990, 958 cm^{-1}. *Anal.* Calcd for $C_{35}H_{68}O_4$: C, 76.03; H, 12.40. Found:[27] C, 76.26; H, 12.76.

cis-**2-Pentadecyl-5-hexadecanoyloxy-1,3-dioxane** (**10a**) had mp 95–96°; R_f 0.32;[25] ir (CS_2, C_2Cl_4)[26] 1732 (s), 1408, 1340, 1244 (m), 1170, 1152 (s), 1104 (m), 1073 (m), 1008 (m), 950, 902, 791 cm^{-1}. *Anal.* Calcd for $C_{35}H_{68}O_4$: C, 76.03; H, 12.40. Found:[27] C, 76.30; H, 12.70.

trans-**2-Pentadecyl-5-hexadecanoyloxy-1,3-dioxane** (**10a**) had mp 87–89°; R_f 0.65;[25] ir (CS_2, C_2Cl_4)[26] 1740 (s), 1420, 1350 (sh), 1215, 1150 (s), 1115 (m), 1095 (sh), 1075 (sh), 1043 (m), 960, 900 cm^{-1}. *Anal.* Calcd for $C_{35}H_{68}O_4$: C, 76.03; H, 12.40. Found:[27] C, 75.90; H, 12.63.

Cyclic diol acetals **11a–d** were prepared by acid-catalyzed condensation[28] of the corresponding diols with hexadecanal followed by tlc purification with toluene as developing solvent.

(27) Elemental analyses were by I. Beetz, Mikroanalytisches Laboratorium, Kronach, Germany.

(28) P. V. Rao, S. Ramachandran, and D. G. Cornwell, *J. Lipid Res.*, **8**, 380 (1967).

Acknowledgment.—The authors are indebted to Drs. K. Biemann and C. E. Hignite, Massachusetts Institute of Technology, and to Dr. W. E. Baitinger, Purdue University, for recording high-resolution mass spectra.

Registry No.—**1a**, 555-44-2; **1b**, 41562-98-5; **1c**, 41562-99-6; **1d**, 6110-59-4; **2a**, 624-03-3; **2a-d_4**, 34083-13-1; **2b**, 818-21-3; **2c**, 26719-63-1; **2d**, 26933-79-9; **2e**, 23130-50-9; **2f**, 34083-10-8; **2f-d_4**, 41563-08-0; **2g**, 29899-13-6; **2g-d_4**, 41563-10-4; **9a**, 41563-11-5; **9b**, 41563-12-6; *cis*-**9c**, 30889-29-3; *trans*-**9c**, 30889-32-8; **9c-d_1**, 41563-15-9; *cis*-**10a**, 41563-16-0; *trans*-**10a**, 41563-17-1; *cis*-**10b**, 34298-21-0; *trans*-**10b**, 34315-34-9; *cis*-**10c**, 30889-23-7; *cis*-**10c-d_1**, 41563-21-7; *trans*-**10c**, 30889-26-0; *trans*-**10c-d_1**, 41563-23-9; **11a**, 4360-57-0; **11a-d_1**, 41563-25-1; **11a-d_4**, 41563-26-2; **11b**, 17352-27-1; **11b-d_1**, 41563-28-4; **11c**, 41563-29-5; **11c-d_1**, 41563-30-8; **11d**, 41583-11-3.

Phenacyl Photosensitive Blocking Groups

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The *p*-methoxyphenacyl group and α-methylphenacyl group have been found useful photosensitive protecting groups for the carboxyl function. Both types of esters are cleavable in ethanol or dioxane solution at 20° by uv light. The reaction has been applied to esters of N-protected alanine, glycine, phenylalanine, tryptophane, glycylglycine, and benzylaspartylserine and to benzoic acid.

Most useful protecting groups are removed by common chemical reactions. In principle, however, it should be possible to design protecting groups which could be removed by photolysis. In accord with the progress of organic photochemistry, several photosensitive blocking groups have been designed. The advantage of photosensitive blocking groups is that they can be removed under completely neutral and mild conditions.

The first photochemical removal of a blocking group was observed in the photolysis of carbobenzoxyglycine.[1] The irradiation of an aqueous solution of the sodium salt of carbobenzoxyglycine with the 2537-Å mercury line gave a small amount of glycine along with a mixture of other products.

$$PhCH_2OCONHCH_2COONa \xrightarrow{h\nu} H_2NCH_2COONa + \text{mixture}$$

The use of *o*-nitrobenzyl derivatives as photosensitive blocking reagents for amino and carboxyl functions has been reported.[2,3] Irradiation of these derivatives at wavelengths longer than 3200 Å cleaves the protecting group without affecting light-sensitive amino acids.

The potential of certain aromatic azides as photosensitive blocking groups has also been explored.[4] The photolysis of alkyl or acyl derivatives of β-(*o*-azidophenyl)ethyl alcohol yields indole and the corresponding alcohol or acid. This reaction is interesting as a photocyclization reaction. However, since the yield is low, it is not attractive as a photoremoval reaction of a protecting group.

Benzoin esters and other desyl compounds yield 2-phenylbenzofuran upon irradiation with uv light.[5]

A preliminary investigation of the application of this furanization reaction in the unmasking of carboxylic acid esters of appropriately substituted benzoins has been reported.[6] The irradiation of the benzoin derivatives of phthaloylglycine by uv light at 3200 Å formed phthaloylglycine and the corresponding furan derivatives.

These photosensitive blocking groups are all unique and interesting. However they are somewhat complicated to use practically in syntheses, and are far from being widely applicable protecting groups. Since the search for a photosensitive blocking group has just begun, more practical and simple blocking groups can be expected.

Discussion

The phenacyl group has low-lying excited states because of the interaction of the electrons between the carbonyl group and the phenyl ring. Therefore the photolysis of substituted phenacyl esters was first attempted. When *p*-methoxyphenacyl benzoate was irradiated in benzene, no observable reaction occurred and starting material was recovered. But when *p*-methoxyphenacyl benzoate was irradiated in dioxane with a Pyrex filter, the ester cleavage reaction occurred to give benzoic acid in good yield. Encouraged by this observation the photolysis of phenacyl esters was investigated in considerable detail.

(1) J. A. Barltrop and P. Schofield, *Tetrahedron Lett.*, 697 (1962).

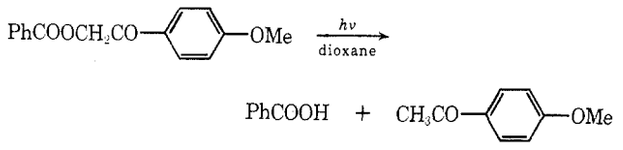
(2) J. A. Barltrop, P. J. Plant, and P. Schofield, *Chem. Commun.*, 822 (1966).

(3) A. Patchornik, B. Amit, and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 6333 (1970).

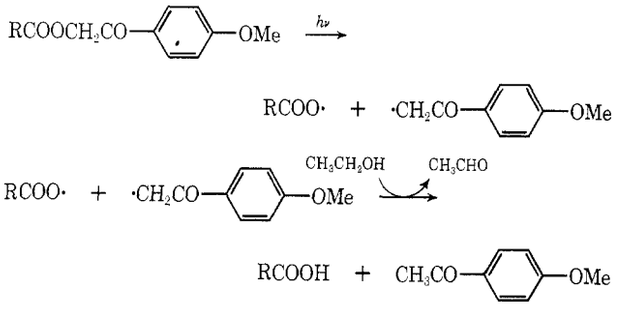
(4) D. H. R. Barton, P. G. Sammes, and G. G. Weingarten, *J. Chem. Soc. C*, 721 (1971).

(5) J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.*, **86**, 5277 (1964).

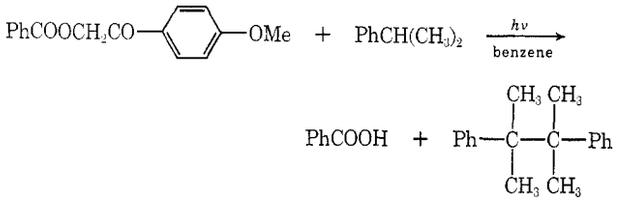
(6) J. C. Sheehan, R. M. Wilson, and A. W. Oxford, *J. Amer. Chem. Soc.*, **93**, 7222 (1971).



In the photocleavage reaction of a phenacyl ester, the other product is acetophenone, which is obtained in good yield. Dioxane serves as a hydrogen donor. Further study showed that ethanol is a better donor, provided that the phenacyl ester is soluble. Ethanol presumably is dehydrogenated to acetaldehyde as the reaction proceeds.[7] The mechanism is considered to be a simple radical scission of the carbon–oxygen bond since in some cases partial decarboxylation was observed.



When a small amount of water was added to the solution, the yield of carboxylic acid was decreased. Photocleavage of phenacyl benzoate also occurred with cumene in benzene to give benzoic acid and 2,3-dimethyl-2,3-diphenylbutane. Cumene is a typical hydrogen radical donor.



These phenomena support the concept of a radical scission.

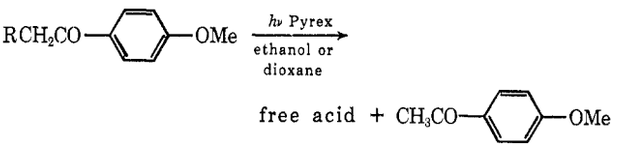
When the photocleavage reaction was carried out in 1 *M* benzophenone or naphthalene in dioxane, the reaction was quenched completely. Benzophenone and naphthalene can quench excited triplet states when their lifetime is longer than 10^{-10} sec.[6] This is evidence that the reaction proceeds through a long-lived triplet state, having a lifetime longer than 10^{-10} sec.

Photolysis of *p*-Methoxyphenacyl Esters.—The phenacyl photocleavage reaction was applied to many blocked amino acids and peptides. The results are summarized in Table I. All these reactions were carried out below room temperature at concentrations of 5×10^{-3}–10^{-2} *M* with a Pyrex filter. Pyrex filters pass uv light of 313 mμ and greater. The reaction is complete in 6 hr in ethanol, and in 11–17 hr in dioxane.

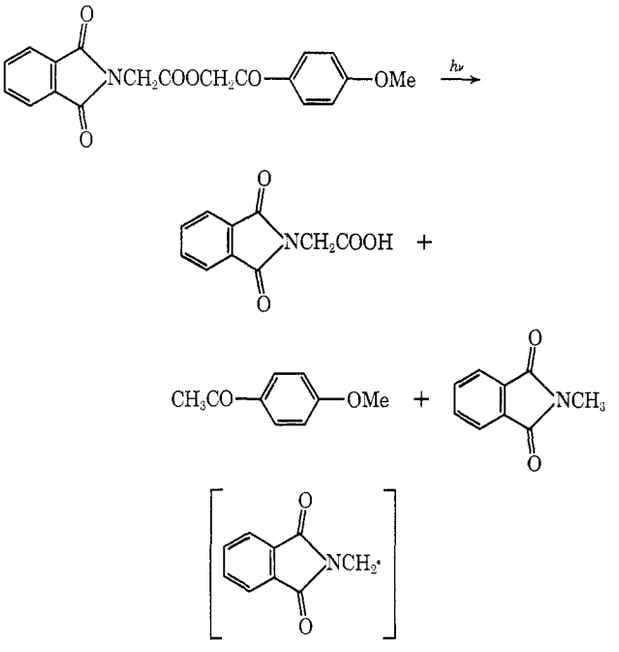
As listed in Table I, under the conditions used for the cleavage, the carbobenzoxy and *tert*-butoxycarbonyl groups are completely stable, although the carbobenzoxy group is sensitive to ultraviolet light of shorter wavelength.[1] However, when phthaloylglycine phenacyl ester was irradiated for 17 hr, partial decarboxylation occurred to give *N*-methylphthalimide. This

(7) R. A. Finnegan and J. A. Matson, *J. Amer. Chem. Soc.*, **94**, 4780 (1972).

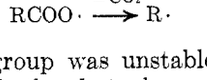
TABLE I



Registry no.	R	Solvent	Irradiation time, hr	Yield of RCOOH, %
41499-11-0	PhCOO	Dioxane	11	78
	PhCOO	Dioxane	17	81
	PhCOO	Ethanol	6	96
41476-77-1	Boc-L-Ala	Dioxane	17	82
	Boc-L-Ala	Ethanol	6	93
41499-12-1	Boc-Gly	Ethanol	6	94
41476-78-2	Boc-L-Phe	Dioxane	17	89
41476-79-3	Z-D, L-Ala	Dioxane	6	84
41558-28-5	Phthaloyl-Gly	Dioxane	17	80
41498-13-2	Tri-Gly	Dioxane	17	58
41476-80-6	Z-L-Trp	Ethanol	4	33
41499-14-3	Z-Gly-Gly ⌐L-Ser	Ethanol	5.5	77
41476-81-7	Z-L-Asp-OBz	Dioxane	9	49



may occur because the phthalimide methylene radical is stabilized by conjugation. When the alkyl radical R· is very stable, partial decarboxylation becomes more likely.



The *N*-trityl group was unstable to uv irradiation to some extent. In the photocleavage reaction of carbobenzoxyglycylglycine phenacyl ester, the peptide bonds were shown to be stable under the reaction conditions. The more complex dipeptide, carbobenzoxy-L-asparagyl-L-serine, was also examined, and gave the desired product in 49% yield. The phenacyl ester of the most photosensitive amino acid, tryptophane, gave only 30% yield after 4-hr irradiation.

The substitution of the phenyl ring of the phenacyl group by electron-donating groups may lower the stability of the derivatives toward acid. Therefore the stability of *p*-methoxyphenacyl ester was examined in trifluoroacetic acid and in 33% hydrogen bromide in acetic acid. It was shown that *p*-methoxyphenacyl acetate was stable under these conditions.

α-Methylphenacyl Blocking Group.—*p*-Methoxyphenacyl esters are more photoreactive than unsubstituted phenacyl esters. One reason could be that the methoxy substitution causes a bathochromic shift and requires radiation of lower energy. The other reason could be that the intermediate radical is stabilized by the electron-donating group.

The α-methylphenacyl blocking group was designed and investigated in accord with the idea of radical stabilization. The results of the photocleavage reactions of α-methylphenacyl esters are summarized in Table II. The treatment is the same as for *p*-

TABLE II

$$RCH(CH_3)COPh \xrightarrow[\text{dioxane or ethanol}]{h\nu} \text{free acid} + CH_3CH_2COPh$$

Registry no.	R	Solvent	Time, hr	Yield of RCOOH, %
1030-23-5	PhCOO	Dioxane	6	78.2
	PhCOO	Ethanol	6	87.4
41499-16-5	Boc-Gly	Ethanol	6	87.3
41476-82-8	Boc-L-Ala	Dioxane	6	95.7
	Boc-L-Ala	Ethanol	6	93.3
41476-83-9	Boc-L-Phe	Dioxane	6	95.6
	Boc-L-Phe	Ethanol	6	85.7
41499-17-6	Phthaloyl-Gly	Ethanol	6	70.6

methoxyphenacyl esters. The α-methylphenacyl group was as reactive as the *p*-methoxyphenacyl group. The cleavage reaction is complete in 6 hr in dioxane. For the α-methylphenacyl blocking group, dioxane seems to be a better solvent than ethanol. The mechanism of the reaction presumably is the same as that of *p*-methoxyphenacyl esters. The coproduct, propiophenone, is obtained in good yield. In the case of phthaloylglycine phenacyl ester, the yield is low because of partial decarboxylation of the product.

Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Hilger-Watts H1200 Infragraph. The nmr spectra were recorded on a Varian T-60. Microanalyses were supplied by Hiroko Hino, Institute of Applied Microbiology, University of Tokyo, and Mrs. Nancy Alvord, MIT. Thin layer chromatography was performed on Baker-Flex silica gel 1B-F plates.

Photolysis Apparatus and Procedures.—The light source was a 450-W Hanovia mercury immersion lamp. The reactions were carried out in a Hanovia no. 19434 quartz immersion well fitted with a Pyrex 7740 absorption sleeve. The apparatus was flushed with nitrogen which had been purified using a sodium anthraquinone-β-sulfonate solution, a solution of sodium hydrosulfite in aqueous potassium hydroxide, and a saturated lead acetate solution.[8]

Photolysis of *p*-Methoxyphenacyl Benzoate. A. In Dioxane.—A solution of 1.20 g (4.45 mmol) of *p*-methoxyphenacyl benzoate in 300 ml of dioxane was irradiated for 17 hr. After the removal of the solvent under reduced pressure, 60 ml of ethyl acetate was added. This solution was extracted with 1 *N* potassium carbonate and the extract was acidified with 2 *N* hydrochloric acid. The product was extracted into ether and the organic layer was dried with anhydrous magnesium sulfate and evaporated to give 0.44 g (81%) of benzoic acid. The identity of the product was confirmed by mixture melting point and comparison of ir spectra. The ethyl acetate solution after the extraction was dried with anhydrous sodium sulfate and evaporated. The residue was chromatographed on 55 g of Florisil (100–200 mesh) using cyclohexane–ethyl acetate (4:1) to give 0.45 g (73%) of *p*-methoxyacetophenone: mp 33–36°; ir ($CHCl_3$) 1670 cm^{-1}; nmr ($CDCl_3$) δ 8.1 (d, 2 H), 7.0 (d, 2 H), 3.9 (s, 3 H), 2.6 (s, 3 H); tlc R_f 0.39 [cyclohexane–EtOAc (4:1)].

B. In Ethanol.—A solution of 1.20 g (4.45 mmol) of *p*-methoxyphenacyl benzoate in 300 ml of ethanol was irradiated for 6 hr. The solution was treated as already described to give 0.52 g (96%) of benzoic acid and 0.38 g (62%) of *p*-methoxyacetophenone.

Photolysis of *p*-Methoxyphenacyl Benzoate with Cumene.—A solution of 0.70 g (2.6 mmol) of *p*-methoxyphenacyl benzoate in 100 ml of cumene and 200 ml of benzene was irradiated for 17 hr. The solution was concentrated under reduced pressure to 150 ml and extracted with 1 *N* aqueous potassium carbonate. Upon acidification of the alkaline extract with 2 *N* hydrochloric acid, the product was extracted with ether. The ether solution was dried with anhydrous magnesium sulfate. After the removal of ether, 0.218 g (69.0%) of benzoic acid was obtained.

***p*-Methoxyphenacyl Benzoate.**—A solution of 1.22 g (0.01 mol) of benzoic acid, 1.01 g (0.01 mol) of triethylamine, and 2.29 g (0.01 mol) of *p*-methoxyphenacyl bromide in 20 ml of dimethylformamide was refrigerated for 24 hr. The mixture was triturated with 140 ml of ice water and the resulting precipitate was filtered and dried. This material was suspended in 80 ml of petroleum ether (bp 40–60°) and stirred for 5 min. The crude product was filtered and recrystallized from ethanol to give 60% colorless needles: mp 108°; ir ($CHCl_3$) 1732, 1700 cm^{-1}; nmr ($CDCl_3$) δ 8.2–6.8 (m, 9 H), 5.5 (s, 2 H), 3.8 (s, 3 H). *Anal.* Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.16; H, 5.18.

***p*-Methoxyphenacyl Esters of N-Blocked Amino Acids.**—The product was prepared in the same way as described for *p*-methoxyphenacyl benzoate.

p-Methoxyphenacyl ester of *tert*-butoxycarbonyl-L-alanine had mp 137°; 71%; ir ($CHCl_3$) 3480, 1760, 1715 cm^{-1}. *Anal.* Calcd for $C_{17}H_{23}NO_6$: C, 60.52; H, 6.87; N, 4.16. Found: C, 60.59; H, 6.78; N, 4.27.

p-Methoxyphenacyl ester of carbobenzoxy-DL-alanine had mp 133°; 85%; ir ($CHCl_3$) 3440, 1755, 1725, 1700 cm^{-1}. *Anal.* Calcd for $C_{20}H_{21}NO_6$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.56; H, 5.71; N, 3.75.

p-Methoxyphenacyl ester of *tert*-butoxycarbonyl-L-phenylalanine had mp 110°; 80%; ir ($CHCl_3$) 3420, 1750, 1700 cm^{-1}. *Anal.* Calcd for $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58; N, 3.39. Found: C, 67.14; H, 6.52; N, 3.45.

p-Methoxyphenacyl ester of *tert*-butoxycarbonylglycine had mp 73°; yield 65%; ir (CCl_4) 3470, 1765, 1730, 1705 cm^{-1}. *Anal.* Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.04; H, 6.49; N, 4.28.

p-Methoxyphenacyl ester of tritylglycine had mp 169°; 73%; ir ($CHCl_3$) 3450, 1750, 1695 cm^{-1}. *Anal.* Calcd for $C_{30}H_{27}NO_4$: C, 77.40; H, 5.85; N, 3.01. Found: C, 76.35; H, 5.72; N, 2.96.

p-Methoxyphenacyl ester of carbobenzoxy-L-tryptophan had mp 119°; 82%; ir ($CHCl_3$) 3480, 1760, 1720, 1700 cm^{-1}. *Anal.* Calcd for $C_{28}H_{26}N_2O_6$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.12; H, 5.29; N, 5.65.

p-Methoxyphenacyl ester of phthaloylglycine had mp 87°; 30%; ir ($CHCl_3$) 1770, 1730, 1700, 1600 cm^{-1}. *Anal.* Calcd for $C_{19}H_{15}NO_6$: C, 64.64; H, 4.28. Found: C, 64.83; H, 4.34.

***p*-Methoxyphenacyl Esters of N-Blocked Dipeptides.**—The products were prepared from the corresponding N-blocked dipeptides in the same way as described for *p*-methoxyphenacyl *tert*-butoxycarbonylglycinate.

Carbobenzoxyglycylglycine *p*-methoxyphenacyl ester had mp 136–138°; 67%; ir ($CHCl_3$) 3410, 1755, 1725, 1695 cm^{-1}. *Anal.* Calcd for $C_{21}H_{22}N_2O_7$: C, 60.86; H, 5.35; N, 6.76. Found: C, 60.73; H, 5.37; N, 6.83.

(8) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957, p 299.

Carbobenzoxy-β-benzyl-L-aspartyl-L-serine *p*-methoxyphenacyl ester had mp 145–150°; 75%; ir ($CHCl_3$) 3400, 1755, 1725, 1680 cm^{-1}. *Anal.* Calcd for $C_{31}H_{32}N_2O_{10}$: C, 62.83; H, 5.44; N, 4.73. Found: C, 62.98; H, 5.36; N, 4.65.

Photolysis of *p*-Methoxyphenacyl Esters of N-Blocked Amino Acids and Peptides.—These photocleavage reactions were carried out in the same way as described for *p*-methoxyphenacyl benzoate with solvents and irradiation times as indicated in Table I.

α-Methylphenacyl Esters.—The products were prepared from α-methylphenacyl bromide and the corresponding carboxylic acid in the same way as described for *p*-methoxyphenacyl benzoate.

α-Methylphenacyl benzoate had mp 108°; 76%; ir (CCl_4) 1730, 1705 cm^{-1}. *Anal.* Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.25; H, 5.39.

α-Methylphenacyl phthaloylglycinate had mp 86°; 76%; ir (CCl_4) 1770, 1740, 1710 cm^{-1}. *Anal.* Calcd for $C_{19}H_{15}NO_5$: C, 67.65; H, 4.48; N, 4.15. Found: C, 67.53; H, 4.49; N, 4.13.

α-Methylphenacyl *tert*-butoxycarbonylglycinate had mp 87°; 91%; ir (CCl_4) 3460, 1760, 1725, 1705 cm^{-1}. *Anal.* Calcd for $C_{16}H_{21}NO_5$: C, 62.52; H, 6.88; N, 4.56. Found: C, 62.48; H, 6.68; N, 4.49.

α-Methylphenacyl ester of *tert*-butoxycarbonyl-L-alanine was recrystallized from petroleum ether: mp 79–83°; 62%; ir (CCl_4) 3450, 1750, 1720, 1710 cm^{-1}. *Anal.* Calcd for $C_{17}H_{23}NO_5$: C, 63.53; H, 7.21; N, 4.36. Found: C, 63.28; H, 7.00; N, 4.72.

α-Methylphenacyl ester of *tert*-butoxycarbonyl-L-phenylalanine was an oil: 80%; ir (CCl_4) 1750, 1725, 1700 cm^{-1}.

Photolysis of α-Methylphenacyl Benzoate.—A solution of 1.06 g (4.0 mmol) of α-methylphenacyl benzoate in 300 ml of dioxane was irradiated for 6 hr at 12°. After removal of the solvent under reduced pressure, 60 ml of ethyl acetate was added. The solution was extracted with 1 *N* aqueous potassium carbonate. Upon acidification of the alkaline extract with 2 *N* hydrochloric acid, the product was extracted with ether. After the removal of ether, the colorless solid was triturated in petroleum ether. Filtration gave 0.382 g (78.2%) of benzoic acid, mp 102°.

The ethyl acetate solution after the extraction was dried and evaporated. The residue was chromatographed on 50 g of Florisil (100–200 mesh) using cyclohexane–ethyl acetate (4:1) to give 0.190 g (35.4%) of propiophenone: ir (CCl_4) 1690 cm^{-1}; nmr δ 8.2–7.9 (m, 2 H), 7.7–7.3 (m, 3 H), 3.1 (q, 2 H), 1.3 (t, 3 H); tlc R_f 0.73 (cyclohexane–EtOAc (4:1)].

The other reactions of α-methylphenacyl esters were similarly conducted with solvents as indicated in Table II.

Quenching Experiments of *p*-Methoxyphenacyl Benzoate Photocleavage Reactions.—A solution of 1.2 g (4.45 mmol) of *p*-methoxyphenacyl benzoate and 38.4 g (0.30 m) of naphthalene in 300 ml of dioxane was irradiated for 17 hr. After the removal of the solvent, 200 ml of benzene was added. The solution was extracted with 1 *N* aqueous potassium carbonate. Upon acidification of the alkaline extract with 2 *N* hydrochloric acid, the solution was extracted with ether. The thin layer chromatography of the ether solution using cyclohexane–ethyl acetate (4:1) showed no product. After the removal of ether, no benzoic acid was obtained.

Acknowledgment.—We are grateful to the Sloan Basic Research Fund for support of this work.

Registry No.—*p*-Methoxyacetophenone, 100-06-1; propiophenone, 93-55-0; benzoic acid, 65-85-0; triethylamine, 121-44-8; *p*-methoxyphenacyl bromide, 2632-13-5.

Reaction Kinetics of 3-Thenoyl Chloride with Anilines in Benzene

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The rate of the reaction of 3-thenoyl chloride with substituted anilines has been measured in benzene at different temperatures. The reaction follows a second-order kinetics. The activation parameters and the slopes of the Hammett (−3.21) and Brønsted (1.08) plots are similar to those of the reactions of benzoyl and 2-thenoyl chlorides with aniline. In the 3-thenoyl chloride reaction the effect of the substituents in the aniline is to modify the activation energy, log *A* remaining approximately constant. The reaction mechanism of the 3-thenoyl chloride with aniline is the same as for the reactions of benzoyl and 2-thenoyl chlorides. 3-Thenoyl chloride, however, does not react as expected from the pK_a of 3-thenoic acid. The Tommila equation points out that the carbonyl carbon atom of 3-thenoyl chloride is less electrophilic than that of benzoyl chloride but more electrophilic than that of 2-thenoyl chloride.

The Hammett relation is valid for correlating the reaction data of 3-thenoic and 3-furoic acid esters.[1]

Oae and Price[2] found that the ethyl ester of 3-thenoic acid saponified as expected from the pK_a of 3-thenoic acid. Imoto and coworkers[3] studied the hydrolysis of thiophene and furancarboxylic acid esters and they found a linear relationship between the hydrolysis rates and the dissociation constants for the 3-carboxylic acids; the 2-analogs, instead, deviated from the straight line. The same results were obtained recently by Ten Thije and Janssen.[4]

In a previous paper we reported the rates of the reaction of 2-thenoyl chloride with various substituted anilines in benzene solution in order to investigate whether 2-thenoyl chloride, in comparison with benzoyl chloride, reacted as expected from the pK_a of 2-thenoic acid.[5] We found that 2-thenoyl chloride reacted more slowly than benzoyl chloride, although 2-thenoic acid was stronger than benzoic acid. The Tommila equation pointed out that the carbonyl carbon atom of 2-thenoyl chloride was less positively charged than that of benzoyl chloride.

Recently we reported the data relating to the reactions of 3-thenoyl 2- and 3-furoyl chlorides with aniline in benzene.[6] We found that only 2-furoyl chloride reacted as expected from the pK_a of 2-furoic acid. The reactivity decreased from benzoyl to 3-thenoyl, 3-furoyl, and 2-thenoyl chlorides, while the order of the acidity constants was 2-thenoic acid > 3-furoic acid > 3-thenoic acid > benzoic acid.

In the present paper we report a study of the reaction

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