which would be much better solvated by TFE through London dispersion forces than by water. Addition of TFE would decrease $\gamma_\ddagger$ relative to water causing the $\gamma_{H^+}/\gamma_\ddagger$ ratio to increase. Therefore, for an A1 mechanism the solvation effect of TFE on both H^+ and the transition state is to cause $\gamma_{H^+}/\gamma_\ddagger$ to increase.

The situation should be similar in the AS_E2 case. The effect on γ_{H^+} would be identical as above. The AS_E2 transition state for ethyl vinyl ether would be structurally related to that for diethyl acetal—the difference being a water molecule and an ethanol molecule, respectively. There is considerable charge dispersal in both cases. The expectation would be that TFE would have the same solvation effect on $\gamma_\ddagger$ for AS_E2 as it did for A1. One would predict, therefore, that addition of TFE would increase γ_{H^+} and decrease $\gamma_\ddagger$ causing the $\gamma_{H^+}/\gamma_\ddagger$ ratio to increase.

It has been argued[3] that dimethyl sulfoxide solvates H^+ better than water, giving rise to a decrease in γ_{H^+}. The same argument probably applies to dioxane which can only function as a hydrogen bond acceptor. The opposite argument was applied above for TFE. It appears that the solvent effect on both A1 and AS_E2 reactions can be predicted qualitatively by considering the solvent effect on γ_{H^+}, and the effect on γ_{H^+} can be surmised by looking at the H^+ solvating ability of the organic solvent with respect to that of water.

Experimental Section

Diethyl acetal, ethyl vinyl ether, and 2,2,2-trifluoroethanol were obtained commercially (Aldrich Chemical Co.), were distilled once, and were used without further purification. An aqueous stock solution of perchloric acid was prepared and then standardized by the usual analytical techniques.[7] A series of water/TFE solutions of known acid concentration were then prepared.

The rate of hydrolysis of both diethyl acetal and ethyl vinyl ether was followed by monitoring the buildup of acetaldehyde at 270 nm with time. The reactions were initiated by injecting 30–50 μL of substrate into 3 mL of reaction solution contained in a spectrophotometer cell. All solutions and the spectrophotometer cell holder were thermostated at 25.0 ± 0.2 °C. All reactions were followed for at least 3 half-lives. The pseudo-first-order rate constants could be replicated with discrepancies of no more than 10%. In the case of ethyl vinyl ether the rate was also followed by monitoring the disappearance of the vinyl ether at 236 nm. Identical rate constants were obtained by whichever method was used. The second-order rate constants were calculated from the pseudo-first-order rate constants and the acid concentration.

The molar activity coefficients of diethyl acetal were determined from the distribution ratios in the two-phase system of cyclohexane/water–TFE at 25 ± 1 °C. The acetal concentration in the water–TFE layer was determined by adding acid and titrating the released aldehyde by the method of Siggia and Maxcy.[8] The concentration in the cyclohexane layer was calculated by the difference between the total amount of acetal added and the amount in the water–TFE. The activity coefficient, γ_S, relative to pure water as the standard state was then calculated by dividing the distribution ratio for cyclohexane/water by the distribution ratio for each cyclohexane/water–TFE system. This method depended on the insolubility of water and especially TFE in cyclohexane. Since TFE was the most likely candidate, its presence in cyclohexane was determined. Cyclohexane and TFE were shaken together. Gas chromatographic analysis of the cyclohexane layer using a column of 10% Carbowax on 60/80 Chrom W resulted in no detection of TFE in the cyclohexane.

Acknowledgment. This paper was written while R.E. was on sabbatical leave, and he wishes to express his appreciation to Dr. Vernon Parker and the Organic Chemistry Institute, Norwegian Institute of Technology, Trondheim, for their hospitality and to thank the Norwegian Marshall Fund for a fellowship.

Registry No. Ethyl vinyl ether, 109-92-2; diethyl acetal, 105-57-7; proton, 12586-59-3.

---

[7] Kolthoff, I. M.; Sandell, E. B. "Textbook of Quantitative Inorganic Analysis"; The Macmillan Co.: New York, 1952.

[8] Siggia, S.; Maxcy, W. *Anal. Chem.* **1947**, *19*, 1023.

Photochemical Reactions in the Benzophenone/*tert*-Butyl Alcohol/Oxygen System. Some Unexpected Results

Jean-Claude Gramain* and Roland Remuson

Laboratoire de Chimie et Biochimie des Substances Naturelles. Equipe de Recherche Associée au CNRS 392, Université de Clermont-II, B.P. 45, 63170 Aubiere, France

Received June 26, 1984

tert-Butyl alcohol is often used as a solvent for photochemical reactions (especially photoreductions) due to its inertness. Its primary aliphatic hydrogen atoms are not expected to be readily abstracted by a carbonyl triplet state. However, it has been reported that aromatic ketones may be photoreduced by *tert*-butyl alcohol in the absence of any more reactive hydrogen donors.[1] Thus, irradiation of a solution of benzophenone in *tert*-butyl alcohol (0.5 g in 150 mL) for 2.5 h (Hanovia 250-W, medium pressure mercury lamp, Pyrex) in the absence of oxygen led to the complete disappearance of benzophenone.[1d] The benzophenone–*tert*-butyl alcohol adduct 1 was isolated in a 26% yield[1c] (Scheme I).

This unexpected result shows that the photoreduction of benzophenone by *tert*-butyl alcohol is a rather fast process.[2] We reported also that during long irradiations of nitrogen containing heterocycles in the presence of benzophenone and *oxygen* products derived either from benzophenone or from *tert*-butyl alcohol were formed.[3] These findings prompted us to undertake a detailed study of the mechanism of formation of these side products which could interfere with the main photochemical reaction.

Irradiation (medium pressure mercury lamp, MEDA 400-W, Pyrex) of an oxygen-saturated solution of benzophenone in *tert*-butyl alcohol (150 mL) for 168 h gave the mixture of products shown in Table I. These may be split into three groups according to their origin: (1) products of coupling reactions of radicals resulting from the photoreduction of benzophenone by *tert*-butyl alcohol, (2) products of oxidation of radicals derived from *tert*-butyl alcohol (in particular, a rather important amount of acetone was formed), and (3) products derived from benzophenone by other reactions.

(1) Ph_2CO/*t*-BuOH Coupling Products. 1,1-Diphenylethylene is obtained even though oxygen is present, presumably by fragmentation of the 1,3-diol 1[1c,4] already

---

[1] (a) Lwowski, W.; Mattingly, T. W. *J. Am. Chem. Soc.* **1965**, *87*, 1947. (b) Wubbels, G. G.; Monaco, W. J.; Johnson, D. F.; Meredith, R. S. *Ibid.* **1976**, *98*, 1036. (c) Alexander, D. W.; Prate, A. C.; Tripping, A. E. *Tetrahedron Lett.* **1976**, 2893. (d) Gramain, J. C.; Troin, Y. unpublished results.

[2] The rate constant of reduction of triplet benzophenone by *tert*-butyl alcohol has been determined in CCl_4: $k_r = 5.35 \times 10^4$ mol^{-1} s^{-1}.[10] This value is a hundred times smaller than the rate constant of reduction of triplet benzophenone by isopropyl alcohol ($k_r = 4.10 \times 10^6$ mol^{-1} s^{-1} in the same conditions). Our observation is consistent with these values since in our[1d] and others[1c] experiments *tert*-butyl alcohol is used as a solvent in a very high concentration.

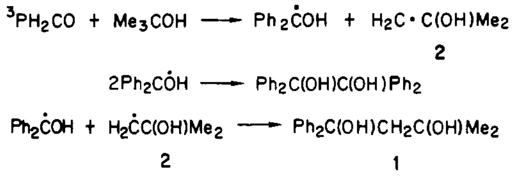
[3] Remuson, R. Doctorate Thesis, Clermont II, University, 1981, No. 287.

0022-3263/85/1950-1120$01.50/0

Table I. Products Resulting from the Irradiation of Benzophenone in Oxygen-Saturated *tert*-Butyl Alcohol (168 h)

product	quantity (mmol)	origin	detection method
benzophenone (initial	11		
benzophenone (final)	6.5		
consumed benzophenone	4.5		
benzene	0.1	Norrish I type fragmentation of Ph_2CO	GC, UV
phenol	0.2		isolated
benzoic acid	2.5		isolated
phenyl benzoate	0.25	Baeyer–Villiger oxidation of benzophenone	isolated
1,1-diphenylethylene	0.6	Ph_2CO/t-BuOH coupling	isolated
acetone	7.5	oxidation of t-BuOH (and Ph_2CO/t-BuOH coupling)	GC, UV
formic acid	0.15	oxidation of t-BuOH	crystalline derivative

Scheme I

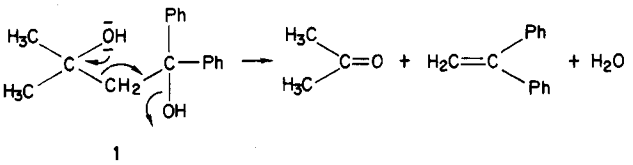


$$^3PH_2CO + Me_3COH \longrightarrow Ph_2\dot{C}OH + H_2\dot{C}\cdot C(OH)Me_2 \quad \mathbf{2}$$

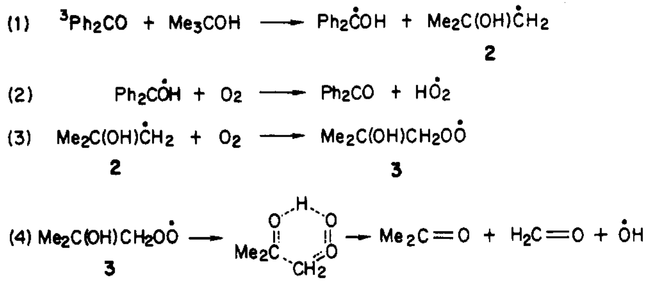
$$2Ph_2\dot{C}OH \longrightarrow Ph_2C(OH)C(OH)Ph_2$$

$$Ph_2\dot{C}OH + H_2\dot{C}C(OH)Me_2 \,(\mathbf{2}) \longrightarrow Ph_2C(OH)CH_2C(OH)Me_2 \,(\mathbf{1})$$

Scheme II



Scheme III



$$(1)\quad ^3Ph_2CO + Me_3COH \longrightarrow Ph_2\dot{C}OH + Me_2C(OH)\dot{C}H_2 \quad \mathbf{2}$$

$$(2)\quad Ph_2\dot{C}OH + O_2 \longrightarrow Ph_2CO + H\dot{O}_2$$

$$(3)\quad Me_2C(OH)\dot{C}H_2 \,(\mathbf{2}) + O_2 \longrightarrow Me_2C(OH)CH_2O\dot{O} \,(\mathbf{3})$$

$$(4)\quad Me_2C(OH)CH_2O\dot{O} \,(\mathbf{3}) \longrightarrow \cdots \longrightarrow Me_2C{=}O + H_2C{=}O + \dot{O}H$$

shown to be formed during the photoreduction of benzophenone by *tert*-butyl alcohol. Formation of 1,1 diphenylethylene must be accompanied by the formation of an equimolar amount of acetone (Scheme II).

(2) *tert*-Butyl Alcohol Oxidation Products. Photoreduction of benzophenone by *tert*-butyl alcohol gives a hydroxy benzhydryl radical and the 2-hydroxy isobutyl radical **2**. In the presence of oxygen the former is reoxidized to give benzophenone.[11] The radical **2** is oxidized to the peroxy radical **3** and the decomposition of **3** (eq 4)[5] gives acetone and formaldehyde which is subsequently oxidized into formic acid (Scheme III).

The formation of the main part of acetone is explained by this mechanism. The amount formed is proportional to the time of irradiation, and the overall reaction does not consume benzophenone. Hence, this side reaction will generally go unnoticed in preparative work since the first step of the workup is the evaporation of the solvent.

(3) Other Products Derived from Benzophenone. The structure of the other products suggests that they derive from a Norrish I type fragmentation of benzophenone leading to PhCO· and Ph· radicals which undergo subsequent reactions. Actinometry measurements give a value of 5×10^{-4} for the quantum yield of this reaction. Therefore, the corresponding products can be only observed during long irradiation times.

Though this particular reaction does not seem to have been studied in detail, a weak EPR signal, attributable to the benzoyl radical, has been observed during photolysis of benzophenone in the gas phase or in a solid matrix at 77 K.[6]

Mechanism (Scheme IV). Biphenyl is not isolated because the very low concentration of phenyl radicals does not favor coupling. Equations 3 and 4 account for the formation of benzene and phenol. The oxidation of the benzoyl radical by oxygen can give perbenzoic acid via a perbenzoxy radical.[7] Some of the benzoic acid found could come from thermal or photochemical decomposition of perbenzoic acid. Phenyl benzoate results from a Baeyer–Villiger type reaction[8] between the perbenzoic acid formed in eq 6 and benzophenone; such a reaction takes place in *tert*-butyl alcohol solution in the absence of irradiation at concentrations similar to those encountered in the photochemical system. The ratio of phenyl benzoate to benzoic acid is consistent with this mechanism.

Scheme IV

$$(1)\ PhCOPh + h\nu \rightarrow PhCO\cdot + Ph\cdot$$

$$(2)\ 2Ph\cdot \rightarrow Ph\text{–}Ph$$

$$(3)\ Ph\cdot + RH \rightarrow PhH + R\cdot$$

$$(4)\ Ph\cdot + O_2 \rightarrow \ldots \rightarrow PhOH$$

$$(5)\ PhCO\cdot + O_2 \rightarrow PhCO_3\cdot$$

$$(6)\ PhCO_3\cdot + RH \rightarrow PhCO_3H + R\cdot$$

Two control experiments substantiate the validity of a low quantum yield Norrish I type fragmentation of benzophenone: (1) in acetonitrile and in the absence of oxygen the irradiation of benzophenone leads to the formation of benzene and benzoin (PhCOCHOHPh), indicating the presence of Ph· and PhCO· radicals; (2) in the same solvent (CH_3CN) and in the presence of oxygen benzoic acid and phenyl benzoate are formed in the same amount as in *tert*-butyl alcohol.

In summary, we have shown that benzophenone undergoes a low quantum yield Norrish I type fragmentation leading to phenyl and benzoyl radicals either in *tert*-butyl alcohol or in acetonitrile. These radicals lead to a variety of compounds whose structure depends on the solvent and the conditions (presence or absence of oxygen). Due to the low quantum yield of the process (5×10^{-4}) the products are formed in small amount and become noticeable only when long irradiation times are used.

Moreover, the reputedly inert *tert*-butyl alcohol reduces efficiently the benzophenone triplet state leading to rad-

---

(4) English, J.; Brutcher, F. V. *J. Am. Chem. Soc.* **1952**, *74*, 4279.

(5) Ray, D. J. M.; Redfearn, A.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 540.

(6) Murai, H.; Obi, K. *J. Phys. Chem.* **1975**, *79*, 2446.

(7) Weaver, J.; Meagher, J.; Heicklen, J. *J. Photochem.* **1976**, *6*, 111.

(8) Hassal, C. H. *Org. React.* **1978**, *9*, 73.

icals derived from both compounds. In the presence of oxygen, formic acid and a rather important amount of acetone are formed. The hydroxy benzhydryl radicals are simultaneously reoxidized to benzophenone which therefore does not seem to be consumed.

Formation of benzene and acetone are likely to go unnoticed in practice due to the workup techniques generally employed. The other products, which are obtained in small quantities, may well remain undetected when photochemical reactions with higher quantum yields are in competition for photons. All of these products can pertub the photochemical processes in very unexpected ways. Therefore, the results of long-duration irradiations carried out in *tert*-butyl alcohol when using benzophenone as a sensitizer, with or without oxygen, have to be interpreted carefully.

Experimental Section

GC analyses were carried out on 10 ft × $^1/_8$ in. 5% Carbowax 20M on Chromosorb W columns at a flow rate of 30 mL/min. *tert*-Butyl alcohol was distilled before use; acetonitrile (Aldrich spectrophotometric grade) was used as supplied. Both solvents were checked spectrophotometrically for absence of traces of acetone and benzene before use. Irradiations were performed in a Pyrex glass vessel (capacity 150 mL, optical path length 0.5 cm) using a medium pressure mercury lamp (MEDA 400 W). The solution was flushed with a stream of dry oxygen or dry nitrogen. In all experiments, benzophenone (*c* 0.07 M) absorbed 99% of the incident light. The intensity of the lamp used was calculated by a $\mathrm{Ph_2CO/Ph_2CHOH}$ actinometry (c_0 0.1 M/0.05 M; $I = 4.5 \times 10^{-4}$ E/min). Thus, the quantum yield of the benzophenone cleavage was $\Phi = 5 \times 10^{-4}$.

Irradiation of the $\mathrm{Ph_2CO}/t\text{-}\mathrm{BuOH/O_2}$ System. A solution of benzophenone (2 g, 11 mmol) in *t*-BuOH (150 mL) was irradiated under a slow stream of oxygen for 168 h. The following compounds were detected or isolated from several similar experiments.

(a) Acetone and Benzene. GC Detection: Determination of concentrations was performed using a Perkin-Elmer F30 instrument and an electronic integrator (Perkin-Elmer M2). Concentrations were determined by comparison with standard *t*-BuOH/acetone and *t*-BuOH/benzene mixtures.

UV Detection: Determination of concentrations was performed on a CARY 15 instrument. Optical densities of benzene and acetone in *t*-BuOH solution were measured at the relevant $\lambda_{\max}$. Both measures gave the same values: acetone 7.5 mmol and benzene 0.1 mmol (from 150 mL of *t*-BuOH).

(b) Formic Acid. Formic acid was isolated as *p*-bromophenacyl formate by action of *p*-bromophenacyl bromide on the reaction mixture. Weighing gave 0.15 mmol of formic acid.

(c) Phenol and Benzoic Acid.[9] After evaporation of solvent, the reaction mixture was dissolved in dichloromethane and washed with 10% aqueous sodium hydroxide, and the washings were neutralized with dilute hydrochloric acid. Benzoic acid and phenol were extracted with dichloromethane and the extracts were washed with sodium bicarbonate solution. The washings were acidified with dilute hydrochloric acid and extracted with dichloromethane. Evaporation gave benzoic acid (0.3 g, 2.5 mmol). Evaporation of the washed extract gave phenol (0.02 g, 0.2 mmol).

(d) 1,1-Diphenylethylene and Phenyl Benzoate. After evaporation of solvent, column chromatography on silica gel yielded 1,1-diphenylethylene (0.110 g, 0.6 mmol) and phenylbenzoate (0.05 g, 0.25 mmol) identified by IR, NMR, melting point, and comparison with authentic samples.

Irradiation of the $\mathrm{Ph_2CO/CH_3CN/O_2}$ System. A solution of benzophenone (2 g) in acetonitrile (150 mL) was irradiated under a slow stream of dry oxygen for 170 h. UV detection of the reaction mixture gave 1 mmol of benzene/150 mL of $\mathrm{CH_3CN}$. After evaporation of solvent, chromatography on silica gel gave benzoic acid (0.300 g, 2.5 mmol) and phenyl benzoate (0.04 g, 0.2 mmol). No formic acid, acetone, and 1,1-diphenylethylene could be detected by the appropriate methods.

Irradiation of the $\mathrm{Ph_2CO/CH_3CN/N_2}$ System. A solution of benzophenone (2 g) in acetonitrile (150 mL) was irradiated under nitrogen for 170 h. UV detection of the reaction mixture gave 1 mmol of benzene/150 mL of $\mathrm{CH_3CN}$. After evaporation of solvent, chromatography on silica gel gave 0.1 g of benzopinacol ($\mathrm{CH_2Cl_2}$/hexane (1:1)) and 0.05 g of benzoin (hexane/AcOEt (4:1)).

Baeyer–Villiger Type Reaction of Benzophenone. A solution of benzophenone (2 g) and *m*-chloroperbenzoic acid (0.1 g) in *t*-BuOH (70 mL) was stirred at 30 °C for 172 h. After evaporation of solvent, chromatography on silica gel gave 0.07 g (60%) of phenyl benzoate eluted with $\mathrm{CH_2Cl_2}$/hexane (1:1).

Acknowledgment. We are grateful to Pr. J. Levisalles for helpful discussions and to Pr. J. Lemaire for his comments.

Registry No. $\mathrm{Ph_2CO}$, 119-61-9; *t*-BuOH, 75-65-0; $\mathrm{O_2}$, 7782-44-7; $\mathrm{Ph_2\dot{C}OH}$, 4971-41-9; $\cdot\mathrm{CH_2C(OH)Me_2}$, 5723-74-0; $\mathrm{Ph\dot{C}O}$, 2652-65-5; Ph·, 2396-01-2; phenyl benzoate, 93-99-2.

---

(9) Vogel, A. L. "Practical Organic Chemistry", 3rd ed.; Longman: 1956; p 362.

(10) Jeandrau, J. P.; Gramain, J. C.; Lemaire, J. *J. Chem. Res., Synop.* **1979**, 186; *J. Chem. Res., Miniprint* **1979**, 2240.

(11) Pitts, J. W.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Recktenwald, G.; Martin, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 1068.

Synthesis of Allenes by Nickel-Catalyzed Grignard Reactions with Silylpropargyl Alcohols

Ernest Wenkert,* Michael H. Leftin, and
Enrique L. Michelotti

Department of Chemistry (D-006), University of
California—San Diego, La Jolla, California 92093

Received September 11, 1984

In continuation of a study of nickel-catalyzed Grignard reactions with allyl alcohols and their derivatives[1] it became of interest to investigate the behavior of propargyl alcohols in such reactions.[2] In the absence of any possibility for the formation of (π-allyl)nickel intermediates and in view of the known tendency for acetylenes to undergo nickel-catalyzed Grignard addition reactions,[3] three

---

(1) (a) Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735. (b) Buckwalter, B. L.; Burfitt, I. R.; Felkin, H.; Joly-Goudket, M.; Naemura, K.; Salomon, M. F.; Wenkert, E.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 6445. (c) Swindell, C. S., Ph. D. Dissertation 1979, Rice University, Houston, TX 77001. (d) Wenkert, E. *Chimia* **1981**, *35*, 257. (e) Wenkert, E.; Ferreira, T. W. *Organometallics* **1982**, *1*, 1670. (f) Wenkert, E.; Fernandes, J. B.; Michelotti, E. L.; Swindell, C. S. *Synthesis* **1983**, 701.

(2) For reactions of propargyl alcohols and their derivatives with organometallic reagents in the presence of other transition-metal species, see the following examples. (a) Pasternak, Y.; Delepine, M. *C. R. Acad. Sci. Fr.* **1962**, 3429. (b) Serratosa, F. *Tetrahedron Lett.* **1964**, 895. (c) Rona, P.; Crabbé, P. *J. Am. Chem. Soc.* **1968**, *90*, 4733. (d) Luche, J. L.; Barreiro, E.; Dollat, J. M.; Crabbé, P. *Tetrahedron Lett.* **1975**, 4615. (e) Moreau, J. L.; Gaudemar, M. *J. Organomet. Chem.* **1976**, *108*, 159. (f) Pasto, D.; Shultz, R.; McGrath, J.; Waterhouse, A. *J. Org. Chem.* **1978**, *43*, 1382. (g) Pasto, D.; Chou, S.; Waterhouse, A.; Shultz, R.; Hennion, G. *J. Org. Chem.* **1978**, *43*, 1385. (h) Pasto, D.; Chou, S.; Fritzen, E.; Shultz, R.; Waterhouse, A.; Hennion, G. *J. Org. Chem.* **1978**, *43*, 1389. (i) Vermeer, P., Westmijze, H.; Kleijn, H.; van Dijeck, L. A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 56. (j) Jeffery-Luong, T.; Linstrumelle, G. *Tetrahedron Lett.* **1980**, *21*, 5019. (k) Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1981**, *22*, 1451. (l) Kleijn, H.; Meijer, J.; Overbeek, G. C.; Vermeer, P. *Recl. Trav. Chem. Pays-Bas* **1982**, *101*, 97. (m) Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103. (n) Ruitenberg, K.; Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 405. (o) Elsevier, C. J.; Kleijn, H.; Ruitenberg, K.; Vermeer, P. *J. Chem Soc., Chem. Commun.* **1983**, 1529. (p) Colas, Y.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 845.

0022-3263/85/1950-1122$01.50/0