Reaction of Thallous Isopropoxide with CS_2.—Thallous isopropoxide (**1c**) (10.5 g, 40 mmol) was allowed to react with CS_2 (0.80 g, 10.5 mmol) as in the case of thallous ethoxide. Distillation of the filtrate from the reaction mixture afforded tetraisopropyl orthocarbonate (**5c**) in 55% yield (1.35 g, 5.5 mmol): bp 47–51° (3.5 mm); ir ($CHCl_3$) 1471, 1384, 1188, 1155, 1080 (strong), and 961 cm^{-1}; nmr ($CHCl_3$) τ 8.85 (d, 24, J = 6.0 Hz, CH_3C) and 5.94 (heptet, 4, J = 6.0 Hz, CHO).

Anal. Calcd for $C_{13}H_{28}O_4$: C, 62.87; H, 11.37. Found: C, 62.51; H, 10.98.

The orthocarbonate **5c** was rapidly hydrolyzed by moisture in air to give diisopropyl carbonate, and the $\nu_{C=O}$ band of the carbonate at 1738 cm^{-1} emerged during the ir measurement.

When the crude thallous isopropoxide, prepared by the alcoholysis of thallous ethoxide with isopropyl alcohol, and containing about 20 mol % of thallous ethoxide, was submitted to reaction with CS_2, a small amount of diisopropyl dithiocarbonate was formed along with the ethyl and isopropyl orthocarbonates. The dithiocarbonate in the reaction mixture was detected by its characteristic peaks at τ 4.23 (heptet, J = 6.0 Hz) in the nmr spectrum.

Reaction of Dithallous Ethylene Glycolate with CS_2. A.—Dithallous ethylene glycolate (**6a**) (1.32 g, 2.81 mmol) was dispersed in dry benzene (30 ml), and CS_2 (0.083 g, 1.1 mmol) was introduced slowly into the dispersion, which was stirred for 2 hr at room temperature. The thallous sulfide formed was filtered off, and benzene in the filtrate was evaporated to separate the crude crystals of the spiroorthocarbonate **10a** in 60% yield (0.070 g, 0.50 mmol). This compound showed a strong ν_{C-O} band at 1058 cm^{-1} in the ir spectrum (benzene) and a peak at τ 6.40 (s, 8, CH_2) in the nmr spectrum (benzene), which were the same values as for an authentic sample,[2] mp (CCl_4) 140.5–141.0° (lit.[2] mp 143–144°).

B.—Dithallous ethylene glycolate (**6a**) (0.49 g, 1.04 mmol) was allowed to react with an excess of CS_2 (3.05 g, 40 mmol) for 2.5 hr at room temperature with stirring. The ir spectrum in carbon disulfide of the crude product displayed absorption bands at 1360, 1250, 1210, 1140, 1058, 1018, and 958 cm^{-1} (but a ν_{OH} band at ~3600 cm^{-1} was not observed), and the nmr peaks at τ 5.45 (s) and 6.13 (s) coincided with those of a mixture of 40 mol % of ethylene thioncarbonate and 60 mol % of bis(ethylene) orthocarbonate (**10a**).

Reactions of CS_2 with Dithallous 1,2- or 1,3-Propylene and 1,4-Butylene Glycolates.—The dithallous glycolates **6b**, **6c**, and **6d** were allowed to react with CS_2 as in procedure A described above, giving the crude orthocarbonates **10b** (about 50% yield), **10c** (73% yield), and **10d** (35% yield), respectively. The products, purified by distillations or by recrystallizations, were identified by comparisons of boiling point, melting point, ir, and nmr spectra with those of authentic samples.

Registry No.—**5a**, 78-09-1; **5c**, 36597-49-6; **6a**, 36597-50-9; **6c**, 36601-78-2; **6d**, 36601-79-3; **10a**, 24471-99-6; carbon disulfide, 75-15-0.

Observations Related to the Alkylation of Thallium Enolates of β-Keto Sulfoxides, β-Diketones, and β-Keto Esters. An Alternative Viewpoint

JOHN HOOZ* AND JOHN SMITH

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

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The alkylation[1,2] of β-keto sulfoxides[3] (as their sodium enolates), followed by reductive fission of the sulfoxide function,[1,4] represents a useful alternative to the acetoacetic ester route for the synthesis of ketones. Mono- and dialkylated derivatives are formed in good yields,

$$RCOCH_2SOCH_3 \longrightarrow \underset{Na^+}{RCO\bar{C}HSOCH_3} \longrightarrow \underset{R'}{RCOCHSOCH_3} \longrightarrow RCOCH_2R'$$

but attempts to extend this method to secondary halides have as yet been unpromising, resulting in "extremely poor yields of alkylation product."[2]

In the light of prior results, we investigated the use of thallium enolates for this purpose, since Tl derivatives of 1,3-dicarbonyl compounds (β-diketones or β-keto esters) are reported to possess a variety of attractive synthetic features.[5-7] Thallium enolates (i) are easily formed in virtually quantitative yield, (ii) are crystalline, stable, nonhygroscopic solids, and (iii) react with alkyl iodides to give *exclusively*, in essentially quantitative yield, *the product of C-alkylation*—even for secondary substrates (isopropyl iodide). In addition, the heterogeneous thallium cation–ambident anion combination reportedly avoids *all* the traditionally encountered obstacles associated with β-dicarbonyl anion alkylations (O-alkylation, dialkylation, Claisen-type condensations, β-keto cleavage, oxidative coupling, etc.).[5]

For exploratory synthetic purposes we considered that Tl β-dicarbonyl enolates might serve as reasonable models for Tl β-keto sulfoxides since in each parent substrate the active methylene is flanked by two atoms each of which is "doubly" bonded to oxygen. Moreover, Tl enolates are highly insoluble, and, among the several factors responsible for promoting predominant C- rather than O-alkylation of ambident anions, heterogeneity[8] plays a significant role.[9]

Reaction of keto sulfoxide **1** with thallous ethoxide[10] led to quantitative precipitation of salt **2** (eq 1). The

$$\underset{\mathbf{1}}{C_6H_5COCH_2SOCH_3} \xrightarrow{TlOC_2H_5} \underset{\mathbf{2}}{C_6H_5CO\bar{C}HSOCH_3\ Tl^+} \qquad (1)$$

results of heterogeneous alkylation experiments employing **2** with methyl, ethyl, or isopropyl iodide are summarized in eq 2 (see Experimental Section for

$$\underset{Tl^+}{C_6H_5CO\bar{C}HSOCH_3} \xrightarrow{RI} \underset{\mathbf{3}}{C_6H_5COCHSOCH_3} + \underset{\mathbf{4}}{C_6H_5C(OR)=CHSOCH_3} + \underset{\mathbf{5}}{C_6H_5COCH_2SCH_3} \qquad (2)$$

Alkylating agent	Isolated product yield, % 3	4	5
CH_3I	81		
C_2H_5I	38	17	28
i-C_3H_7I		42	36

(1) G. A. Russell and G. J. Mikol, *J. Amer. Chem. Soc.*, **88**, 5498 (1966); G. A. Russell and G. Hamprecht, *J. Org. Chem.*, **35**, 3007 (1970).

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(5) E. C. Taylor, G. H. Hawks, III, and A. McKillop, *ibid.*, **90**, 2421 (1968).

(6) E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, **3**, 338 (1970).

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(8) N. Kornblum and A. Lurie, *J. Amer. Chem. Soc.*, **81**, 2705 (1959).

(9) An excellent and extensive discussion appears in H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, Chapter 9.

(10) Available from Aldrich Chemical Co., Inc., Milwaukee, Wis.

details). Only methylation resulted in the exclusive formation of C-alkylate. Since reaction of CH_3I with the corresponding sodium enolate of **1** gave yields of 86%[1] (or 70%[2]) of **3** (R = CH_3), no advantage accrues using the Tl enolate. Ethylation of **2** was complex and clearly inferior to ethylation of the Na analog in promoting efficient C-alkylation.[1,2] Keto sulfide **5**[11-13] is not reported to be a product of Na enolate alkylations of **1**. No C-alkylate was obtained from reaction of **2** with isopropyl iodide.

To gain additional experience and confirm our technique, we sought to duplicate prior findings.[5] In our hands, heterogeneous alkylation of **6** (from $TlOC_2H_5$ and acetylacetone) with methyl, ethyl, or isopropyl iodide, gave exclusively C-alkylation products only with methyl iodide, but alkylate **7** (R = CH_3, 85%) was also accompanied by formation of *ca.* 6% of dialkylate **8** (R = CH_3). Reaction of **6** with C_2H_5I produced a mixture of **7** (R = C_2H_5, 65%), **8** (R = C_2H_5, 4%), and enol ether **9** (R = C_2H_5, 13%). Isopropyl iodide reacted with **6** to produce O-alkylate **9** (R = *i*-C_3H_7 as the major product (62%), accompanied by a 20% yield of **7** (R = *i*-C_3H_7).

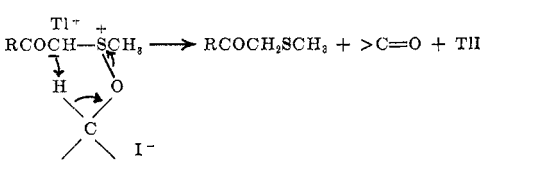
To check independently our synthetic **6**, commercially available **6**[10] was alkylated with isopropyl iodide. Under conditions identical with those employed for synthetic **6** (and as previously described[5]), there was obtained enol ether **9** (R = *i*-C_3H_7, 62%) and C-alkylate **7** (R = *i*-C_3H_7, 20%).

Reaction of the Tl enolate of ethyl acetoacetate (**10**) with C_2H_5I produced a mixture of alkylates **11** (R = C_2H_5, 80%), **12** (R = C_2H_5, 2%), and **13** (R = C_2H_5, 5%). Isopropyl iodide reacted with **10** to furnish a mixture of **11** (R = *i*-C_3H_7, 67%) and **12** (R = *i*-C_3H_7, 20%).

In contrast to the heterogeneous acetylacetone–Tl enolate reactions, it is difficult for us to state with confidence that the latter alkylations were totally heterogeneous.[5-7] Admixture of **10** with either C_2H_5I or *i*-C_3H_7I led to the formation of cloudy mixtures (no solid particles were evident) with the gradual development of a yellow coloration and ultimate deposition of (yellow) TlI.

In view of the complex array of products observed, we conclude that Tl enolates of β-keto sulfoxides or β-diketones, despite their heterogeneity, and Tl enolates of β-keto esters (despite their apparent "heterogeneity"), offer no special synthetic advantages for promoting *exclusive* mono-C-alkylation.

(11) Although the mechanism for keto sulfide formation has not been established, one plausible pathway involves initial O-alkylation (on sulfoxide oxygen), followed by inter- or intramolecularly promoted elimination, *viz.*



The reduction of dimethyl sulfoxide by alkyl halides is well documented.[12,13]

(12) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Amer. Chem. Soc.*, **79**, 6562 (1957).

(13) A. P. Johnson and A. Pelter, *J. Chem. Soc.*, 520 (1964).

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nmr spectra were run on a Varian A-60 or Hr-100 spectrometer in deuteriochloroform with tetramethylsilane as internal standard and are reported in τ units. Gas chromatographic (gc) analyses were performed using the following columns: column A, 10 ft × 1/4 in. 15% XF-1150 on 60/80 Chromosorb W; column B, 5 ft × 1/8 in. 10% QF-1 on 60/80 Chromosorb W; column C, 10 ft × 1/4 in. 15% Apiezon L on 60/80 Chromosorb W; column D, 15 ft × 1/8 in. 15% SE-30 on 60/80 Chromosorb W; column E, 10 ft × 1/4 in. 10% SE-30 on 60/80 Chromosorb W. All alkylation products, in both the quantitative (corrected for peak response) analytical and preparative gc work, are listed in order of elution. Infrared spectra were recorded on a Unicam SP 1000 spectrometer. Mass spectra were determined by Dr. A. Hogg and his associates at 70 eV using an A.E.I. MS-2 or MS-9 mass spectrometer. Analytical thin layer chromatography (tlc) was performed on silica gel plates. Precoated silica gel F_{254} plates, 20 × 20 × 0.2 cm (E. Merck, Darmstadt), were used for preparative tlc. Microanalyses were performed by the Microanalytical Laboratory, University of Alberta.

Caution! Thallium compounds are insidious poisons and should be handled with great care.

Reaction of Thallous Ethoxide with ω-(Methylsulfinyl)acetophenone (1) to Form Salt 2.—To a solution of 1.5 g (6.0 mmol) of thallous ethoxide[10] in 25 ml of anhydrous tetrahydrofuran, magnetically stirred under a nitrogen atmosphere, was added a solution of 0.91 g (5.0 mmol) of ω-(methylsulfinyl)acetophenone in 25 ml of tetrahydrofuran. After stirring for *ca.* 5 min, the initially formed yellow coloration disappeared, and a white precipitate formed. The mixture was stirred (30 min), 40 ml of anhydrous ligroin was added, and stirring was continued for an additional 15 min. The solid was filtered, washed (ligroin), and dried to provide 1.9 g (100%) of product: mp 139–141°; mass spectrum *m/e* (rel intensity) M^+ 386, 384 (2), 371 (31), 369 (13), 205 (100), 203 (37), 120 (6), 105 (95), 77 (58).

Anal. Calcd for $C_9H_9O_2STl$: C, 28.04; H, 2.33; S, 8.32. Found: C, 28.00; H, 2.11; S, 8.31.

Alkylation of 2 with Alkyl Iodides. General Procedure.—To 5.0 mmol of **2** was added 40 ml of the freshly distilled alkyl iodide under a nitrogen atmosphere. After the magnetically stirred mixture had reacted for the times and at the temperatures indicated below, it was filtered through a Florisil column. The column was washed with tetrahydrofuran (two 40-ml portions), and the solutions were combined and concentrated on a rotary evaporator. Products were isolated by column chromatography using Florisil as adsorbent.

With Methyl Iodide.—After a reaction time of 30 min at 25°, there was obtained 0.87 g of colorless oil. Chromatography on 50 g of Florisil (elution with ether–acetone, 7:3 by volume) afforded 0.79 g (81%) of diastereomeric sulfoxides **3**: ir ($CHCl_3$) 1675 (C=O), 1050 cm^{-1} (SO); nmr (60 MHz, $CDCl_3$) τ 8.44 (d, 3, CH_3), 8.40 (d, 3, CH_3), 7.55 (s, 3, $SOCH_3$), 7.50 (s, 3, $SOCH_3$), 5.35 (q, 1, CH), 5.10 (q, 1, CH), 2.80–1.95 (m, 10, arom).

Crystallization from ether–ethyl acetate yielded white crystals, mp 74–76° (lit.[2] mp 77–78°).

With Ethyl Iodide.—After 1.5 hr at 55° there was obtained 0.97 g of pale yellow oil. Chromatography on 50 g of Florisil (elution with ether) afforded 0.24 g (28%) of **5**, the ir and nmr spectra of which were identical with those of a sample independently prepared from reduction of **1** with sodium metabisulfite.[14]

Further elution with ether–acetone (4:1) provided 0.64 g of colorless oil, shown to be a two-component mixture by analytical tlc. By preparative tlc (ethyl acetate development) there was obtained as the more mobile component, 0.39 g (38%) of diastereomeric keto sulfoxides, **3** (R = C_2H_5): ir (liquid film) 1670 (C=O), 1060 cm^{-1} (SO); nmr (60 MHz, $CDCl_3$) τ 8.95 (t, 3, CH_3), 7.60–8.10 (m, 2, CH_2), 7.45 (s, 3, $SOCH_3$), 5.10–5.45 (m, 1, CH), 2.65–1.75 (m, 5, arom); mass spectrum M^+ 210. The less mobile component, **4** (0.175 g, 17%), was a colorless oil: ir (liquid film) 1605 (C=C), 1070 (C–O), 1040 cm^{-1} (SO); nmr (60 MHz, $CDCl_3$) τ 8.68 (t, 3, CH_3), 7.27 (s, 3, $SOCH_3$), 6.00 (q, 2, CH_2), 3.98 (s, 1, C=CH), 2.30–2.65 (m, 5, arom); mass spectrum M^+ 210.

With Isopropyl Iodide.—After 6 hr at 65° there was obtained 0.91 g of pale yellow oil. Column chromatography on Florisil (ether elution) provided 0.325 g of pale yellow oil. Molecular distillation at 90–100° (bath temperature) (1 mm) yielded 0.300 g (36%) of **5**. The ir and nmr spectra were identical with those of an authentic sample.[14]

Further elution with ether–acetone (4:1) provided 0.467 g (42%) of **4** (R = i-C_3H_7): ir (liquid film) 1605 (C=C), 1060 (CO), 1040 cm^{-1} (SO); nmr (60 MHz, $CDCl_3$) τ 8.70 (q, 6, CH_3), 7.27 (s, 3, $SOCH_3$), 5.72 (m, 1, CH), 4.00 (s, 1, C=CH), 2.40–2.75 (m, 5, arom); mass spectrum M^+ 224. The structure was further confirmed by conversion (2 *N* HCl, 50°, 15 min) into the Pummerer rearrangement product $C_6H_5COCH(OH)SCH_3$:[1] ir ($CHCl_3$) 1670 (C=O), 3460 cm^{-1} (OH); nmr (60 MHz, $CDCl_3$) τ 8.00 (s, 3, SCH_3), 5.66 (s, 1, OH), 3.83 (s, 1, CH), 1.80–2.70 (m, 5, arom); mass spectrum M^+ 182.

Preparation of 6.—To a solution of 11.0 g (110 mmol) of 2,4-pentanedione in 20 ml of anhydrous ligroin was added, all at once, a solution of 25 g (100 mmol) of thallous ethoxide in 30 ml of anhydrous ligroin. A heavy white precipitate formed immediately, and the mixture was magnetically stirred for *ca.* 30 min. The solid was collected (vacuum filtration) and dried to afford 30.3 g (100%) of **6**, mass spectrum M^+ 304.

Reaction of 6 with Alkyl Iodides. General Procedure.—A heterogeneous mixture of 50 mmol of **6** in 45 ml of the freshly distilled alkyl iodide was magnetically stirred and refluxed (N_2 atmosphere) for the times indicated.[5] The mixture was then cooled to room temperature and the supernatant passed through a Florisil column. The solid residue was washed with tetrahydrofuran (2 × 25 ml), and the THF washings were also passed through the Florisil column. Yields were established by quantitative gc analysis. Each component was isolated by preparative gc, and where amounts permitted, further purified by molecular distillation.

With Methyl Iodide.—After a reflux period of 4 hr and processing as described above, quantitative gc analysis (column B, 125°) gave the following results: 2,4-pentanedione, 5%; **7** (R = CH_3), 85%; and **8** (R = CH_3), 6%. The isolated (column A, 155°) materials had the following properties: 2,4-pentanedione: ir and nmr spectra identical with those of an authentic sample;[10] **7** (R = CH_3), after molecular distillation at 75–77° (bath) (20 mm): ir (liquid film) 3410 (enol OH), 1720, 1700 (C=O), 1610 cm^{-1} (C=C enol); nmr (60 MHz, $CDCl_3$) τ 8.68 (d, 3, CH_3), 7.80 (s, 6, CH_3CO), 6.33 (q, 1, CH), and in addition signals due to *ca.* 25% enol content, τ 8.17 (s, 3, C=CCH_3), 7.89 (s, 3, $CH_3C(O)$=C), 7.80 (s, 3, CH_3CO), −6.42 (OH, exch by D_2O); mass spectrum M^+ 114; **8** (R = CH_3): ir (liquid film) 1710 cm^{-1} (C=O); nmr (60 MHz, $CDCl_3$) τ 8.65 (s, 6, CH_3), 7.87 (s, 6, $COCH_3$); mass spectrum M^+ 128.

With Ethyl Iodide.—After a reflux period (16 hr) and processing as above, quantitative gc (column D, 155°) indicated: 2,4-pentanedione, 3%; **7** (R = C_2H_5), 65%; **9** (R = C_2H_5), 13%; and dialkylate **8** (R = C_2H_5), 4%. Properties of isolated (column E, 170°) materials follow: 2,4-pentanedione: spectroscopically (ir, nmr) identical with authentic material;[10] **7** (R = C_2H_5), after molecular distillation at 73–75° (bath) (20 mm): ir (liquid film) 3410 (OH enol), 1725, 1700 (CO), 1600 cm^{-1} (C=C enol); nmr (60 MHz, $CDCl_3$) τ 9.08 (t, 3, CH_3), 8.11 (m, 2, CH_2), 7.82 (s, 6, CH_3CO), 6.44 (t, 1, CH); mass spectrum M^+ 128; **9** (R = C_2H_5): ir (liquid film) 1680 (CO), 1585 cm^{-1} (C=C); nmr (60 MHz, $CDCl_3$) τ 8.65 (t, 3, CH_3), 7.87 (s, 3, $CH_3C(O)$=C), 7.73 (s, 3, CH_3CO), 6.17 (q, 2, CH_2), 4.57 (s, 1, C=CH); mass spectrum M^+ 128; **8** (R = C_2H_5): ir (liquid film) 1700 cm^{-1} (CO); nmr (60 MHz, $CDCl_3$) τ 9.28 (t, 6, CH_3), 8.06 (q, 4, CH_2), 7.92 (s, 6, CH_3CO); mass spectrum M^+ 156.

With Isopropyl Iodide.—The reaction mixture was processed as above after being refluxed for 14 hr. The yields (quantitative gc analysis, column D, 170°) were 20% for **7** (R = i-C_3H_7), and 62% for **9** (R = i-C_3H_7). Isolation (column C, 200°) provided **7** (R = i-C_3H_7), which after molecular distillation at 72–76° (bath) (18 mm) displayed ir (liquid film) 1725, 1700 cm^{-1} (CO); nmr (100 MHz, $CDCl_3$) τ 9.10 (d, 6, CH_3), 7.83 (s, 6, CH_3CO), 7.20–7.80 (m, 1, CH), 6.60 (d, 1, COCH); mass spectrum M^+ 142; and **9** (R = i-C_3H_7): ir (liquid film) 1675 (CO), 1580 cm^{-1} (C=C); nmr (60 MHz, $CDCl_3$) τ 8.74 (d, 6, CH_3), 7.88 (s, 3, $CH_3C(O)C$=C), 7.76 (s, 3, CH_3CO), 5.60 (m, 1, CH), 4.58 (s, 1, C=CH); mass spectrum M^+ 142.

Preparation of 10.—To ethyl acetoacetate (110 mmol) in a mixture of 20 ml of ligroin and 20 ml of toluene was added, all at once, a solution of thallous ethoxide (100 mmol) in 30 ml of ligroin. A white precipitate formed, and the mixture was magnetically stirred under N_2 for *ca.* 30 min. After filtration and drying there was obtained 32 g (96%) of **10**, mp 90–91°, mass spectrum M^+ 334.

Alkylation of 10 with Alkyl Iodides. General Procedure.—A mixture of 50 mmol of **10** in 45 ml of the freshly distilled alkyl iodide was magnetically stirred and refluxed under a nitrogen atmosphere for the times indicated. The mixtures were then processed as described for the alkylations of **6**.

With Ethyl Iodide.—Admixture of the reagents resulted in cloudiness, but no solid particles were evident. Upon reflux (4 hr) the mixture turned yellow and TlI precipitated. After processing as described above, the yields (column D, 170°) were ethyl acetoacetate, 2%; **11** (R = C_2H_5), 80%; **12** (R = C_2H_5), 2%, and **13** (R = C_2H_5), 5%. Isolation (column A, 200°) provided materials with the following properties: ethyl acetoacetate: ir and nmr identical with authentic sample; **12** (R = C_2H_5): ir (liquid film) 1710, 1625 cm^{-1}; nmr (100 MHz, $CDCl_3$) τ 8.70 (m, 6, CH_3), 7.72 (s, 3, $CH_3C(O)$=C), 6.20 (q, 2, C=$C(O)CH_2$), 5.86 (q, 2, $COOCH_2$), 5.01 (s, 1, C=CH); mass spectrum M^+ 158; **11** (R = C_2H_5) (after molecular distillation at 87–88° (bath) (20 mm): ir (liquid film) 1740, 1720 cm^{-1}; nmr (60 MHz, $CDCl_3$) τ 9.07 (t, 3, $CCCH_3$), 8.73 (t, 3, $OCCH_3$), 8.11 (m, 2, CCH_2C), 7.78 (s, 3, CH_3CO), 6.65 (t, 1, CH), 5.79 (q, 2, OCH_2C); mass spectrum M^+ 158; **13** (R = C_2H_5): ir (liquid film) 1735, 1710 cm^{-1}; nmr (60 MHz, $CDCl_3$) τ 9.24 (t, 6, $CCCH_3$), 8.74 (t, 3, $OCCH_3$), 8.07 (q, 4, CCH_2C), 7.88 (s, 3, CH_3CO), 5.80 (q, 2, OCH_2C); mass spectrum M^+ 186.

With Isopropyl Iodide.—The initial cloudy mixture (no solid particles) turned yellow, and TlI precipitated upon refluxing the mixture (19 hr). After processing as above, the yields (column A, 165°) were 20% for **12** (R = i-C_3H_7) and 67% for **11** (R = i-C_3H_7). Separation (column A, 195°) afforded **12** (R = i-C_3H_7), which after molecular distillation at 86–88° (bath) (18 mm) displayed ir (liquid film) 1700 (C=O), 1615 cm^{-1} (C=C); nmr (100 MHz, $CDCl_3$) τ 8.74 (d, 6, $C(CH_3)_2$), 8.74 (t, 3, CH_3C), 7.75 (s, 3, $CH_3C(O)$=C), 5.89 (q, 2, CH_2), 5.62 (m, 1, OCH), 5.03 (s, 1, C=CH); and **11** (R = i-C_3H_7), after molecular distillation at 83–86° (bath) (20 mm) showed ir (liquid film) 1740, 1715 cm^{-1}; nmr (60 MHz, $CDCl_3$) τ 9.06 (q, 6, $C(CH_3)_2$), 8.75 (t, 3, $OCCH_3$), 7.81 (s, 3, CH_3CO), 7.3–7.8 (m, 1, CH), 6.83 (d, 1, COCH), 5.85 (q, 2, CH_2).

Registry No.—**2**, 36623-33-3; **3** (R = Me), 7715-08-4; **3** (R = Et), 36623-35-5; **4** (R = Et), 24378-06-1; **4** (R = i-Pr), 36623-37-7; **6**, 25955-51-5; **7** (R = Me), 815-57-6; **7** (R = Et), 1540-34-7; **7** (R = i-Pr), 1540-38-1; **8** (R = Me), 3142-58-3; **8** (R = Et), 15119-66-1; **9** (R = Et), 1540-24-5; **9** (R = i-Pr), 1540-25-6; **10**, 36623-46-8; **11** (R = Et), 607-97-6; **11** (R = i-Pr), 1522-46-9; **12** (R = Et), 998-91-4; **12** (R = i-Pr), 1540-21-2; **13** (R = Et), 1619-57-4.

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