Oxythallation Adduct Intermediate in Hydration of Terminal Acetylenes by Thallium(III) Salt Catalyst

By Sakae Uemura,* Haruo Miyoshi, and Masaya Okano, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Katsuhiko Ichikawa, Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Reaction of several terminal acetylenes with thallium(III) acetate in chloroform or acetic acid gives a white solid in good yield which is believed to be a new type of oxythallation adduct, $(AcO)CR=C-Tl(OAc)-C[Tl(OAc)]=CR(OAc)$ (2), on the evidence available to date. From the fact that it is converted into the corresponding ketone and inorganic thallium(III) salt by heating in acetic acid or methanol, it is concluded that it is one of the intermediates in the thallium(III) salt-catalysed conversion of terminal acetylenes into ketones.

THALLIUM(III) salts are known to be catalysts for the conversion of terminal acetylenes into ketones.[1] The reaction has been assumed to proceed via oxythallation,[2] but the intermediate oxythallation adduct has never been isolated. McKillop and his co-workers[3] have criticized the previous work[1] on thallium(III) salt-catalysed conversion of acetylenes into ketones, arguing that the reactions being studied were merely the acid-catalysed hydration of phenylacetylene. However, their criticisms neglected the definite observation[1] that acetophenone was formed in a yield of 67% by heating phenylacetylene at 65 °C for 11 h in the presence of thallium(III) acetate (0.14M), while no acetophenone was obtained without addition of thallium(III) acetate under similar conditions (see Table 1 of ref. 1). In order to obtain more information on these systems, we have extended the work on acetoxythallation of alkylphenylacetylenes[4] to terminal acetylenes and now find that a new type of organothallium(III) compound can be isolated in the reaction of several terminal acetylenes with thallium(III) acetate.[5] These compounds are shown to be at least one of the intermediates in the conversion of acetylenes into ketones; the catalysis of the hydration of terminal acetylenes by thallium(III) acetate is clarified.

RESULTS AND DISCUSSION

Reaction of the terminal acetylenes (1; R = Ph, Me, Bu^n, or n-hexyl) with thallium(III) acetate [acetylene : Tl(OAc)$_3$ = 1.0—1.1 : 1] in chloroform at 20 or 0 °C for 1—2 h, followed by evaporation, gave an almost colourless oil which was washed several times with n-hexane to afford a white amorphous solid (Scheme 1). The solid is soluble in various organic solvents such as methanol, acetic acid, nitromethane, acetonitrile, dimethyl sulphoxide, NN-dimethylformamide, acetone, dichloromethane, pyridine, chloroform, ethyl acetate, 1,4-dioxan, and benzene, and insoluble in carbon tetrachloride, diethyl ether, n-hexane, and water. The solubility of the product from (1; R = Ph) in such solvents is higher than the solubility of those from (1; R = alkyl). The solids were somewhat unstable and

blackened or decomposed to brown oils when kept in the air for a few weeks; yields and m.p.s are given in the Table. The reaction also proceeded in acetic acid to give the same compounds, the yields being slightly lower than those obtained in chloroform. We assign structure
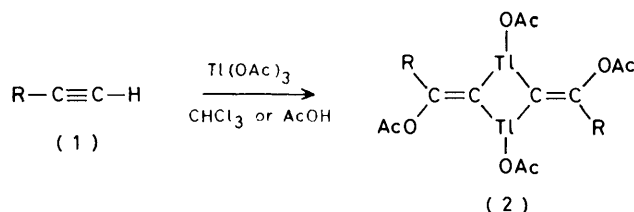
SCHEME 1   R = Ph, Me, Bu^n, or n-hexyl

(2) to these compounds, as shown in Scheme 1, on the evidence available to date. The stereochemistry of R and OAc in (2) is tentative at this stage.

Products of acetoxythallation of terminal acetylenes

| R	% Yield of (2)^a	M.p. (decomp.) $(T/°C)$ ^{b}
Ph	94	140—142 ^{c}
Me	90	137—140
Bu^n	73	116—120
n-Hexyl	80	90—95

^{a} Yield of crude product. ^{b} M.p. of crude product. ^{c} M.p. of pure compound.

The formation of (2) may be explained by assuming an intermolecular acetoxythallation between two alkynylthallium diacetate (A) molecules which can be produced by replacement of the acidic hydrogen of acetylene by a diacetoxythallium unit (Scheme 2). Compound (2) seems to be in equilibrium to some extent with (A) in solution (shown by n.m.r. spectroscopy; see Experimental section). Several examples of four-membered M-C-M-C rings are known, e.g. with M = Al,[6] Be,[6] Nb,[7] and Ta[7] etc. Application of the same reaction to mercury(II) acetate resulted in the quantitative formation of the bis(alkynyl)mercury(II) compound [(R-C≡C-)$_2$Hg] as reported elsewhere.[8]

Sodium borohydride reduction of (2; R = Ph) in tetrahydrofuran (THF)–D$_2$O at 0 °C for 1 h afforded

(3D; R = Ph) in a yield of 75% together with some acetophenone and phenylacetylene (Scheme 3). The introduction of two deuterium atoms on one carbon atom should correspond to the presence of two C–Tl bonds to that atom, because it is known that a thallium substituent on a vinyl carbon atom can be replaced by a

ketone and thallium(III) salt, (2; R = Ph) was heated in acetic acid at 65—70 °C for 3 h, and acetophenone (68% yield) and inorganic trivalent thallium (91% by iodometry) were obtained, none of α-acetoxystyrene being detected, as expected from Scheme 4. This is in accord with the result that acetophenone was obtained
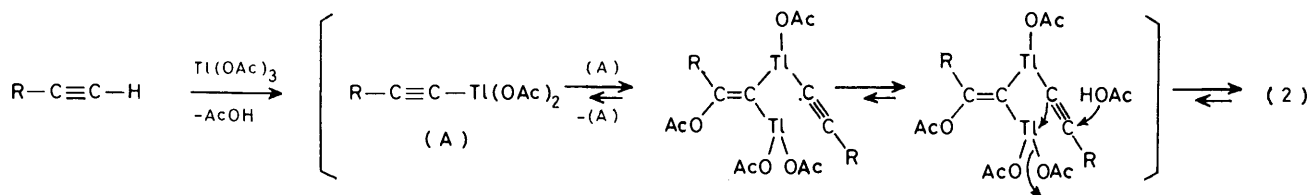
SCHEME 2

hydrogen of the solvent under sodium borohydride reduction conditions.[4] This result provides some chemical evidence for the structure of (2). Similar treatment of (2; R = n-hexyl) in methanol gave mainly octan-2-one (27%) and octan-2-ol (24%) together with a 5% yield of 2-acetoxyoct-1-ene (3; R = n-hexyl) (Scheme 3). We have confirmed in separate experiments that the last compound is a primary product as

in a yield of 62% (based on acetylene employed) from phenylacetylene under similar conditions [acetylene : Tl(OAc)₃ = 2 : 1], the amount of thallium(III) present after the reaction being determined as 81% of the starting amount. Similarly, when (2; R = n-hexyl) was heated in acetic acid at reflux temperature for 1 h, octan-2-one was formed in a yield of 36%. Further, the addition of an equimolar amount [with respect to (2)] of
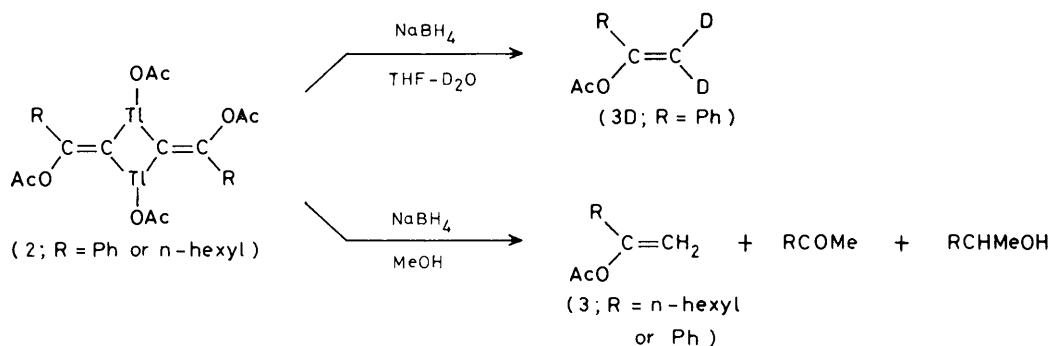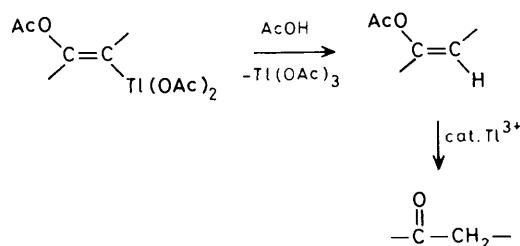

SCHEME 3

expected, since it was converted into the corresponding ketone and alcohol under the reaction conditions. Under alkaline conditions the reduction products were only the ketone and alcohol. *E.g.* the reduction of (2; R = Ph) with NaBH₄ in sodium borohydride in methanol–aqueous 3M-sodium hydroxide at 20 °C for 1 h gave acetophenone (18%) and 1-phenylethanol (35%). Similarly, a mixture of octan-2-one (12%) and octan-2-ol (44%) was obtained from (2; R = n-hexyl). Treatment of (2; R = Ph) with aqueous 3M-sodium hydroxide or 1M-hydrochloric acid at room temperature for 3 h gave acetophenone in a yield of 55 or 21% respectively.

It has been shown that vinylthallium(III) compounds react with acetic acid to give a protodethallated compound (Scheme 4),[4] and that α-acetoxystyrene is readily converted into acetophenone when heated in acetic acid in the presence of a thallium(III) salt.[1] In order to clarify whether protodethallation occurs with (2) and acetic acid to give the corresponding vinyl acetate or

thallium(III) acetate to the reaction system resulted in an increase in the yield of the ketone to 68%, probably because thallium(III) acetate also acts as a catalyst for
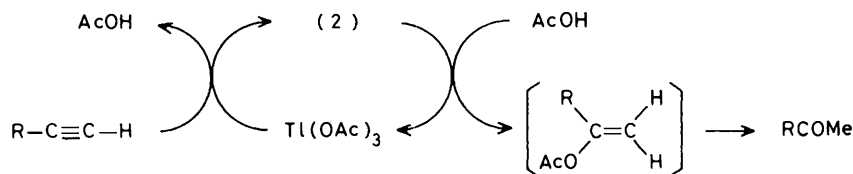

SCHEME 4

the protodethallation step. When oct-1-yne (2 mol. equiv.) was heated in acetic acid at reflux temperature for 1 h in the presence of thallium(III) acetate (1 mol. equiv.) without isolation of (2), octan-2-one was pro-

duced in a yield of 41% (based on the amount of acetylene employed). Under similar conditions, without the addition of thallium(III) acetate, hardly any ketone was obtained from either phenylacetylene or oct-1-yne. These results clearly show that thallium(III) acetate catalyses the hydration of acetylenes and that (2) is at least one of the intermediates in the conversion of terminal acetylenes into ketones as shown in Scheme 5. The addition of thallium(III) acetate, acetic acid, or water to the intermediate (A) in Scheme 2, followed by protodethallation may be another possibility for these conversions especially when these were carried out without isolation of (2).

It should be noted here that the addition of aromatic amines to phenylacetylene is also catalysed by thallium(III) acetate,[9] the aminothallation adduct having

diethyl ether as catalyst. α-Acetoxystyrene (3; R = Ph) was similarly prepared from phenylacetylene.[12]

Reaction of Terminal Acetylenes with Thallium(III) Acetate in Chloroform.—To an orange heterogeneous solution of thallium(III) acetate (3.89 g, 10 mmol on the basis of pure Tl^{III} in chloroform (20 ml) was added phenylacetylene (1.02 g, 10 mmol) at 0—5 °C and the resulting mixture was stirred for 2 h. Chloroform was evaporated from the resulting clear solution, and n-hexane was added to the residual oil to afford crude (2; R = Ph) (4.0 g, 94%) as a white solid, m.p. 137—140 °C (decomp.), which was purified as follows. The solid was dissolved in chloroform, the solution filtered, chloroform then evaporated off, and the residual oil (or solid in some case) washed with n-hexane to give a white solid. Analytical and spectral data for pure (2; R = Ph) thus obtained [m.p. 140—142 °C (decomp.)] are as follows: ^1H n.m.r. $\delta(CD_3OD)$ 1.71 (3 H, s, TlOAc), 2.0 (3 H, s, =C–OAc), 7.2—7.7 (3 H, m, Ph), and 7.8—8.2

AcOH ← → (2) ← AcOH

$R–C{\equiv}C–H$ → $Tl(OAc)_3$ ← → [structure: R, H, C=C, AcO, H, H] → RCOMe

SCHEME 5

been assumed to be the intermediate which suffers protodethallation by acetic acid to give the product.

Conversion of phenylacetylene into acetophenone also occurred in methanol in the presence of thallium(III) acetate where thallium(III) species may be present in the form $Tl(OAc)_2(OMe)$. For example, a yield of 15% (based on acetylene employed) of the ketone was obtained by heating phenylacetylene in methanol at 65 °C for 3 h [acetylene : $Tl(OAc)_3$ = 2 : 1]. In accordance with this slow conversion, compared with that in acetic acid, (2; R = Ph) was also slowly converted into acetophenone when heated in methanol (23% yield after 3 h at 65 °C), probably because protodethallation of the vinyl carbon–thallium bond with methanol is slower than with acetic acid.

EXPERIMENTAL

All commercially available organic and inorganic materials were used without further purification. Thallium(III) acetate was prepared by the reported method;[10] its purity was shown to be 98% by iodometry. The impurities may be acetic acid, water, and/or thallium(I) salts. I.r. spectra (KBr disc and paraffin and hexachlorobutadiene mulls) were recorded with a Hitachi EPI-S2 spectrometer. ^1H N.m.r. spectra were taken with Varian A-60 and Varian EM-360 instruments for solution in $CDCl_3$, CCl_4, or CD_3OD with tetramethylsilane as internal standard. G.l.c. analyses were carried out with Shimadzu 5APTF and 4BMPF apparatus using EGSS-X (30%) on Chromosorb W (1 m), Apiezon-L (30%) on Celite (1 m), and PEG-6000 (25%) on Chromosorb-W (3 m) columns (N_2 as carrier gas). The authentic sample of (3; R = n-hexyl) was prepared by the reported method[11] from oct-1-yne and acetic anhydride in the presence of mercury(II) acetate and boron trifluoride–

(2 H, m, Ph); i.r. (paraffin and hexachlorobutadiene mulls) $\nu(C=O)$ 1 765, $\nu(C=C)$ 1 625, $\nu_{as}(CO_2)$ 1 540, $\nu_s(CO_2)$ 1 395, $\nu(C–O)$ 1 185, and Ph, 770 and 700 cm^{-1}; mass spectrum m/e 249 and 247 ($TlCO_2^+$), 221 and 219 (TlO^+), 205 and 203 (Tl^+); no molecular ion peak was observed;[13] M(cryoscopy in benzene), 835 (calc. 847) (Found: C, 34.2; H, 2.7. $C_{24}H_{22}O_8Tl_2$ requires C, 34.0; H, 2.6%). During ^1H n.m.r. measurements on this sample in $CDCl_3$, the intensity of the signal at δ 1.71 increased and that at δ 2.0 decreased gradually (within 4—5 h at 20 °C), the ratio of the integrals of the acetate and acetoxy signals to the phenyl signal being almost unchanged. This suggests the slow conversion of (2) into the intermediate (A) in Scheme 2 or an equilibrium between (2) and (A). No signal due to the acetylenic proton of (1; R = Ph) appeared. Similar phenomena were also observed with (2; R = alkyl).

Compounds (2; R = Bu^n) and (2; R = n-hexyl) were prepared by a similar method. From hex-1-yne (5 mmol scale) at 20 °C for 5 min, or 0 °C for 1 h, 1.47 g (73% yield) of crude (2; R = Bu^n) was obtained [m.p. 116—120 °C (decomp.)]; ^1H n.m.r. $\delta(CDCl_3)$ 0.8—1.2 (3 H, m, Me), 1.2—1.7 (4 H, m, CH_2), 1.7—2.8 (2 H, m, =CCH_2), 1.97 (3 H, s, TlOAc), and 2.17 (3 H, s, =COAc); i.r. $\nu(C=O)$ 1 760, $\nu(C=C)$ 1 630, $\nu_{as}(CO_2)$ 1 540, and $\nu_s(CO_2)$ 1 400 cm^{-1} (Found: C, 28.0; H, 3.7. $C_{20}H_{30}O_8Tl_2$ requires C, 29.75; H, 3.75%). From oct-1-yne (5 mmol scale) at 20°C for 1 h, 1.73 g (80% yield) of crude (2; R = n-hexyl) was obtained [m.p. 90—95 °C (decomp.)]; ^1H n.m.r. $\delta(CDCl_3)$ 0.7—1.1 (3 H, m, Me), 1.1—1.8 (8 H, m, CH_2), 1.8—2.9 (2 H, m, =CCH_2), 2.00 (3 H, s, TlOAc), and 2.20 (3 H, s, =COAc); i.r. $\nu(C=O)$ 1 760, $\nu(C=C)$ 1 630, $\nu_{as}(CO_2)$ 1 540, and $\nu_s(CO_2)$ 1 400 cm^{-1} (Found: C, 33.2; H, 4.7. $C_{24}H_{38}O_8Tl_2$ requires C, 33.4; H, 4.4%).

In the case of methylacetylene, gaseous methylacetylene (1.0 g) was passed into a stirred heterogeneous solution of thallium(III) acetate (3.89 g, 10 mmol on the basis of pure

T^{III} in chloroform (20 ml) at 20—25 °C for 40 min. Chloroform was evaporated from the resulting clear solution, and the residual colourless oil was washed with n-hexane to afford crude (2; R = Me) as a white solid (3.25 g, 90% yield), m.p. 137—140 °C (decomp.); ^{1}H n.m.r. δ(CDCl$_3$), 1.7—2.5 (3 H, m, =CMe), 1.98 (3 H, s, TlOAc), and 2.17 (3 H, s, =COAc); i.r. ν(C=O) 1 760, ν(C=C) 1 635, ν_{as}(CO$_2$) 1 540, and ν_s(CO$_2$) 1 400 cm^{-1} (Found: C, 21.75; H, 2.8. C$_{14}$H$_{18}$O$_8$Tl$_2$ requires C, 23.3; H, 2.5%).

The purification of compounds (2) with R alkyl by the method described for (2; R = Ph) resulted in slow decomposition to inorganic Tl salts and ketones, and microanalytical results for C gradually decreased on repeating the purification. In these cases, we have accordingly given analytical results for crude (2) which seems to contain inorganic Tl salt, and shows a lower C content than the calculated value.

Reduction of (2) *with Sodium Borohydride.*—Solid (2; R = Ph) (1.69 g, 2 mmol) was dissolved in tetrahydrofuran (THF) (10 ml) at 32 °C and then D$_2$O (99.8%, 10 ml) was added. The resulting white heterogeneous mixture was then cooled to 0 °C, solid sodium borohydride (0.075 g, 2 mmol) was added in portions during 10 min, and the mixture was stirred for 1 h at 0 °C. The mixture was poured into aqueous sodium chloride and extracted with benzene. The extract was washed with water and dried (Na$_2$SO$_4$). G.l.c. and n.m.r. analyses of the extract [using phenyl n-propyl ketone (for ester and ketone) and cumene (for acetylene) as internal standards] showed the presence of α-acetoxy-ββ-dideuteriostyrene (3D; R = Ph) (75% yield), αα-dideuterioacetophenone (20%), and phenylacetylene (5%). The retention times of the deuteriated products were the same as those for α-acetoxystyrene or acetophenone, respectively. Distillation of the extract afforded 0.18 g of (3D; R = Ph) (b.p. 80—110 °C at 29 Torr) which was contaminated with a small amount of the non-deuteriated compound (3; R = Ph) (D/H = 96/4 by n.m.r.). Similar treatment in aqueous THF afforded (3; R = Ph) (50—70%) and acetophenone (20%).

Compound (2; R = n-hexyl) (0.863 g, 1 mmol) was similarly treated in methanol (20 ml) with sodium borohydride (0.038 g, 1 mmol) at 0 °C for 1 h. G.l.c. analysis (n-hexanol as an internal standard) of the benzene extract of the reaction mixture showed the presence of octan-2-one (27% yield), octan-2-ol (24%), and 2-acetoxyoct-1-ene (3; R = n-hexyl) (5%).

Compound (3; R = n-hexyl) (0.85 g, 5 mmol) was treated with sodium borohydride (0.190 g, 5 mmol) in methanol (20 ml) at 0 °C for 1 h. The mixture was poured into aqueous sodium chloride and extracted with ether. G.l.c. analysis of the ether extract revealed the presence of octan-2-one (12% yield), octan-2-ol (35%), and the starting material (3; R = n-hexyl) (13%).

To a yellow heterogeneous mixture of methanol (15 ml)–aqueous 3M-sodium hydroxide (5 ml) containing (2; R = Ph) (0.847 g, 1 mmol) was added sodium borohydride (0.038 g, 1 mmol) and the mixture stirred at 25 °C for 1 h. The mixture was then poured into aqueous sodium chloride and extracted with benzene. G.l.c. analysis of the benzene extract using p-methylacetophenone as an internal standard showed the presence of acetophenone (18% yield) and 1-phenylethanol (35%).

Reaction of (2; R = Ph) *with Aqueous Sodium Hydroxide*

or Hydrochloric Acid.—Solid (2; R = Ph) (0.847 g, 1 mmol) was added to aqueous 3M-sodium hydroxide (20 ml) at 20—25 °C and the resulting brown heterogeneous solution was stirred for 2 h. It was then poured into aqueous sodium chloride and extracted with benzene. G.l.c. analysis of the benzene extract showed the presence of acetophenone in a yield of 55% (p-methylacetophenone as internal standard).

Solid (2; R = Ph) (0.847 g, 1 mmol) was added to 1M-hydrochloric acid (20 ml) and the resulting white heterogeneous solution was stirred at 20—25 °C for 2 h. It was then poured into aqueous sodium chloride and extracted with benzene. G.l.c. analysis of the extract showed the presence of acetophenone (21% yield) and phenylacetylene (trace).

Reaction of (2) *with Acetic Acid.*—A solution of (2; R = Ph) (0.847 g, 1 mmol) in acetic acid (20 ml) was heated at 65 °C for 3 h. The solution was allowed to cool to room temperature, poured into aqueous sodium chloride, and then extracted with benzene. G.l.c. analysis of the extract revealed the presence of acetophenone [1.36 mmol, 68% yield based on (2)] (p-methylacetophenone as internal standard). Iodometry of the aqueous solution combined with several aqueous washings showed the presence of 1.83 mmol of thallium(III) ion [91.3% based on (2) which would give 2 mmol of thallium(III) ion]. It was confirmed separately that no thallium(III) ion was detected in the iodometry of (2; R = Ph) itself under similar analytical conditions.

The analogous reaction of (2; R = n-hexyl) (1 mmol) was carried out in refluxing acetic acid (20 ml) for 1 h in the presence or absence of thallium(III) acetate (1 mmol), and the results given earlier were obtained.

We thank Dr. T. Ueno, Department of Hydrocarbon Chemistry, Kyoto University, for the measurement of the mass spectrum of (2; R = Ph).

REFERENCES

[1] S. Uemura, R. Kitoh, K. Fujita, and K. Ichikawa, *Bull. Chem. Soc. Jpn.,* 1967, **40**, 1499.

[2] K. Ichikawa and S. Uemura, *Yuki Gosei Kagaku Kyokai Shi,* 1971, **29**, 400; A. G. Lee, ' The Chemistry of Thallium,' Elsevier, Amsterdam, 1971, p. 237.

[3] A. McKillop, O. H. Oldenziel, B. P. Swann, E. C. Taylor, and R. L. Robey, *J. Am. Chem. Soc.,* 1973, **95**, 1296.

[4] S. Uemura, H. Tara, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Jpn.,* 1974, **47**, 2663.

[5] Preliminary communication: S. Uemura, H. Miyoshi, H. Tara, M. Okano, and K. Ichikawa, *J. Chem. Soc., Chem. Commun.,* 1976, 218.

[6] F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' Interscience, London, 1972, pp. 306—307.

[7] F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.,* 1971, 1477.

[8] S. Uemura, H. Miyoshi, and M. Okano, *J. Chem. Soc., Perkin Trans. 1,* 1980, 1098.

[9] J. Barluenga and F. Aznar, *Synthesis,* 1977, 195.

[10] L. F. Fieser and M. Fieser, ' Reagents for Organic Synthesis,' Wiley, New York, 1967, vol. 1, p. 1150.

[11] R. F. Hudrlik and A. M. Hudrlik, *J. Org. Chem.,* 1973, **38**, 4254.

[12] A. I. Bol'shukin and V. L. Zhitorchuk, *Zh. Obshch. Khim.,* 1955, **25**, 1459 (*Chem. Abstr.,* 1956, **50**, 4832).

[13] A. T. T. Hsieh, A. G. Lee, and P. L. Sears, *J. Org. Chem.,* 1972, **37**, 2637.