The unusual rate enhancement with piperazine was observed in aqueous solution earlier by Dahlgren and Schell.[4] In that study piperazine was a factor of 665 more effective a catalyst for the complete hydrolysis of MOFB than morpholine. In the present lactonization study the second-order rate constant for piperazine is a factor of 126 larger than that for morpholine or one-half of that if we make the statistical correction for the second amine group of piperazine.

Standard equations were used to determine the activation parameters over the temperature range 21–39° and the results are recorded in Table VI. It is interesting to note that the enthalpy of activation determined for the piperazine-catalyzed lactonization of MOFB in dioxane is essentially the same as that for the piperazine-catalyzed hydrolysis of MOFB in water.[4]

TABLE VI

THERMODYNAMIC FUNCTIONS OF ACTIVATION FOR THE LACTONIZATION OF MOFB BY SELECT CYCLIC SECONDARY AMINES[a]

Amine	$\Delta H^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Morpholine	1.6 ± 0.2	2.8 ± 0.1	15 ± 1
Piperazine	1.2 ± 0.1[b]	2.58 ± 0.07	12.6 ± 0.6
1-Methylpiperazine	1.7 ± 0.3	3.0 ± 0.1	16 ± 2

[a] Dioxane at 21° except for piperazine where 5% MeOH/dioxane was used. [b] Reference 4 reports a value of 1.3 ± 0.1 kcal/mol in aqueous media.

Finally, where pK_B values were available the second-order rate constants and the pK_B's were found to obey the Brønsted relation (eq 2). That is, in the case of

$$\log k_2 = 0.33\ (\pm 0.02) \log K_B + 2.39\ (\pm 0.07) \qquad (2)$$

pyrrolidine (pK_B = 2.695),[10] piperidine (2.877),[10] 1-methylpiperazine (4.50),[11] and morpholine (5.64),[12] the rate of nucleophile attack on the carbonyl carbon of the aldehyde function of MOFB parallels the affinity of the nucleophile for the protons of water. However, piperazine (pK_B = 4.21),[10] whose second-order rate constant according to eq 2, should equal 10.2 l. mol^{-1} sec^{-1}, actually gave an observed value of 500 l. mol^{-1} sec^{-1} at 25°. It is this latter observation which has piqued our curiosity and led us to preparing bicyclic systems containing the piperazine geometry but preventing participation by the second amine group in, perhaps, a proton abstraction role.

Registry No.—I, 4122-56-9; II, 4122-57-0; III, 4195-21-5; pyrrolidine, 123-75-1; piperidine, 110-89-4; 1*H*-hexahydroazepine, 111-49-9; 4-pipecoline, 626-58-4; 3-pipecoline, 626-56-2; 2-pipecoline, 109-05-7; piperazine, 110-85-6; 1-methylpiperazine, 109-01-3; morpholine, 110-91-8.

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Thermal Decomposition of Benzyl Triphenylacetate and Benzyl Diphenyl-*p*-tolylacetate. The Possibility of 1,4-Aryl Migration and α-Lactone Formation[1a,b]

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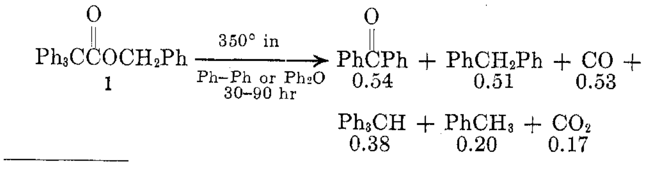
The thermal decomposition of benzyl triphenylacetate at 350° for 30–90 hr in the liquid phase gives 0.54, 0.51, and 0.53 mol/mol ester of benzophenone, diphenylmethane, and carbon monoxide, respectively, in addition to 0.38, 0.20, and 0.17 mol/mol ester of triphenylmethane, toluene, and carbon dioxide, respectively. The thermal decomposition of benzyl diphenyl-*p*-tolylacetate under comparable conditions for 30 hr gives 0.29, 0.27, 0.15, and 0.34 mol/mol ester of benzophenone, phenyl-*p*-tolylmethane, *p*-methylbenzophenone, and diphenylmethane, respectively, plus 0.30 mol/mol ester of diphenyl-*p*-tolylmethane. A mechanism is proposed for the formation of the arylphenylmethanes and benzophenones which involves a 1,4-aryl migration to produce the arylphenylmethane and α-lactone which rapidly decarbonylates to give the benzophenone.

The thermal decomposition of benzyl triphenylacetate (1) at 350° in biphenyl or diphenyl ether (*ca.* 15% 1 in solution) for 30–90 hr in a sealed tube gives rise to fairly high and approximately equal yields of benzophenone, diphenylmethane, and carbon monoxide in addition to triphenylmethane, toluene, and carbon dioxide (throughout this paper yields are given in mol/mol ester unless otherwise indicated).



$$\underset{\mathbf{1}}{\mathrm{Ph_3C\overset{O}{\overset{\|}{C}}OCH_2Ph}} \xrightarrow[\text{Ph-Ph or Ph}_2\text{O, 30-90 hr}]{350^\circ \text{ in}} \underset{0.54}{\mathrm{Ph\overset{O}{\overset{\|}{C}}Ph}} + \underset{0.51}{\mathrm{PhCH_2Ph}} + \underset{0.53}{\mathrm{CO}} + \underset{0.38}{\mathrm{Ph_3CH}} + \underset{0.20}{\mathrm{PhCH_3}} + \underset{0.17}{\mathrm{CO_2}}$$

Yields were determined by glpc and nmr analyses and are averages of 6–8 runs. The use of biphenyl or diphenyl ether as solvent made no significant difference. In fact, the pyrolysis of a neat sample of 1 for 5 hr at 350° gave 0.52, 0.46, and 0.25 mol/mol ester of benzophenone, diphenylmethane, and triphenylmethane, respectively. The gaseous products were collected and determined as described previously.[2]

Ester 1 was reported[3] to decompose at its boiling point to give triphenylmethane, 37% carbon dioxide,

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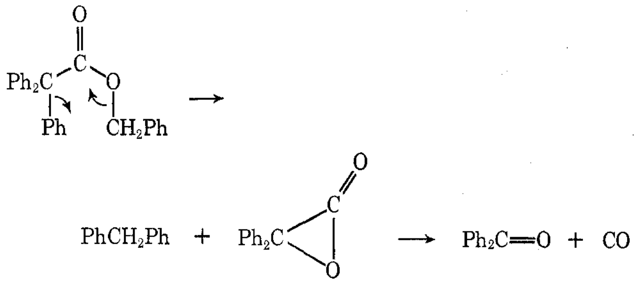
and 42% carbon monoxide. Because of the high yield of carbon monoxide, benzaldehyde was postulated but not demonstrated to be a pyrolysis product. We found no benzaldehyde, benzyl triphenylmethyl (trityl) ether, trityl phenylacetate, 1,1,1,2-tetraphenylethane, or **1** in the product mixture.

A possible explanation for the formation of benzophenone and diphenylmethane is that a 1,4-phenyl migration occurs giving rise to diphenylmethane and diphenylacetolactone (**2**) which rapidly decarbonylates



2

to give benzophenone. Triphenylmethane and toluene probably come from hydrogen abstraction reactions by the trityl and benzyl radicals, which would be produced by homolytic cleavage of the trityl–carbonyl bond of **1**

$$\mathbf{1} \longrightarrow \text{Ph}_3\text{C}\cdot + \cdot\text{COOCH}_2\text{Ph} \longrightarrow \text{CO}_2 + \cdot\text{CH}_2\text{Ph}$$

followed by decarboxylation of the benzyloxycarbonyl radical.[2] The sources of hydrogen atoms are probably species formed by the addition of radicals into solvent molecules.

1,4-Aryl migrations are rare but known[4] and α-lactones have been isolated at low temperatures.[5,6] The decarbonylation of α-lactones has been shown to be a primary photochemical reaction[6] and a thermal reaction of di(trifluoromethyl)acetolactone.[7] Although polymerization has been shown to be a thermal reaction of α-lactones, including **2**,[5,6] the thermal decarbonylation of **2** at high temperatures is not an unreasonable process. In fact, fair yields of benzophenone have been obtained from reactions which are thought to involve **2**, although decarbonylation of **2** has not been invoked as the route to benzophenone.[8]

Other mechanisms, such as a bimolecular one which is analogous to the above unimolecular mechanism, can be written, but a key point which they must account for is the approximately equal yields of diphenylmethane and benzophenone.

The thermal decomposition of neat benzyl diphenyl-*p*-tolylacetate (**3**) under comparable conditions gives

$$\underset{\mathbf{3}}{\text{Tol(Ph)}_2\text{CCOOCH}_2\text{Ph}} \xrightarrow[30\text{ hr}]{350°}$$

Tol ≡ p-$\text{CH}_3\text{C}_6\text{H}_4$

$$\underset{\substack{\mathbf{4}\\0.29}}{\text{PhCOPh}} + \underset{\substack{\mathbf{5}\\0.27}}{\text{PhCH}_2\text{Tol}} + \underset{\substack{\mathbf{6}\\0.15}}{\text{PhCOTol}} + \underset{\substack{\mathbf{7}\\0.34}}{\text{PhCH}_2\text{Ph}}$$

the products expected from both phenyl and *p*-tolyl migrations. Nmr and glpc analysis also indicated that 0.30 mol/mol ester of diphenyl-*p*-tolylmethane was produced. In Table I are presented the yields of products from runs for varying lengths of time. From these yields, it is seen that for all of these runs the ratio of **4** to **5** is *ca.* 1, as expected, but the ratio of **6** to **7** is *ca.* 0.5 for all the runs except the one which was stopped after 1 hr. For the 1-hr run, the ratio of **6** to **7** is *ca.* 1. Thus **6** seems to be unstable to reaction conditions.

TABLE I

DECOMPOSITION PRODUCTS OF BENZYL DIPHENYL-*p*-TOLYLACETATE AT 350°

Reaction time, hr	Yields,[a] mol/mol ester				
	PhCOPh	PhCH_2Tol	PhCOTol	PhCH_2Ph	$\text{Tol-(Ph)}_2\text{CH}$
1[b]	0.16	0.14	0.12	0.13	0.20
5	0.21	0.20	0.14	0.23	0.40
15	0.35	0.31	0.20	0.36	0.49
30	0.29	0.27	0.15	0.34	0.30
47	0.27	0.26	0.13	0.32	0.34
66	0.28	0.23	0.13	0.28	0.24
91	0.27	0.22	0.14	0.26	0.22

[a] Analysis for toluene was not carried out. [b] 61% of ester **3** was recovered.

The ratio of *p*-tolyl to phenyl migration calculated from diarylmethanes is 0.86 and that calculated from the benzophenones from the 1-hr run is 1.3. Thus the rate of migration of the *p*-tolyl is *ca.* two times that of the phenyl group taking into consideration the fact that there are two phenyl groups to every *p*-tolyl group. It is difficult to interpret these comparable rates of migration for the *p*-tolyl and phenyl groups, since the ratio of these rates has been shown to be *ca.* 1 for a radical rearrangement[9] but range from 1 to 16 for cation rearrangements.[10]

Methyl (**8**) and phenyl (**9**) triphenylacetates were thermally decomposed under similar conditions. Ester **8** gave 0.07, 0.11, and 0.56 mol/mol ester of toluene, benzophenone, and triphenylmethane, respectively. Ester **9** gave 0.70 and 0.75 mol/mol ester of phenol and triphenylmethane, respectively. Thus the methyl ester undergoes a rearrangement reaction analogous to the one observed for the benzyl ester, but the phenyl ester undergoes trityl–carbonyl bond cleavage only. These results for the thermal decomposition of **8** and **9** are consistent with previously published results.[3,11]

When **1** was pyrolyzed in the gas phase at 550° by the technique previously described[12] most of **1** was recovered, no diphenylmethane was produced, and 0.08, 0.08, 0.06, and 0.02 mol/mol ester of benzophenone,

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bibenzyl, triphenylmethane, and biphenyl, respectively, were obtained. Thus a different reaction must take place at the higher temperature in the gas phase.

Experimental Section

Methods and Materials.—Most equipment and methods have been previously described.[2,12] An insulated, electrically heated, aluminum block heater was used for most of the high-temperature sealed-tube pyrolyses. The heater consisted of a round block of aluminum 6 in. in diameter and 6 in. long which was wrapped with asbestos, wound with enough No. 20 Chromel heating wire to attain a maximum temperature of 500°, and again wrapped with asbestos. Ten evenly spaced holes, each 0.875 in. in diameter, 4.5 in. from the axis of the cylinder, and 5 in. deep, were drilled into the block. One hole 0.25 in. in diameter and 3 in. deep for the thermocouple was drilled between two of the sample holes. Each of the ten sample holes was expanded to 1 in. in diameter to a depth of 1 in. Ten stainless steel plugs, 1 in. deep, were ground to fit loosely in the sample holes and rest on the ledge of the inner hole. Each plug had a hook on the bottom side for attaching sample holders and a "knob" on the top for pulling out the plug (and sample). Ten sample holders were made of stainless steel tubing (22 mm) and fitted with wire bails. The block was placed in a box made of Transite insulation board; the box was filled with blown mica and covered with a Transite lid. The heating coil was connected to a Variac, and a thermocouple attached to a Leeds and Northrup potentiometer was used to measure the temperature of the block.

Benzyl triphenylacetate (1) was prepared from the acid chloride[13] and alcohol:[3] mp 98–99° (lit.[3] mp 99–99.5°); nmr ($CDCl_3$) δ 7.17 (s, 20) and 5.21 (s, 2); ir ($CHCl_3$) 1725, 1487, 1170, 1005, and 973 cm^{-1}.

Benzyl trityl ether was prepared as described previously:[14] mp 101–103° (lit.[14] mp 105.5–106°); nmr ($CDCl_3$) 7.35 (m, 20) and 4.26 (s, 2); ir ($CHCl_3$) 1490, 1375, 1150, 1085, 1053, 1000, 982, and 900 cm^{-1}.

Trityl phenylacetate was prepared in 70% yield from trityl bromide and potassium phenylacetate[15] by a method similar to a previously published one:[16] mp 69–71°; nmr ($CDCl_3$) δ 7.17 (m, 20) and 3.60 (s, 2); ir ($CHCl_3$) 1737, 1130, and 983 cm^{-1}.

Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 86.62, 85.05, 84.02; H, 6.05, 5.97, 6.09. (This compound appeared to be sensitive to moisture.)

Diphenyl-*p*-tolylacetic acid was prepared from benzilic acid, toluene, and anhydrous stannic chloride by a procedure similar to that previously described,[17] mp 205–207° (lit.[17] mp 205°).

Benzyl diphenyl-*p*-tolylacetate (**3**) was prepared by treating the acid with an ethereal solution of phenyldiazomethane.[18] The crude product was recrystallized from benzene: mp 68–69°; nmr (CCl_4) δ 7.1 (s, 14), 6.99 (s, 5), 5.15 (s, 2), and 2.3 (s, 3); ir (KBr) 1720, 1495, 1440, 1162, 971, and 813 cm^{-1}.

Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.71; H, 6.12. Found: C, 85.86; H, 6.23.

Methyl triphenylacetate (**8**) was prepared as described previously:[3] mp 182–184° (lit.[19] mp 182°); nmr ($CDCl_3$) δ 7.11 (d, 15) and 3.67 (s, 3); ir ($CHCl_3$) 1725, 1486, 1445, 1430, and 1010 cm^{-1}.

Phenyl triphenylacetate (**9**) was prepared as described previously:[20] mp 124–126° (lit.[20] mp 123–124°); ir ($CHCl_3$) 1755, 1595, 1490, 1156, and 970 cm^{-1}.

Thermal Decomposition of the Esters.—Solutions of the esters in diphenyl ether or biphenyl or neat samples were placed in constricted tubes, degassed three times, and sealed. The tubes were heated in the aluminum block heater, cooled, and opened. A weighed quantity of benzil was added as a standard and the mixture was analyzed by glpc using an SE-30 or Carbowax 20M column. The products were identified by enhancement of glpc trace peaks with authentic samples[21] and nmr spectra of the product mixture. The ir spectrum of the product mixture from 1 had a peak at 1660 cm^{-1} which is characteristic of benzophenone.

Analysis of the Gases Evolved during the Thermal Decomposition of 1.—A total of 0.756 g (2.00 mmol) of 1 in 6.15 g (36.2 mmol) of diphenyl ether was placed in two thick-walled tubes and degassed three times and the tubes were sealed. The tubes were heated at 350° for 32 hr. After cooling the tubes were broken open under a funnel submerged in a large water tank and analyzed as described previously.[2] At 301° K and 707-mm pressure (corrected for water vapor) 9.00 ml of carbon dioxide and 28.40 ml of carbon monoxide were obtained (1.40 ml of gas remained). A second run gave comparable results.

Registry No.— **1**, 37173-04-9; **3**, 37173-05-0; **8**, 5467-21-0; **9**, 34823-77-3; benzyl trityl ether, 5333-62-0; trityl phenylacetate, 37173-09-4.

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