Preparative photolyses were generally carried out in benzene (50-100 mL) by using 0.05 M *trans*-stilbene and 0.5 M ester. Samples were degassed prior to irradiation through Pyrex with a 450-W medium-pressure mercury lamp by bubbling dry nitrogen through the solution for 10-15 min. Reaction progress was monitored by GC. Yields were not optimized. The isolated yield of cycloadducts from the *trans*-stilbene-dimethyl ethylidenemalonate reaction mixture is representative of the reactions studied.

Methyl 4,4-Dimethyl-*c*-2,*t*-3-diphenylcyclobutane-1-carboxylate (1a) and Methyl 4,4-Dimethyl-*t*-2,*c*-3-dicyclobutane-1-carboxylate (1b). The *trans*-stilbene-methyl 3-methylcrotonate reaction mixture was chromatographed on alumina with 0-1% ethyl acetate in hexane as eluant. The major adduct, **1a**, eluted after the stilbenes and was isolated as a 6:1 mixture of **1a** and **1b**. **1b** followed and was isolated as a 1:1 mixture of **1a** and **1b**: the NMR data (Table II) are consistent with those reported by Hirsch;[3] IR (CCl_4, mixture of isomers) 5.75, 7.91 μm.

Methyl *t*-4-Methyl-*c*-2,*t*-3-diphenylcyclobutane-1-carboxylate (2a) and Methyl *t*-4-Methyl-*t*-2,*c*-3-diphenylcyclobutane-1-carboxylate (2b). The *trans*-stilbene-methyl crotonate reaction mixture was chromatographed on alumina with 2% ethyl acetate in hexane as eluant. Attempted crystallization of the isomeric mixture was unsuccessful: the NMR data in Table II is consistent with that reported by Retjö;[4] IR (CCl_4, mixture of isomers) 5.76, 8.55 μm.

Dimethyl *r*-2,*t*-3-Diphenyl-*t*-4-methylcyclobutane-1,1-dicarboxylate (3a) and Dimethyl *r*-2,*t*-3-Diphenyl-*c*-4-methylcyclobutane-1,1-dicarboxylate (3b). A solution of *trans*-stilbene (0.45 g) and dimethyl ethylidenemalonate (4.0 g) in 50 mL of benzene was irradiated 38 h. The solvent was removed, the unreacted ester distilled bulb-to-bulb, and the residue chromatographed on alumina (50 g) with 0-4% ethyl acetate in hexane as eluant. Early product-containing fractions were enriched in the major isomer, **3a**; later fractions were enriched in **3b**. Fractional crystallization afforded no further enrichment of either isomer: yield 0.46 g (54%); NMR (see Table II); IR (CCl_4, mixture of isomers) 5.76, 7.84, 7.97 μm.

Diethyl 4,4-Dimethyl-*t*-2,3-diphenylcyclobutane-1,1-dicarboxylate (4). The *trans*-stilbene-diethyl isopropylidenemalonate reaction mixture was chromatographed on silica gel with 5% ethyl acetate in hexane as eluant. Stilbenes eluted first, followed by **4**. The crude product was recrystallized from hexane: mp 124.5-125 °C; NMR (see Table II).

Dimethyl 1,2-Dimethyl-*t*-3,4-diphenylcyclobutane-*c*-1,2-dicarboxylate (5). The *trans*-stilbene-dimethyl dimethylmaleate reaction mixture was chromatographed on alumina with 0-2% ethyl acetate in hexane as eluant. The crude product was recrystallized from hexane: mp 104.9-105.2 °C; NMR (see Table II); IR (KBr) 5.74, 5.83 μm.

Registry No. 1a, 72727-30-1; **1b**, 72777-29-8; **2a**, 72727-31-2; **2b**, 72777-30-1; **3a**, 72727-32-3; **3b**, 72777-31-2; **4**, 72727-33-4; **5**, 72727-34-5; *trans*-stilbene, 103-30-0; methyl 3-methylcrotonate, 924-50-5; methyl crotonate, 18707-60-3; dimethyl ethylidenemalonate, 17041-60-0; diethyl isopropylidenemalonate, 6802-75-1; dimethyl dimethylmaleate, 13314-92-6.

Photochemical Transformations. 26. Sensitized and Unsensitized Photoreactions of Some Benzyl Chlorides in *tert*-Butyl Alcohol[1]

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Benzyl chloride and a variety of meta- and para-substituted derivatives have been irradiated in *tert*-butyl alcohol at 254 nm or in acetone-*tert*-butyl alcohol mixtures at 300 nm. Quantum and chemical yields of photosolvolysis products (benzyl *tert*-butyl ether and/or benzyl alcohol), photohomolysis products (bibenzyl and 4-phenyl-2-methyl-2-butanol), and corresponding products from substituted benzyl chlorides have been measured as functions of substrate concentration and medium composition. Sensitized reactions favor bond heterolysis, but direct irradiations favor homolysis, although reactions are not clean in either case. There is no correlation between quantum yields for photosolvolysis and Hammett σ or Brown σ^+ constants, and no salt effects of added lithium perchlorate were observed, in either direct or sensitized reactions.

In the decade and a half following the report[2] by Zimmerman and Sandel of the photosolvolysis of certain benzyl derivatives, that is, photochemically induced bond heterolysis, there has been a considerable amount of work on the photochemistry of benzyl compounds in nucleophilic solvents. The compounds studied include benzyl (or substituted benzyl) sulfonium salts,[3] ammonium salts,[4-6] acetates,[2,7,8] phosphonium salts,[9] and halides,[2,10-13] and it has been reported that products resulting from both heterolysis and homolysis of the benzyl-heteroatom bond are formed either upon direct irradiation or upon photosensitization.

The proportion of homolytic and heterolytic cleavage depends on the nature of the leaving group in the molecule and on the apparent multiplicity of the excited state (direct irradiation vs. photosensitization), but how these factors influence the choice of cleavage type is not yet clear. We

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(1) Paper 25: Cristol, S. J.; Kaufman, R. L. *J. Photochem.*, in press.
(2) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.
(3) Maycock, A. L.; Berchtold, G. A. *J. Org. Chem.* **1970**, *35*, 2532.
(4) Ratcliff, Jr., M. A.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 3112.
(5) Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J.; McKenna, J. M.; Walley, A. R. *J. Chem. Soc., Chem. Commun.* **1974**, 473.
(6) Lillis, V.; McKenna, J.; McKenna, J. M.; Williams, I. H. *J. Chem. Soc., Chem. Commun.* **1974**, 474.
(7) Ivanov, V. B.; Ivanov, V. L.; Kuz'min, M. G. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 1263.
(8) Jaeger, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 902.
(9) Griffin, C. E.; Kaufman, M. L. *Tetrahedron Lett.* **1965**, 773.
(10) Ivanov, V. B.; Ivanov, V. L.; Kuz'min, M. G. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 345.
(11) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105.
(12) McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Brocklehurst, B.; Appleton, D. C.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Chem. Commun.* **1977**, 108.
(13) Hyömäki, J.; Koskikallio, J. *Acta Chem. Scand., Ser. A* **1977**, *31*, 321.

0022-3263/80/1945-0951$01.00/0

Table I. Effect of Concentration of Benzyl Chloride on the Quantum Yield of Benzyl *tert*-Butyl Ether in Acetone-Sensitized Solvolysis[a] with 300-nm Light

$[PhCH_2Cl]$, M	quantum yield of $PhCH_2$-O-*t*-Bu	$[PhCH_2Cl]$, M	quantum yield of $PhCH_2$-O-*t*-Bu
0.66	0.28	0.078	0.28
0.46	0.30	0.039	0.26
0.32	0.30	0.021	0.29
0.22	0.28	0.015	0.22
0.15	0.30	0.0073	0.14
0.11	0.29		

[a] 0.35 mol fraction acetone in *tert*-butyl alcohol.

Table II. Effect of Sensitizer-Solvent Composition in the Solvolysis of Benzyl Chloride at 300 nm in Acetone-*tert*-Butyl Alcohol Mixtures

acetone		maximum quantum yield of $PhCH_2O$-*t*-Bu	maximum quantum yield of $PhCH_2OH$
vol %	mol fraction		
10	0.13	0.28	*a*
25	0.30	0.29	*a*
30	0.35	0.30	0.047, 0.050
40	0.46	0.25	*a*
50	0.56	0.23	*a*
60	0.65	0.19	*a*
70	0.74	0.16	*a*
75	0.79	0.15	*a*
80	0.84	0.11, 0.11	0.14, 0.16
100	1.0		0.29, 0.26

[a] Not measured.

decided to undertake a study in some depth of benzyl chloride itself and of several monosubstituted benzyl chlorides to see whether a structure–reactivity relationship might become apparent and to test other factors influencing photoreactivities. This paper discusses quantum yield–multiplicity experiments, environmental factors, sensitizations, etc. Later papers will discuss mechanistic details to the extent that they are apparent to us.

Previous work in this laboratory[11] and elsewhere[12,13] indicated that photosolvolysis of benzyl chloride occurred either with ketone sensitization or upon direct irradiation in a variety of alcohols and organic acids. We decided to focus our attention on the use of *tert*-butyl alcohol as a solvolysis medium, although it has the obvious disadvantage that it is considerably less polar than the lower alcohols and therefore might be anticipated to disfavor heterolysis (the reaction in which we were principally interested), assuming solvent effects similar to ground-state reactions. However, we intended to follow the course of the reaction by gas chromatography, and our experience suggested that confidence in such results with the lower alcohols was often misplaced, in view of relatively rapid solvolysis reactions occurring in the inlet system of chromatographic systems. In addition, ground-state solvolysis was anticipated to be negligible near room temperature in *tert*-butyl alcohol, even for reactive chlorides, which is not true for the lower alcohols, and especially for aqueous methanol. Finally, we noted that ketone sensitizers, such as acetophenone, disappeared rapidly in alcohols with α hydrogen atoms, presumably because of chemical quenching of the ketone triplets by hydrogen atom transfer. Such a reaction, which obviously leads to quantum yield losses, would certainly be minimized and might be negligible with *tert*-butyl alcohol.

Irradiations of Benzyl Chloride. For these reactions we used acetone–*tert*-butyl alcohol as a sensitizer–reactant–solvent system. We were first interested in working in a mixture which would give fairly high efficiencies for solvolysis. In our experiments it was necessary to use conditions where the sensitizer absorbed substantially all of the light and yet where enough substrate was present to quench substantially all of the sensitizer triplets. We therefore did irradiations at 300 nm, where aromatic absorption is low. Table I shows the effect of benzyl chloride concentration on the quantum yield of formation of benzyl *tert*-butyl ether in 0.35 mol fraction acetone in *tert*-butyl alcohol. Clearly, above 0.02–0.05 M benzyl chloride, excitation transfer is, within the limits of experimental error, complete. Similar results were obtained with other mixtures of acetone and *tert*-butyl alcohol. As the amount of acetone was increased in the solvent mixture, the solvolysis product changed from benzyl *tert*-butyl ether to benzyl alcohol. The maximum quantum yields found for various sensitizer-solvent compositions are given in Table II. As can be noted, the highest quantum yields for solvolysis are in the neighborhood of 0.30, so that this is a moderately efficient process.[14]

In addition to benzyl *tert*-butyl ether and benzyl alcohol, lesser amounts of bibenzyl, 4-phenyl-2-butanone, 4-phenyl-2-methyl-2-butanol, and mesityl oxide were observed. Of these, the latter undoubtedly was produced by hydrogen chloride catalyzed aldolization of acetone, followed by dehydration.

The formation of benzyl alcohol may be conceived to be the result of one or more possible reaction paths, of which three seemed most likely. The first of these involved the possibility of adventitious water in the acetone reacting with benzyl cation. The second involved capture of benzyl cations by acetone to form benzylisopropylideneoxonium ion or its deprotonation product, benzyl isopropenyl ether, either of which would be expected to hydrolyze to benzyl alcohol and acetone in the presence of water or acid and water. Third, the benzyl alcohol could have arisen from water formed during the course of the irradiation, either from the reaction of *tert*-butyl alcohol with hydrogen chloride or from that accompanying mesityl oxide formation. That the reaction of *tert*-butyl alcohol with hydrogen chloride was not responsible may be noted (see below) by the fact that irradiation of benzyl chloride in *tert*-butyl alcohol without acetone present did not lead to measurable amounts of benzyl alcohol. Analysis of the acetone which we used indicated that it contained about 0.4% water, and, after the short periods of irradiation we were using, the water content was not significantly increased. Experiments in which the concentration of water was doubled did not give significantly different results from those in Table II. We therefore conclude that the benzyl alcohol results from nucleophilic capture of benzyl cation by acetone, competing with that by *tert*-butyl alcohol.

Table III presents sensitized quantum-yield data (for experiments carried out to about 5% reaction) and chemical-yield data, based on chloride reacted (for experiments carried out to about 42% reaction, and under conditions designed for preparative isolation and identification of products).

Benzyl chloride was also irradiated directly at 254 nm in *tert*-butyl alcohol; quantum-yield and chemical-yield data are given in Table IV.

The products obtained in both the direct and the sensitized irradiations in *tert*-butyl alcohol are the same, with

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(14) McKenna and co-workers[12] report a quantum yield of the ether of 0.20 in 10% acetone in *tert*-butyl alcohol. Unfortunately their communication does not indicate the concentration of benzyl chloride used, so that we cannot clarify this discrepancy.

Table III. Products Resulting from Sensitized Irradiations with 300-nm Light of Benzyl Chloride in Acetone–*tert*-Butyl Alcohol

product	quantum yield[a,e]	chemical yield,[b] %
$PhCH_2O$-*t*-Bu	0.28	63, 64
$PhCH_2OH$	0.047 ± 0.000 (2)	9, 10
$PhCH_2CH_2Ph$	0.060[c] ± 0.006 (3)	19, 18
$PhCH_2CH_2COCH_3$	0.009 ± 0.001 (3)	1
$PhCH_2CH_2C(CH_3)_2OH$	*d*	2, 2

[a] Conditions: 30% acetone in *tert*-butyl alcohol, 0.11–0.2 M benzyl chloride, ca. 5% conversion. [b] Conditions: 30% acetone in *tert*-butyl alcohol, 0.05 M $PhCH_2Cl$, ca. 42% conversion. [c] Calculated as moles of benzyl radical/einstein, that is by doubling moles of bibenzyl/einstein. [d] Not measured, presumably ca. 0.01. [e] Number in parentheses indicates number of replications.

Table IV. Products Resulting from Direct Irradiations with 254-nm Light of Benzyl Chloride in *tert*-Butyl Alcohol

product	quantum yield[a,d]	chemical yield,[b] %
$PhCH_2O$-*t*-Bu	0.12	28, 31
$PhCH_2OH$	0.00	0
$PhCH_2CH_2Ph$	0.090[c] ± 0.000 (2)	28, 29
$PhCH_2CH_2C(CH_3)_2OH$	0.053 ± 0.001 (2)	20, 24

[a] Conditions: 0.1 M $PhCH_2Cl$, ~10% conversion. [b] Conditions: 0.075 M $PhCH_2Cl$, 41% conversion. [c] Calculated as moles of benzyl radical/einstein, that is, by doubling moles of bibenzyl/einstein. [d] Number in parentheses indicates number of replications.

the exception of the acetone-derived products, but the proportions of products in the two processes are clearly different.

Perhaps most interesting is the ratio of heterolytic products (ether plus alcohol) to the radical products (bibenzyl, 4-phenyl-2-methyl-2-butanol, and 4-phenyl-2-butanone). It is clear that the direct irradiation produces less heterolysis and more homolysis products than does the acetone photosensitization and that the direct irradiation process has a higher quantum efficiency for the homolysis products and a lower quantum efficiency for the heterolysis product than does the sensitized reaction. The results with *tert*-butyl alcohol as solvent nucleophile are thus consistent with previous results[11-13] on benzyl chloride, and, as discussed earlier,[11,15] inconsistent with those with other nucleofugal groups or with chlorides in bridged systems[1,16] in that, in such cases, heterolysis occurs upon direct, rather than sensitized, irradiation. The reasons for this remain unclear.[17]

The reaction scheme given by eq 1–6 seems reasonable to rationalize the formation of the radical products.

$$PhCH_2Cl \xrightarrow[{}^3\text{sens}]{h\nu\ \text{or}} PhCH_2Cl^* \rightarrow PhCH_2\cdot + Cl\cdot \quad (1)$$

$$Cl\cdot + CH_3COCH_3 \rightarrow HCl + \cdot CH_2COCH_3 \quad (2)$$

$$Cl\cdot + CH_3C(CH_3)_2OH \rightarrow HCl + \cdot CH_2C(CH_3)_2OH \quad (3)$$

$$2PhCH_2\cdot \rightarrow PhCH_2CH_2Ph \quad (4)$$

$$PhCH_2\cdot + \cdot CH_2COCH_3 \rightarrow PhCH_2CH_2COCH_3 \quad (5)$$

$$PhCH_2\cdot + \cdot CH_2C(CH_3)_2OH \rightarrow PhCH_2CH_2C(CH_3)_2OH \quad (6)$$

It may be noted from the data in Tables III and IV that the sensitized reaction gives a much higher ratio of bibenzyl to the products of coupling of benzyl radical with solvent-derived radicals than does the direct irradiation. The latter products may, of course, be derived from geminate-pair recombination, whereas bibenzyl must be derived from free radicals. One may ascribe the differences to the fact that the sensitized reaction probably leads to a triplet radical pair, which must change multiplicity before covalent-bond formation, giving more time for radical separation. In addition, the results may be rationalized by the differences in the size of the energy package delivered to the benzyl chloride molecules, 110 kcal/mol in direct irradiation vs. 78 kcal/mol in sensitization, or to the solvent viscosity, making the cage tighter in *tert*-butyl alcohol than in the 0.35 mol fraction acetone solvent, or to both. A test of the latter, that is, dilution of *tert*-butyl alcohol with a low viscosity inert solvent, is simple but has not yet been conducted.

The ionic reactions would appear to be well rationalized by nucleophilic capture of the benzyl cation, either free or as a member of an ion pair,[17] produced by the conversion of an excited-state species.

The sums of the quantum yields for both the sensitized and the unsensitized reactions are considerably below unity, in spite of the fact that chemical-yield data indicate that most of the reactant has been accounted for and, for the sensitized reaction, excitation transfer has been maximized. Thus energy wastage represents approximately 60% of the fates of the sensitized molecules and 75% of those excited by direct irradiation. Energy wastage would of course result from radical-pair recombination, ion-pair recombination, formation of excited species with insufficient energy to effect bond cleavage, or internal conversion to a ground-state species with insufficient energy or with lifetime in a vibrationally excited state insufficient to allow reaction. Of these, the first two could be explored, although obviously not with benzyl chloride itself, by experiments with chiral species.[19] Further experiments to test for ion-pair return possibilities are described below. The question of low-energy excited states will be discussed in a later paper.

Irradiations of Substituted Benzyl Chlorides. A number of meta- and para-substituted benzyl chlorides were irradiated, both directly and with acetone sensitization, in an attempt to learn whether there might be any simple structure–quantum yield relationship. The quantum yields for ether, alcohol, and substituted bibenzyl formation for acetone sensitization are given in Table V, along with Hammett[20] σ and Brown[21] σ^+ substituent constants, and corresponding data are given in Table VI for the formation of ether, substituted bibenzyl, and 4-aryl-2-methyl-2-butanol upon direct irradiation. The sensitized data were collected at substrate concentrations where

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[15] Cristol, S. J.; Stull, D. P.; McEntee, Jr., T. E. *J. Org. Chem.* **1978**, *43*, 1150.

[16] Cristol, S. J.; Stull, D. P.; Daussin, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 6674.

[17] We have already[16] discussed the question of whether bond heterolysis occurs in competition with homolysis, is the result of electron transfer following homolysis, or is the result of a mixed process,[18] and we have no evidence with respect to this question as a result of these experiments.

[18] Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonnou, C. G. *J. Am. Chem. Soc.* **1970**, *92*, 4927.

[19] McKenna and co-workers[6] have showed that (α-phenylethyl)trimethylammonium salts photosolvolyze upon direct irradiation in water or methanol to give largely racemized products, but without racemization of quaternary ammonium salt. No such experiment has been conducted with a chiral chloride, to the best of our knowledge, although workers in this laboratory have reported[1,16] isomerizations consistent with ion-pair return.

[20] Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. Swain, C. G.; Lupton, Jr., E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

[21] Brown, H. C.; Okamota, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

Table V. Quantum Yields for Acetone-Sensitized Irradiations of Substituted Benzyl Chlorides in *tert*-Butyl Alcohol at 300 nm[a]

	substituent constant[b]		quantum yield[f]		
substituent	σ	σ^+	ArCH$_2$O-*t*-Bu	ArCH$_2$CH$_2$Ar[c]	ArCH$_2$OH
p-CF$_3$	0.54	0.61	0.21	0.11 ± 0.01 (2)	0.038 ± 0.004 (3)
m-CF$_3$[e]	0.43	0.52	0.18	0.10 ± 0.00 (2)	0.045 ± 0.006 (3)
p-CH$_3$CO	0.50	0.57	0.42	<0.01	*d*
m-F	0.34	0.35	0.24	0.076 (1)	0.038 (1)
p-Cl	0.23	0.11	0.26	0.073 ± 0.006 (2)	0.032 ± 0.001 (2)
m-CH$_3$O	0.12	0.05	0.28	0.048 (1)	0.043 ± 0.004 (3)
p-F	0.06	-0.07	0.14	0.044 (1)	0.014 (1)
H	0.00	0.00	0.30	0.060 ± 0.006 (3)	0.047 ± 0.000 (2)
p-*t*-Bu	-0.20	-0.26	0.30	0.070 ± 0.002 (3)	0.046 ± 0.005 (3)
p-CH$_3$O	-0.27	-0.78	0.13	0.044 (1)	*d*

[a] Sensitizer-solvent 0.35 mol fraction acetone in *tert*-butyl alcohol. [b] Substituent constants (σ = Hammett constants and σ^+ = Brown–Okamoto constants) are taken from ref 20 and 21. [c] Calculated as moles of substituted benzyl radical/einstein. [d] Not measured. [e] Products involving solvolysis at trifluoromethyl group were not detected. [f] Measured at substrate concentrations where solvolysis quantum yields were at a maximum. Number in parentheses indicates number of replications.

Table VI. Quantum Yields for Direct Irradiations of Substituted Benzyl Chlorides in *tert*-Butyl Alcohols

	substituent constant[a]		irradiation wavelength, nm	quantum yield[e]		
substituent	σ	σ^+		ArCH$_2$O-*t*-Bu	(ArCH$_2$)$_2$[c]	ArCH$_2$CH$_2$C(CH$_3$)$_2$OH
p-CF$_3$[b]	0.54	0.61	254	0.095 ± 0.003 (4)	0.13 ± 0.01 (4)	0.097 ± 0.004 (3)
m-CF$_3$[b]	0.43	0.52	254	0.12 ± 0.00 (3)	0.13 ± 0.00 (3)	0.065 ± 0.009 (3)
p-CH$_3$CO	0.50	0.57	254	0.23 ± 0.04 (4)	<0.01	0.029 (1)
p-CH$_3$CO	0.50	0.57	300	0.37 ± 0.00 (2)	<0.01	0.017 ± 0.001 (2)
p-Cl	0.23	0.11	254	0.065 ± 0.004 (7)	*d*	*d*
m-CH$_3$O	0.12	0.05	254	0.10 ± 0.01 (3)	0.051 ± 0.001 (2)	0.055 ± 0.003 (2)
p-F[b]	0.06	-0.07	254	0.093 ± 0.002 (2)	0.072 ± 0.002 (2)	0.078 ± 0.001 (2)
H	0.00	0.00	254	0.12 ± 0.00 (2)	0.090 ± 0.000 (2)	0.053 ± 0.001 (2)
p-*t*-Bu	-0.20	-0.26	254	0.095 ± 0.000 (2)	*d*	0.095 ± 0.005 (2)
p-CH$_3$O	-0.27	-0.78	254	0.051 ± 0.002 (5)	0.050 ± 0.008 (4)	0.067 ± 0.005 (5)

[a] Substituent constants (σ = Hammett constants and σ^+ = Brown–Okamoto constants) are taken from ref 20 and 21. [b] Solvent was 3.8 M acetonitrile in *tert*-butyl alcohol. [c] Calculated as moles of substituted benzyl radical/einstein. [d] Not measured. [e] Number in parentheses indicates number of replications.

solvolysis quantum yields were at a maximum.

Just as with benzyl chloride itself, the principal products of acetone sensitization of the substituted benzyl chlorides were the corresponding *tert*-butyl ethers and alcohols, with small amounts of *sym*-diarylethanes also being produced. This was true regardless of the substituent on the aromatic ring. For the direct irradiations, the quantum yields for solvolysis were substantially lower than those of sensitized irradiations and were, with the exception of the *p*-acetyl derivative (which is discussed below), smaller than the homolysis quantum yields. Thus it would appear that, in general, triplet states produced by sensitization favor heterolysis, whereas the excited states produced as a result of direct light absorption disfavor heterolysis compared with homolysis.

Zimmerman and Sandel[2] observed that *m*-methoxybenzyl acetate, upon direct irradiation, hydrolyzed in aqueous dioxane with a quantum yield of 0.13 and that the corresponding quantum yield for the *p*-methoxy derivative was only 0.016. We observe, similarly, that *m*-methoxybenzyl chloride, either upon direct irradiation or upon sensitization, is more efficient than the *p*-methoxy isomer in alcoholysis, although the effect is not nearly so dramatic (quantum yield doubled). Zimmerman and Sandel suggested that this result may be a reflection of electron distributions in the first excited states of the benzyl derivatives, and their calculations further indicated that, in the first excited state, *m*-methoxybenzyl cation is more stable than the *p*-methoxy cation relative to their respective acetates. In view of the fact that there is no evidence that excited-state cations are produced[2] and that they are certainly not probable in the reactions with the relatively low-energy triplet sensitizers, there may be need for other explanations. One possible explanation may simply be the fact that the *p*-methoxybenzyl radical is formed much more readily than its *m*-methoxy isomer, but our data exclude this.

The data in Tables V and VI suggest that there is no simple correlation between quantum yields and either σ or σ^+. There is perhaps no reason to anticipate such a correlation, as the quantum yield is not the result of one rate constant, but is, of course, in its most simple form, the quotient of the *rate* of transformation of excited state to the product-determining intermediate divided by the sum of all of the *rates* of reaction of the excited state. When all of the product arises from the same excited state, it is possible to determine rate constants for product formation from excited state if the lifetimes of the excited states can be measured. A method to measure such lifetimes has been described recently[22] by workers in this laboratory, and experiments on the compounds in Table V are under way. It will be of obvious interest to learn whether there is a correlation between substituent constants and such rate constants.

Let us consider the question of whether the direct irradiation solvolysis involves transformation of the singlet excited state directly to cation or whether it is first transformed, in part at least, by intersystem crossing to a triplet state which then is the progenitor of the benzylic cation. Quantum-yield data for solvolysis allow either choice (or a combination) as, in all cases except that of *p*-acetyl, the quantum yields of the direct irradiations are substantially lower than those of the sensitized irradiations.

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(22) Ilenda, C. S.; Daughenbaugh, R. J.; Cristol, S. J. *Mol. Photochem.* 1976, 7, 287.

(Parenthetically, this is not true for the radical products.) A possible test of this, involving triplet counting,[23] is in progress and will be reported later.

It should be noted that *p*-acetylbenzyl chloride exhibited a wavelength dependence in direct irradiation. That is, the quantum yield of ether formation was higher at 300 nm than at 254 nm. In addition, the quantum yields are much higher than for other substituents and may be a reflection of the enhanced intersystem crossing ability of ketones.[24] Thus, for this compound the intersystem crossing choice seems plausible. Other explanations are possible and will be discussed in a later paper.

When benzyl chloride, *m*-methoxybenzyl chloride, and *p*-chlorobenzyl chloride were irradiated at 350 nm in 20% acetonitrile in *tert*-butyl alcohol, with benzophenone as sensitizer, the quantum yields for ether formation were found to be 0.003, 0.016, and 0.004, respectively. On the other hand, acetophenone has been reported[11] to be an efficient sensitizer. This means that for efficient photosensitization of solvolysis a triplet energy greater than 69 kcal/mol[25] is required.

It is well-known[26] that the addition of salts increases the rate constants for solvolysis of alkyl halides in protic solvents, and it was of interest to see whether this might be true for photosolvolysis as well. Benzyl chloride was found to solvolyze in 0.35 mol fraction acetone in *tert*-butyl alcohol at 130 °C, and the rate of formation of benzyl *tert*-butyl ether was found to increase about sevenfold when lithium *p*-toluenesulfonate (0.17 M) was added.

On the other hand, photosolvolysis at 300 nm of benzyl chloride in 0.24 mol fraction acetone–*tert*-butyl alcohol in the presence of 0.53 M lithium perchlorate[27] gave product-formation yields slightly less (~90%) than those without the added salt. Similarly, the efficiency of solvolysis resulting from direct irradiation at 254 nm in *tert*-butyl alcohol was unaffected by 0.34 M lithium perchlorate. There clearly is no significant salt effect in these photosolvolyses.

It is difficult to conclude that the presence of lithium perchlorate should not have a large effect on the rate constant (to increase it) for any process that involves transformation of a neutral species into ion pairs or pairs of ions,[29] and that any corresponding effect on a homolysis should be much smaller. If the quantum yield for solvolysis were a reflection of a competition between excited-state decay to an ion pair or to a radical pair, or of a competition of radical pair decay modes to separated radicals or to ion pairs, or of ion-pair return to ion-pair dissociation, one might anticipate an increase in quantum yield with added salt, which was, of course, not observed.

Two tentative explanations seem reasonable to rationalize our failure to observe a salt effect. One is that there is no ion-pair return in this system and that all of the excited-state species which are constitutionally capable of heterolysis already undergo heterolysis. Put another way, if the fraction of excited molecules which solvolyze is, for one reason or another, substantially all that can solvolyze, increasing the rate of their solvolytic process will not increase the fraction of excited molecules which do solvolyze. An alternative, although perhaps connected, explanation is that the excited states (or at least those leading to solvolysis) are highly dipolar (or zwitterionic diradicals[1]), so that the rate of formation of ion pairs may only be mildly affected by added salts. Again, salt effects on lifetimes, which would lead to rate constants for these reactions, are needed but at present have not been measured.

Experimental Section

General Procedures. All melting points were determined with a Thomas-Hoover apparatus. NMR spectra were obtained by using either a Varian Associates EM-390 or an EM-360 instrument. Chemical shifts are reported in parts per million relative to tetramethylsilane. Mass spectra were obtained using a Varian MAT CH-5 spectrometer. Gas chromatography–mass spectrometry (GC–MS) results were obtained from a Hewlett-Packard 5982A GC–MS data system. Irradiations were carried out in the apparatus described earlier[30] by using either 254-, 300-, or 350-nm lamps. Preparative irradiations were carried out by using a water-jacketed quartz immersion well with a 450-W medium-pressure Hanovia Type-L lamp. The gas chromatography was done on a Hewlett-Packard 5754B gas chromatograph linked to a Hewlett-Packard 3380S integrator. The chromatographic columns used were a 6 ft × 0.125 in. stainless-steel 10% UC-W98 on 80/100 mesh Chromosorb W column (column A) and a 3 m × 3 mm aluminum 5% QF-1 on 100/120 mesh Chromosorb W column (column B). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. UV spectra were obtained with a Beckman Model 25 UV-VIS spectrometer.

Materials. *p*-Chlorobenzyl chloride and *p*- and *m*-fluorobenzyl chlorides were obtained from Aldrich and were distilled in vacuo before using. Benzyl chloride was obtained from Matheson, Coleman and Bell and was used without purification. *m*-Methoxybenzyl chloride,[31] *p*-methoxybenzyl chloride,[32] *p*-*tert*-butylbenzyl chloride,[33] *p*-acetylbenzyl chloride,[34,35] *m*-(trifluoromethyl)benzyl chloride,[36] and *p*-(trifluoromethyl)benzyl chloride[37] were synthesized, substantially as described in the literature, and distilled before use. The acetone was Fisher spectral grade. *tert*-Butyl alcohol was analytical reagent quality purchased from Baker or Mallinckrodt. Acetonitrile was Eastman spectrograde. All other compounds mentioned in this paper were from Aldrich unless otherwise specified.

Degassing. All samples for quantitative work were degassed by the freeze–pump–thaw method several times at 2×10^{-5} torr.

Actinometry. Cyclopentanone actinometry[38,39] was used at 254 and 300 nm to measure the light flux of the lamps. Benzophenone–benzhydrol actinometry[25] was used for irradiations at 350 nm.

Acetone-Sensitized Irradiations. A range of concentrations of each chloride in acetone–*tert*-butyl alcohol was made up in which the acetone absorbed at least 99% of the light. After being degassed, the samples were irradiated (in Pyrex tubes) for a period of time which would give about 5% (or lower) conversion of the starting chloride. The samples were then analyzed by gas chromatography using column A and an appropriate internal standard. Column B was used in the alcohol analyses. Each sample was injected at least twice depending upon reproducibility of integration. All starting chlorides were checked for thermal solvolysis

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(23) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

(24) Turro, N. J. "Molecular Photochemistry"; W. A. Benjamin: New York, 1967; p 133.

(25) Murov, S. L. "Handbook of Photochemistry"; Marcel Decker: New York, 1973.

(26) See, for example, Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2763.

(27) We used lithium *p*-toluenesulfonate in the thermal solvolysis, in view of the possibility of danger in the use of perchlorates in alcohol or alcohol–ketone mixtures at elevated temperatures. It is well-known[28] that lithium perchlorate is at least as effective as the toluenesulfonate as an added salt.

(28) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2780.

(29) Hughes, E. D.; Ingold, C. K.; Patel, C. S. *J. Chem. Soc.* **1933**, 526.

(30) Cristol, S. J.; Micheli, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 850.

(31) Pshorr, von R. *Justus Liebigs Ann. Chem.* **1912**, *391*, 44.

(32) Mohammad, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1971**, *93*, 2709.

(33) Levy, A.; Darzens, G. *C. R. Hebd. Seances Acad. Sci.* **1934**, *199*, 1426.

(34) Bergmann, E. D.; Blum, J. *J. Org. Chem.* **1959**, *24*, 549.

(35) Schmid, L.; Swoboda, W.; Wichtl, M. *Monatsh. Chem.* **1952**, *83*, 185.

(36) Fuchs, R.; Carlton, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 104.

(37) Streitwieser, Jr., A.; Perrin, C. *J. Am. Chem. Soc.* **1964**, *86*, 4938.

(38) Dunion, P.; Trumbore, C. N. *J. Am. Chem. Soc.* **1965**, *87*, 4211.

(39) Analysis carried out by using column A.

Table VII

compound irradiated	type of irradiation	mass spectrum, *m/e* (rel int)	irradiation product
$PhCH_2Cl^a$	direct	164 (4), 149 (23), 91 (100), 57 (23)	$PhCH_2OC(CH_3)_3$
		149 (7.8), 146 (48), 131 (57), 91 (72), 59 (100)	$PhCH_2CH_2C(CH_3)_2OH$
		182 (30), 91 (100), 65 (13)	$PhCH_2CH_2Ph$
$PhCH_2Cl^a$	sensitized	165 (0.2), 164 (2.7), 149 (18), 91 (100), 57 (25)	$PhCH_2OC(CH_3)_3$
		148 (37), 105 (46), 91 (100), 43 (75)	$PhCH_2CH_2COCH_3$
		146 (51), 131 (61), 91 (99), 59 (100)	$PhCH_2CH_2C(CH_3)_2OH$
		182 (33), 91 (100), 65 (13)	$PhCH_2CH_2Ph$
p-$CH_3OC_6H_4CH_2Cl$	sensitized	242 (11.6), 121 (100)	$(p$-$CH_3OC_6H_4CH_2)_2$
p-$CH_3OC_6H_4CH_2Cl$	direct	242 (12), 121 (100)	$(p$-$CH_3OC_6H_4CH_2)_2$
		194 (18), 176 (24), 161 (97), 121 (100), 59 (40)	p-$CH_3OC_6H_4CH_2CH_2C(CH_3)_2OH$
m-$CH_3OC_6H_4CH_2Cl$	direct	194 (17), 121 (100), 109 (23), 57 (22)	m-$CH_3OC_6H_4CH_2OC(CH_3)_3$
		161 (36), 121 (100), 59 (50), 32 (36), 28 (64)	m-$CH_3OC_6H_4CH_2CH_2C(CH_3)_2OH$

[a] All of the compounds were confirmed by co-injection of authentic sample.

Table VIII

band	NMR, ppm	*m/e*	products
1	4.59 (s), 2.98 (s)	318, 159	$(m$-$CF_3C_6H_4CH_2)_2$
			m-$CF_3C_6H_4CH_2Cl$
2	4.48 (s), 1.30 (s)	217, 159, 57	m-$CF_3C_6H_4CH_2OC(CH_3)_3$
3	4.78 (s), 2.86 (m), 2.13 (s)	232, 217, 216, 214, 176	m-$CF_3C_6H_4CH_2OH$
	1.26 (s)	173, 159, 59, 43	m-$CF_3C_6H_4CH_2CH_2C(CH_3)_2OH$
			m-$CF_3C_6H_4CH_2CH_2COCH_3$
4	4.78 (s), 1.26 (s)	214, 176, 159, 59, 43	m-$CF_3C_6H_4CH_2OH$
			m-$CF_3C_6H_4CH_2CH_2C(CH_3)_2OH$

in the Rayonet apparatus and in the GC analysis. Only with *p*-methoxybenzyl chloride did solvolysis occur during the GC analysis. In this case the *tert*-butyl alcohol solvent was removed by distillation at reduced pressure, and hexane was substituted. A known solution of the expected *tert*-butyl ether and the internal standard was made up and injected on the gas chromatograph to obtain a relative response factor.[40] In this manner, quantum yields were obtained as a function of starting chloride concentration. Other product quantum yields, except for bibenzyl, were obtained using theoretical relative response factors.[41]

Direct Irradiations. Solutions containing each chloride in *tert*-butyl alcohol or acetonitrile–*tert*-butyl alcohol were prepared so that the concentrations were high enough to absorb substantially all of the light. Samples were irradiated at 300 nm in Pyrex and at 254 nm in Vycor tubes. The solutions were irradiated to 5% conversion or less. The samples were analyzed in a manner similar to that described for the acetone-sensitized irradiation. Some of the peaks were identified by relative retention time (rrt) vis-à-vis the starting chloride and by comparing this to the rrt of compounds formed in the irradiation of benzyl chloride.

GC–MS Analysis of Benzyl Chloride, *p*-Methoxybenzyl Chloride, and *m*-Methoxybenzyl Chloride Irradiations. The indicated chlorides were irradiated (sensitized and direct) to high conversions and then analyzed by GC–MS. The results are given in Table VII.

Sensitized Irradiation of *m*-(Trifluoromethyl)benzyl Chloride. *m*-(Trifluoromethyl)benzyl chloride (425 mg, 2.19 mmol) was dissolved in 0.35 mol fraction acetone in *tert*-butyl alcohol. This solution, in a Pyrex test tube, was irradiated at 300 nm in the Rayonet photoreactor without a merry-go-round for 42 h. GC analysis using column A indicated about 80% loss of starting material. The solvent was removed as carefully as possible from 50 mL of the irradiated solution by vacuum distillation. The residue was then chromatographed by preparative TLC using 3% ether in pentane as the eluting solvent. Three bands along with the origin were extracted with ether and labeled band 1, 2, 3, and 4 in order of decreasing R_f. Bands 1 and 2 contained nearly all of the material by weight. ^1H NMR ($CDCl_3$) absorptions for each band from 3 to 6 ppm, along with other selected absorptions, mass spectrum results, and an identification of compounds present in each band, appear in Table VIII.

Isolation of 4-Phenyl-2-methyl-2-butanol from a Direct Irradiation of Benzyl Chloride. Benzyl chloride (10 g, 0.079 mol) was dissolved in 275 mL of *tert*-butyl alcohol and irradiated in the Hanovia apparatus for 6 days, after which the *tert*-butyl alcohol was removed by evaporation. The resulting residue was chromatographed on alumina and distilled [bp 80 °C (0.7 mm)], yielding a material whose ^1H NMR was identical with that of authentic 4-phenyl-2-methyl-2-butanol[42] (from Aldrich) and whose mass spectrum was consistent with that compound.

Product Yield of Sensitized Irradiation of Benzyl Chloride. Benzyl chloride (73.1 mg, 0.578 mmol) was diluted to 10 mL with 0.35 mol fraction acetone in *tert*-butyl alcohol. Three samples, each containing 2 mL of solution in Pyrex test tubes, were irradiated at 300 nm. The samples were analyzed by gas chromatography, using column A, for benzyl *tert*-butyl ether, bibenzyl, benzyl chloride, and 4-phenyl-2-butanone. In addition, benzyl alcohol was analyzed by using column B.

Product Yield of Direct Irradiation of Benzyl Chloride. Benzyl chloride (95.5 mg, 0.755 mmol) was diluted to 10 mL with *tert*-butyl alcohol. Three 2-mL samples, each in a Vycor tube, were irradiated at 254 nm and analyzed by GC as described in the preceding experiment.

Benzophenone-Sensitized Irradiations. Benzyl chloride, *m*-methoxybenzyl chloride, and *p*-chlorobenzyl chloride were irradiated (350 nm) at concentrations which gave ϕ_{max} in acetone-sensitized irradiations. These concentrations were 0.089, 0.10, and 0.12 M, respectively.

Thermal Solvolyses—"Salt Effect". Two milliliters of a solution of benzyl chloride (0.048 M) in 0.35 mol fraction acetone in *tert*-butyl alcohol and 2 mL of a solution containing 0.048 M benzyl chloride and 0.17 M lithium *p*-toluenesulfonate in the same solvent were placed in screw-cap vials. These vials were placed in an oil bath for 18 h at about 130 °C and were analyzed by GC.

Photochemical "Salt Effects". A solution of 0.07 M benzyl chloride and 0.53 M anhydrous lithium perchlorate in 0.24 mol fraction acetone in *tert*-butyl alcohol and another without lithium perchlorate were prepared. The two solutions were irradiated at 300 nm for 17, 39, and 64 h. In each case, the quantum yield of benzyl *tert*-butyl ether was 10% higher in the absence of lithium perchlorate than in its presence. Analysis for benzyl alcohol in the sample irradiated for 64 h indicated that the amounts of benzyl alcohol present, with and without lithium perchlorate, were not different enough to account for not observing a salt effect for the formation of the ether.

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(40) Relative response factor = [(area of internal standard)/(area of ether)](concentration of ether)/(concentration of internal standard).

(41) David, D. J. "Gas Chromatographic Detectors"; Wiley: New York, 1974.

(42) Klages, A. *Ber.* **1904**, *37*, 2314.

Table IX. Effect of Water and Acetone Concentrations on Quantum Yields of Photosolvolysis of Benzyl Chloride in *tert*-Butyl Alcohol–Acetone Mixtures on Irradiation at 300 nm

mol fraction acetone	total [H_2O], M	quantum yield of $PhCH_2O$-*t*-Bu	quantum yield of $PhCH_2OH$
0.35	0.067	0.28 ± 0.02	0.047 ± 0.006
0.35	0.15	0.28 ± 0.01	0.05 ± 0.01
0.84	0.18	0.11	0.14 ± 0.01
0.84	0.35	0.11	0.16 ± 0.01
1.0	0.22		0.29 ± 0.02
1.0	0.43		0.26 ± 0.01

Determination of the Water Content in Acetone. Using the method of MacDonald and Brady,[43] we found that the acetone contained 0.4% water (w/v).

Analysis for Benzyl Alcohol and Benzyl *tert*-Butyl Ether after Irradiation. Samples containing 0.2 M benzyl chloride and 0.35, 0.84, and 1.0 mol fraction acetone in *tert*-butyl alcohol were prepared. Another set was made up just like the above except that 15 mg, 32 mg, and 37 mg of water were added, respectively. The above solutions were irradiated at 300 nm and analyzed by GC using column B. Results are given in Table IX.

Syntheses of Benzyl *tert*-Butyl Ethers. Benzyl *tert*-butyl ether[44] and *p*-methoxybenzyl *tert*-butyl ether[45] were purified by distillation. **Method A.** Substituted benzyl alcohol, 2 mL of concentrated sulfuric acid, and 75 mL of *tert*-butyl alcohol were mixed together. After a few days the *tert*-butyl alcohol was removed and the resulting residue taken up in ether. The solution was extracted twice with water, once with saturated sodium bicarbonate, and once with brine. The organic layer was distilled in vacuo to remove solvent and the resulting material chromatographed on silica gel.

***p*-*tert*-Butylbenzyl *tert*-Butyl Ether.** *p*-*tert*-Butylbenzyl alcohol (2 g, 0.012 mol) was converted to *p*-*tert*-butylbenzyl *tert*-butyl ether using the above method and then distilled: bp 54 °C (0.05 mm); ^1H NMR ($CDCl_3$) δ 1.29 (s, s, 18 H, CH_3), 4.43 (s, 2 H, CH_2), 7.37 (m, 4 H, Ar H); mass spectrum, *m/e* (rel intensity) 220 (37), 147 (100). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.83; H, 11.05.

***m*-Methoxybenzyl *tert*-Butyl Ether.** *m*-Methoxybenzyl chloride (3 g, 0.019 mol) was dissolved in 250 mL of 20% acetone in *tert*-butyl alcohol and irradiated for 1 day in the Hanovia with Pyrex filter. At the end of 1 day, the solvent was removed, and the residue was chromatographed on alumina and then silica gel and finally distilled: bp 74 °C (0.3 mm); ^1H NMR ($CDCl_3$) δ 7.10 (m, 4 H, Ar H), 4.48 (s, 2 H, CH_2), 3.83 (s, 3 H, OCH_3), 1.29 (s, 9 H, CH_3C); mass spectrum, *m/e* (rel intensity) 194 (33), 121 (100), 57 (30). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.96; H, 9.46.

***p*-Acetylbenzyl *tert*-Butyl Ether.** *p*-Acetylbenzyl alcohol (2 g, 0.013 mol) was subjected to the conditions of method A (1-day reaction time) and yielded 0.9 g (34%) of a colorless oil after distillation: bp 80 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 7.98 (d, 2 H, Ar H), 7.48 (d, 2 H, Ar H), 4.53 (s, 2 H, CH_2), 2.59 (s, 3 H, CH_3CO), 1.30 (s, 9 H, CH_3); mass spectrum, *m/e* (rel intensity) 206 (7), 133 (100), 57 (58). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.54; H, 8.86.

***p*-Chlorobenzyl *tert*-Butyl Ether.** *p*-Chlorobenzyl chloride (12.5 g, 0.016 mol) was dissolved in 230 mL of 40% acetone in *tert*-butyl alcohol and irradiated in the Hanovia apparatus with a Pyrex filter. The irradiation was stopped when GC analysis indicated 87% conversion of starting material (using column A). The solvent was removed, and the sample was chromatographed on silica gel and then on alumina. The purest fraction was distilled to yield *p*-chlorobenzyl *tert*-butyl ether: mp 31–33 °C (lit.[43] mp 34–35 °C).

***m*-(Trifluoromethyl)benzyl *tert*-Butyl Ether.** *m*-(Trifluoromethyl)benzyl alcohol (1.5 g, 0.0085 mol) was treated under the conditions of method A (7-day reaction time) and yielded 1 g (51%) of a colorless oil after distillation: bp 50 °C (0.8 mm); ^1H NMR ($CDCl_3$) δ 7.60 (m, 4 H, Ar H), 4.53 (s, 2 H, CH_2), 1.30 (s, 9 H, CH_3); mass spectrum, *m/e* (rel intensity) 232 (small), 159 (100), 57 (25). Anal. Calcd for $C_{12}H_{15}F_3O$: C, 62.06; H, 6.51. Found: C, 61.81; H, 6.69.

***p*-(Trifluoromethyl)benzyl *tert*-Butyl Ether.** *p*-(Trifluoromethyl)benzyl alcohol (1.5 g, 0.0085 mol) was reacted under the conditions of method A (2-day reaction time), yielding a colorless oil after distillation: bp 50 °C (1 mm); ^1H NMR ($CDCl_3$) δ 7.60 (q, 4 H, Ar H), 4.56 (s, 2 H, CH_2), 1.30 (s, 9 H, CH_3); mass spectrum, *m/e* (rel intensity) 232 (0.9), 159 (100), 57 (50). Anal. Calcd for $C_{12}H_{15}F_3O$: C, 62.06; H, 6.51. Found: C, 62.36; H, 6.75.

***p*-Fluorobenzyl *tert*-Butyl Ether.** *p*-Fluorobenzyl alcohol (2 g, 0.011 mol) was treated according to method A and distilled to yield 0.9 g (31%) of a colorless oil: bp 39 °C (0.4 mm); ^1H NMR ($CDCl_3$) δ 7.30 (m, 2 H, Ar H), 7.00 (m, 2 H, Ar H), 4.37 (s, 2 H, CH_2), 1.28 (s, 9 H, CH_3); mass spectrum, *m/e* (rel intensity) 182 (7), 109 (100), 57 (32). Anal. Calcd for $C_{11}H_{15}FO$: C, 72.50; H, 8.30. Found: C, 72.31; H, 8.29.

***m*-Fluorobenzyl *tert*-Butyl Ether.** *m*-Fluorobenzyl alcohol (2 g, 0.011 mol) was treated according to method A and distilled to yield a colorless oil: bp 34 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 7.18 (m, 4 H, Ar H), 4.47 (s, 2 H, CH_2), 1.29 (s, 9 H, CH_3); mass spectrum, *m/e* (rel intensity) 182 (5), 109 (100), 57 (31). Anal. Calcd for $C_{11}H_{15}FO$: C, 72.50; H, 8.30. Found: C, 72.25; H, 8.35.

4,4′-Diacetylbibenzyl was synthesized according to the method of Lutz et al.[46]

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Registry No. $PhCH_2Cl$, 100-44-7; $PhCH_2O$-*t*-Bu, 3459-80-1; $PhCH_2OH$, 100-51-6; $PhCH_2CH_2Ph$, 103-29-7; $PhCH_2CH_2COCH_3$, 2550-26-7; $PhCH_2CH_2C(CH_3)_2OH$, 21438-74-4; *p*-$CF_3C_6H_4CH_2Cl$, 939-99-1; *m*-$CF_3C_6H_4CH_2Cl$, 705-29-3; *p*-$CH_3COC_6H_4CH_2Cl$, 54589-56-9; *m*-$FC_6H_4CH_2Cl$, 456-42-8; *p*-$ClC_6H_4CH_2Cl$, 104-83-6; *m*-$CH_3OC_6H_4CH_2Cl$, 41908-12-7; *p*-$FC_6H_4CH_2Cl$, 352-11-4; *p*-*t*-$BuC_6H_4CH_2Cl$, 19692-45-6; *p*-$CH_3OC_6H_4CH_2Cl$, 824-94-2; *p*-$CF_3C_6H_4CH_2O$-*t*-Bu, 72390-16-0; *m*-$CF_3C_6H_4CH_2O$-*t*-Bu, 72390-17-1; *p*-$CH_3COC_6H_4CH_2O$-*t*-Bu, 72390-18-2; *m*-$FC_6H_4CH_2O$-*t*-Bu, 72402-80-3; *p*-$ClC_6H_4CH_2O$-*t*-Bu, 56636-79-4; *m*-$CH_3OC_6H_4CH_2O$-*t*-Bu, 72390-19-3; *p*-$FC_6H_4CH_2O$-*t*-Bu, 72390-20-6; *p*-*t*-$BuC_6H_4CH_2O$-*t*-Bu, 72390-21-7; *p*-$CH_3OC_6H_4CH_2O$-*t*-Bu, 56636-80-7; *p*-$CF_3C_6H_4CH_2CH_2C_6H_4$-*p*-CF_3, 42134-71-4; *m*-$CF_3C_6H_4CH_2CH_2C_6H_4$-*m*-CF_3, 72390-22-8; *p*-$CH_3COC_6H_4CH_2CH_2C_6H_4$-*p*-$COCH_3$, 793-06-6; *m*-$FC_6H_4CH_2CH_2C_6H_4$-*m*-F, 351-22-4; *p*-$ClC_6H_4CH_2CH_2C_6H_4$-*p*-Cl, 5216-35-3; *m*-$CH_3OC_6H_4CH_2CH_2C_6H_4$-*m*-$OCH_3$, 72390-23-9; *p*-$FC_6H_4CH_2CH_2C_6H_4$-*p*-F, 458-76-4; *tert*-butyl alcohol, 75-65-0; *p*-*t*-$BuC_6H_4CH_2CH_2C_6H_4$-*p*-*t*-Bu, 22927-07-7; *p*-$CH_3OC_6H_4CH_2CH_2C_6H_4$-*p*-$OCH_3$, 1657-55-2; *p*-$CF_3C_6H_4CH_2OH$, 349-95-1; *m*-$CF_3C_6H_4CH_2OH$, 349-75-7; *m*-$FC_6H_4CH_2OH$, 456-47-3; *p*-$ClC_6H_4CH_2OH$, 873-76-7; *m*-$CH_3OC_6H_4CH_2OH$, 6971-51-3; *p*-$FC_6H_4CH_2OH$, 459-56-3; *p*-*t*-$BuC_6H_4CH_2OH$, 877-65-6; *p*-$CF_3C_6H_4CH_2CH_2C(CH_3)_2OH$, 14248-40-9; *m*-$CF_3C_6H_4CH_2CH_2C(CH_3)_2OH$, 72390-24-0; *p*-$CH_3COC_6H_4CH_2CH_2C(CH_3)_2OH$, 72390-25-1; *m*-$CH_3OC_6H_4CH_2CH_2C(CH_3)_2OH$, 72390-26-2; *p*-$FC_6H_4CH_2CH_2C(CH_3)_2OH$, 63416-82-0; *p*-*t*-$BuC_6H_4CH_2CH_2C(CH_3)_2OH$, 72390-27-3; *p*-$CH_3OC_6H_4CH_2CH_2C(CH_3)_2OH$, 14305-29-4; *m*-$CF_3C_6H_4CH_2CH_2COCH_3$, 57132-19-1.

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(43) MacDonald, J. C.; Brady, C. A. *Anal. Chem.* **1975**, *47*, 947.

(44) Rüchardt, C.; Grundmeier, M. *Chem. Ber.* **1975**, *108*, 2448.

(45) Pratt, E. F.; Erickson, P. W. *J. Am. Chem. Soc.* **1956**, *78*, 76.

(46) Lutz, R. E.; Allison, R. K.; Ashburn, G.; Bailey, P. S.; Clark, M. T.; Codington, J. F.; Deinet, A. J.; Freek, J. A.; Jordon, R. H.; Leake, N. H.; Martin, T. A.; Nicodemus, K. C.; Rowlett, Jr., R. J.; Shearer, Jr., N. H.; Smith, J. D.; Wilson, J. W., III. *J. Org. Chem.* **1947**, *12*, 617.