_6H_5$, $R_2 = C_2H_5$

sured by the distribution of label in the keto ester (Table I).

Table I. Yield and Distribution of Label in Dieckmann Products

Ester	% yield[a]	Mol % of benzyl product[b]	Specific activity, dpm/mmol × 10^{-4} Keto ester	BaCO$_3$	Ketone	% activity in ester carbonyl
1a	46		7.8	0.025	7.8	0.31
1b	34	10	7.8	0.13	7.7	1.70
1c	15		53	1.5	52	2.75
1d	37	21	53	1.7	51	3.20

[a] Radiochemical yield, *i.e.*, total disintegrations per minute of chromatographically pure keto ester/total disintegrations per minute of pure diester or resin ester. [b] Benzyl–*tert*-alkyl ratio determined from ratio of aromatic **H**, δ 7.30, to triethylcarbinyl **CH$_3$**, δ 0.77.

Monoethyl pimelic acid-*1*-^{14}C was prepared and the unique location of its label established in the following way. Dibenzyl sodiomalonate-*1*-^{14}C was alkylated with ethyl 5-bromovalerate in DMF. Crude triester was converted to diacid mono ester by hydrogenolysis after which rapid distillation (170–190° (5 mm)) and fractionation yielded monoethyl pimelic acid-*1*-^{14}C. That the label was exclusively in the carboxylic acid carbon was established by decarboxylation[5,6] to radioinactive ethyl 6-bromohexanoate. Monotriethylcarbinyl pimelic acid-*1*-^{14}C was obtained from the monoethyl ester by transesterification.

To prepare the polystyrene beads, SX-2,[7] as support for the pimelate ester, the benzoate groups resulting from the benzoyl peroxide used to catalyze polymerization of the styrene were removed by refluxing with potassium *tert*-butoxide in toluene for 1 hr. These debenzoylated beads were chloromethylated by a modified procedure permitting greater control of the extent of chloromethylation. Using one-fifth as much stannic chloride as originally[1] in chloromethyl methyl ether at 0° we obtained resin with 1.5% chlorine in 8 min.

The pimelic half-ester was converted to its potassium salt by heating with a 10% excess of potassium carbonate in DMF for 30 min at 150°. Chloromethylated beads equivalent to 67 mol % of the carboxylate groups were added and the mixture held at 150° for 10 hr. The resin ester **1a** was removed, washed serially with dioxane, water, methanol, methylene chloride, methanol, methylene chloride, methanol, and ether, and dried (12 hr at 55° (5 mm)). Esterifications employing triethylammonium salts[1] resulted in the competitive production of quaternary ammonium sites[8] on the resin while the use of hydroxylic solvents[9,10] led to the solvolytic formation of hydroxy- and alkoxybenzylic moieties as well as resin ester.

Changes in the resin functionality were followed by direct[11] scintillation counting of the resin and by infrared difference spectra employing pellets containing 10 mg of resin and 190 mg of potassium bromide. Reference beam pellets contained debenzoylated polystyrene. The resulting difference spectra were much more easily interpreted than were the direct spectra of functionalized beads and a satisfactory Beer's law plot could be obtained for chloromethylation based upon the H–C–Cl bending vibration at 1250 cm^{-1}. In a number of other cases, the difference spectra were essentially superimposable upon the spectra of *p*-cym-7-yl model compounds.

Cyclization was accomplished by addition of resin ester to a refluxing toluene solution of potassium triethylcarbinylate, 4.5 *M* equiv of base in 15 ml of toluene per gram of resin ester. After 2 min, the reaction was cooled, quenched with glacial acetic acid, and filtered, and the resin was washed twice with toluene. Concentration of the filtrate and washings, after aqueous bicarbonate extraction, yielded keto ester which was chromatographed on silica gel,[12] eluting with hexane followed by hexane–ether, 50:1, to yield keto ester: tlc R_F 0.35 (hexane–ether, 10:1); nmr (CCl$_4$) δ 0.77 (t, 9 H, CH$_3$), 1.67 (m, 6 H, CH$_2$), 1.75 (q, 6 H, CH$_2$), 2.13 (t, 2 H, CH$_2$), 12.3 (s, 1 H, enol).

The alkyl-substituted pimeloyl resin ester **1c** was prepared[13] and cyclized in an analogous manner, except that the triethylcarbinyl half-ester of 3-ethylpimelic acid could not be obtained by transesterification. The *tert*-butyl half-ester was prepared by transesterification, converted to the 1-*tert*-butyl 7-methyl diester with methyl iodide, cleaved with anhydrous TFA to 7-methyl half-ester, and converted through the ester acid chloride to 1-triethylcarbinyl 7-methyl diester with lithium triethyl carbinylate.[14] The methyl ester of this diester was selectively hydrolyzed with 1 equiv of potassium hydroxide in diglyme–water–THF, then lyophilized, and the lyophilizate in DMF was attached to the resin and cyclized as above to give keto ester: nmr (CCl$_4$) δ 0.77 (overlapping triplets, 12 H, CH$_3$); 1.05–2.40 (m, br, 13 H, CH$_2$, CH), includes 1.80 (q, 0.7 H, CO$_2$-CHC=O); 12.5 (s, 0.3 H, enol).

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We obtained the unsubstituted benzyl triethylcarbinyl diester **1b** from benzyl bromide and potassium monotriethylcarbinyl pimelate. Transesterification of the 1-triethylcarbinyl-7-methyl 3-ethylpimelate at 25° (25 mm) yielded 7-benzyl 1-triethylcarbinyl 3-ethylpimelate (**1d**). Cyclization by the procedure already described yielded mixtures of triethylcarbinyl and benzyl β-keto esters, which could not be separated by chromatography. The mixed keto esters were hydrogenolyzed using 10% Pd–C as catalyst in ether, washed with aqueous bicarbonate, and concentrated to yield triethylcarbinyl keto esters; nmr established the presence of less than 1% of benzyl esters in both cases.

The distribution of label in the keto esters was determined by decarboxylation in refluxing 25% aqueous ethanolic 3 *N* hydrochloric acid; the evolved CO_2 was counted as barium carbonate.[15] The cyclohexanone and 3-ethylcyclohexanone were extracted into benzene and total activity was determined; the solutions then were analyzed by glpc to obtain ketone specific activities. Cyclization yields and distribution of label in the β-keto esters are shown in Table I.

The unidirectional closure of 1-triethylcarbinyl-7-aralkyl pimelates described here provides a route to unambiguously labeled or substituted triethylcarbinyl cyclohexanone-2-carboxylates which is superior to the existing multistep method.[16–18] Our method requires fewer steps, can be used with compounds containing acid-sensitive substituents, and is capable of extension to the synthesis of other than six-carbon rings.

The use of esters in which one carboxyl provides attachment to a resin support affords a clear benefit over the benzyl case in specificity and greatly simplified isolation and purification of the mixed diester and β-keto ester. We are presently investigating the generalization of this method, including the utilization of any hyperentropic effects available from solid phase mixed esters.

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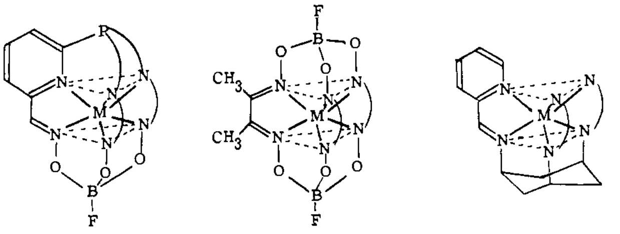
Trigonal-Prismatic Coordination. Complexes of Intermediate Geometry

Sir:

Trigonal-prismatic coordination has recently been reported for $[M(PccBF)]^+$,[1] $[Co(dmg)_3(BF)_2]$,[2] and $[M(py_3tach)]^{2+}$.[3] Each of these complexes contains three five-membered diimine chelate rings as shown in I.



$M(PccBF)^+$ $Co(dmg)_3(BF)_2$ $M(py_3tach)^{2+}$

I

Both $[Co(dmg)_3(BF)_2]$ and $[M(PccBF)]^+$ have each set of imine functions, those that make up a triangular face of the coordination polyhedron (one from each diimine chelate ring), bound through nitrogen to "capping groups" forming "clathro chelates" that encapsulate the metal ions. However, $[M(py_3tach)]^{2+}$ is of an open-trifurcated type,[4] and only the imine functions of one triangular face are bound to a capping group. We wish to report on complexes of 1,1,1-tris(pyridine-2-aldiminomethyl)ethane, $[M(py_3TPN)]^{2+}$, which are of the second, or open-trifurcated type.

In the absence of metal ions, condensation of 1,1,1-tris(aminomethyl)ethane (TPN) with pyridine-2-carboxaldehyde results in 1-methyl-4,6,10-tri(α-pyridyl)-3,5,2-triazatricyclo[3.3.1.1.^{3,7}]decane.[5] When the condensation takes place in the presence of ferrous ions, the uncaged diimine form of the ligand (py_3TPN) is obtained as the Fe(II) complex.[5] The Fe(II) complex of tris(pyridine-2-aldiminomethyl)methane has also been prepared.[6]

Condensation of TPN with pyridine-2-carboxaldehyde in refluxing methanol in the presence of metal perchlorates [Zn(II), Ni(II), Fe(II), Co(II), and Mn(II)] and recrystallization from acetonitrile or acetonitrile–ethanol results in the pure[7] complexes $[M(py_3TPN)](ClO_4)_2$: Zn(II), colorless and diamagnetic; Ni(II), dark red orange, 3.04 BM; Fe(II), dark violet, 0.93 BM; Co(II), dark red orange, 4.66 BM; Mn(II), light orange, 5.85 BM.

Precession photographs indicate that the Zn(II), Ni(II), Co(II), and Mn(II) complexes crystallize in the monoclinic space group $P2_1/c$ and are isomorphous and, therefore, probably isostructural. The Fe(II) complex separates as asymmetric crystals of the orthorhombic space group $P2_12_12_1$ and is probably not isostructural with the other complexes. We are currently engaged in single-crystal X-ray studies of the Zn(II) and Fe(II) complexes. Preliminary results for the Zn(II) complex (present refinement, $R = 11.7$) indicate a large distortion from trigonal-prismatic coordination with an average twist of the two triangular faces of 28°; the geometry is approximately midway between trigonal prismatic and octahedral. Two triangular faces of an octahedron are twisted by an angle of 60°, while the two triangular faces of a trigonal prism are twisted by 0°. Distortion from trigonal prismatic coordination is considerably less for $[Zn(py_3tach)]^{2+}$ (average twist

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