centrated under reduced pressure. The resulting solid (1.6 g) contained two components, which were separated by column chromatography on neutral alumina. The faster moving material (1.18 g) appeared pure, but melted over a 6° range. A 140-mg portion was sublimed to give 55 mg of bicyclic ether **9a**: mp 54.5–56°; nmr δ 2.25–2.83 (m, 2), 3.60–4.50 (m, 3, CH_2OCH); mass spectrum molecular ion m/e 140.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.05; H, 11.59.

The distillation was resumed and a fraction was collected at 110–125° (8–9 mm), dissolved in ether, washed three times with water, dried (Na_2SO_4), and concentrated. The resulting material (11.5 g, 56% yield) was found to be the desired enol **8a** contaminated with a small amount of methoxyalkene **10a** (nmr δ 3.35, sharp singlet). Column chromatography on neutral alumina permitted the desired separation of pure 3-methylenecyclooctanol (**8a**): ir 3350, 3090, 1640 cm^{-1}; nmr δ 2.00 (s, 1, OH), 2.10–2.80 (m, 4, allylic), 3.86 (m, 1, CHO), 4.90 (m, 2, vinylic); mass spectrum molecular ion m/e 140.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.22; H, 11.43.

3-Methylenecyclodecanol (8b). Hofmann elimination of quaternary hydroxide **7b** was performed by the above procedure and was accompanied by serious foaming problems. After removal of water and trimethylamine, a 6.68-g fraction was obtained at 105–122° (4 mm), and another fraction (5.96 g) was obtained at 125–135° (4 mm). The first fraction consisted of approximately 85% bicyclic ether **9b** and about 15% methoxyalkene **10b**. Sequential column chromatography and preparative tlc permitted isolation of the methoxyalkene **10b** in about 90% purity: ir 1650, 3100 cm^{-1}; nmr δ 2.00–2.80 (m, 4, allylic), 3.30 (s, 3, OCH_3), 3.40–3.80 (m, 1, CHO), 4.88 (m, 2, vinylic).

The second fraction, approximately 50% of hydroxyalkene **8b**, 13% of methoxy amine **11b**, and 35% of bicyclic ether **9b**, was separated by column chromatography on neutral alumina. Approximately 600 mg of 3-methoxy-1-dimethylaminomethylcyclodecane (**11b**) was recovered and purified by vacuum distillation, nmr δ 2.07 (broad, 2, CH_2N), 2.20 (s, 6, NCH_3), 3.31 (s, 3, OCH_3), 3.40–3.80 (m, 1, CHO).

Anal. Calcd for $C_{14}H_{29}NO$: C, 73.95; H, 12.85. Found: C, 74.17; H, 12.83.

The desired 3-methylenecyclodecanol (**8b**, 1.78 g) was obtained in later chromatography fractions. A 380-mg sample was further purified by preparative tlc. Approximately one-third of the 300 mg of material recovered was vacuum distilled to give a clear liquid: ir 3200–3500 and 1650 cm^{-1}; nmr δ 1.66 (s, 1, OH), 2.10–2.75 (m, 4, allylic), 4.25 (m, 1, CHO), 4.95 (m, 2, vinylic); mass spectrum molecular ion m/e 168.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.42; H, 12.08.

Spiro[2.7]decan-5-ol. The Simmons–Smith procedure[13] was used for the cyclopropanation of 3-methylenecyclooctanol (**8a**). A 9.52-g (68 mmol) sample of slightly impure **8a** was treated twice with methylene iodide and Zn–Cu couple to produce 4.7 g of a liquid estimated to contain about 85% of the desired spiro alcohol (by nmr), nmr δ 0.10–0.70 (m, 4, cyclopropyl), 2.60 (s, 1, OH), 3.03–4.13 (broad m, 1, CHO).

Spiro[2.9]dodecan-5-ol. The Simmons–Smith procedure[13] was applied to 1.4 g (83.3 mmol) of 3-methylenecyclodecanol (**8b**) to give 500 mg of a crude oil which crystallized on standing. A 430-mg sample of this material was purified by preparative tlc followed by vacuum distillation to give pure spiro alcohol: mp 41–44°; nmr δ 0.10–0.46 (m, 4, cyclopropyl), 4.00 (m, 1, CHO).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.99; H, 12.10.

Spiro[2.7]decan-5-one (1a). The Collins oxidation as modified by Ratcliffe and Rodehorst[14] was used to oxidize 0.46 g (3 mmol) of spiro[2.7]decan-5-ol to the corresponding ketone. The resulting 0.39 g (85.5% yield) of product was distilled at 70–78° (0.9 mm): ir 1705 cm^{-1}; uv λ_{max} (EtOH) 280 nm (ϵ 44.5); nmr δ 0.29–0.70 (m, 4, cyclopropyl), 2.25 (s, 2, c-Pr($CH_2C{=}O$), 2.33–2.66 (m, 2, $CH_2C{=}O$); mass spectrum molecular ion m/e 152.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.74; H, 10.65.

Spiro[2.9]dodecan-5-one (1b). The Ratcliffe–Rodehorst procedure[14] was used to oxidize 80 mg (4.4 mmol) of spiro[2.9]dodecan-5-ol. A 73-mg sample of crude ketone was vacuum distilled to give 60 mg (75.8% yield) of pure ketone **1b**: ir 1700 cm^{-1}; uv λ_{max} (EtOH) 282 nm (ϵ 120); nmr δ 0.20–0.60 (m, 4, cyclopropyl), 2.33 (s, 2, c-Pr$CH_2C{=}O$), 2.50–2.80 (m, 2, $CH_2C{=}O$); mass spectrum molecular ion m/e 180.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.96; H, 11.26.

Registry No.—1a, 51364-58-0; **1b,** 51364-59-1; **4a,** 51364-60-4; **4b,** 51364-61-5; **5a,** 51364-62-6; **5b,** 51364-63-7; **6a,** 51364-64-8; **6a** methiodide, 51364-65-9; **6b,** 51364-66-0; **6b** methiodide, 51364-67-1; **7a,** 51364-68-2; **7b,** 51364-69-3; **8a,** 51364-70-6; **8b,** 51364-71-7; **9a,** 18417-66-8; **9b,** 24995-59-3; **10b,** 51364-72-8; **11b,** 51364-73-9; methyl 3-hydroxycyclooctanecarboxylate tetrahydropyranyl ether, 51364-74-0; methyl 3-hydroxycyclodecanecarboxylate tetrahydropyranyl ether, 51364-75-1; spiro[2.7]decan-5-ol, 51364-76-2; spiro[2.9]dodecan-5-ol, 51364-77-3.

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Quantitative Conversion of Carboxylic Acids and Phenols to Esters and Ethers by Reaction of Their Salts with Alkyl Halides

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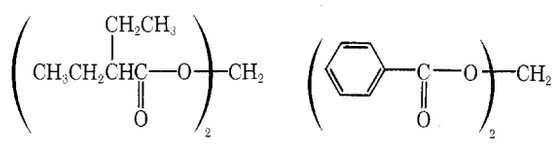
Recently we reported that carboxylic acids can be quantitatively converted to esters by reaction of their salts with alkyl bromides or iodides in hexamethylphosphoramide (HMPA) at room temperature.[1] We now wish to report results of further studies which extend the scope of this reaction. These include the rapid reaction of ethyl iodide with salts of hindered acids, the use of anhydrous potassium carbonate as base to prevent decarboxylation of certain acids, the use of geminal dihalides as the alkylating agent, and the quantitative O-alkylation of phenoxide ions.

Reaction of mesitoic acid and triethylacetic acid with sodium hydroxide (aqueous 25% NaOH) in HMPA followed by addition of ethyl iodide (4 equiv) gave the ethyl esters in quantitative yield. In each case the time required for alkylation was less than 5 min at room temperature. The short reaction time, simple procedure, and quantitative yield of this reaction make it a valuable method for preparing ethyl esters.[2] Other solvent systems such as dimethyl sulfoxide and dimethylformamide required the use of longer reaction times. Reaction of sodium triethylacetate with ethyl iodide at room temperature was only two-

thirds complete after 5 min in dimethyl sulfoxide and about one-third complete after 15 min in dimethylformamide.

Esterification of certain carboxylic acids required the use of anhydrous potassium carbonate as base, since sodium hydroxide caused some decarboxylation. When a solution of malonic acid, sodium hydroxide (aqueous 25% NaOH), and HMPA was stirred for 15 min at room temperature followed by addition of ethyl iodide and continued stirring overnight, only a 36% yield of diethyl malonate was produced. The sodium hydroxide caused some decarboxylation of malonic acid as evidenced by the precipitation of sodium carbonate from the solution. Some decarboxylation was also observed when triphenylacetic acid was treated with sodium hydroxide in HMPA. When a mixture of malonic acid, powdered anhydrous potassium carbonate, ethyl iodide, and dry HMPA was stirred for 24 hr at room temperature, a much higher yield (91%) of diethyl malonate was obtained. The same procedure used for triphenylacetic acid gave a 100% yield of ethyl triphenylacetate.[3]

Reaction of the sodium salts of 2-ethylbutanoic acid and benzoic acid with dibromomethane in HMPA at room temperature gave 100 and 86% yields of diesters **1** and **2**, respectively. Sodium benzoate required a longer reaction



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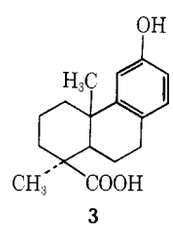
time (48 hr) than sodium 2-ethylbutanoate (24 hr). This is probably because sodium benzoate, unlike sodium 2-ethylbutanoate, is not completely soluble in HMPA. Traditionally, diesters like **1** and **2** have been prepared by reaction of paraformaldehyde or polyoxymethylene with an acid anhydride in the presence of a mineral or Lewis acid.[4,5] Reaction of sodium carboxylates with dibromomethane provides a useful alternative to this procedure.[6] Sodium carboxylates failed to react with bromoform or carbon tetrabromide to give tri- or tetrasubstituted products even when higher temperatures were used.

Phenols were quantitatively converted to ethers by reaction of their sodium salts with alkyl iodides in HMPA at room temperature. Reaction of podocarpic acid (**3**) with sodium hydroxide and methyl iodide in HMPA gave a quantitative yield of the methyl ester and ether **4**. The so-



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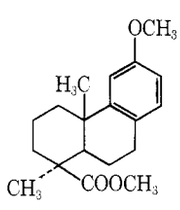

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dium salt of phenol reacted with isopropyl iodide in less than 2.5 hr to give a 100% yield of isopropyl phenyl ether. The reaction time was substantially less than that reported for the same reaction using tetrahydrofuran as solvent.[7] In the THF case a 22% yield of isopropyl phenyl ether was reported after 24 hr at 23° and at 80% yield after 24 hr at 80°. An attempt was made to prepare isopropyl cyclohexyl ether. However, when cyclohexanol, sodium hydride, isopropyl iodide, and HMPA were stirred at room temperature, much propene and only a trace of the desired ether were produced. This result is not surprising, since the alkoxide of cyclohexanol is a much stronger base than phenoxide.

Experimental Section[8]

Ethyl Mesitoate and Ethyl Triethylacetate. These esters were prepared by the procedure we previously reported for methyl mesitoate.[1] The yields of ethyl mesitoate and ethyl triethylacetate were determined by glpc[8] to be 99 and 96%, respectively.

Diethyl Malonate. To a solution of 1.04 g (10 mmol) of malonic acid in 25 ml of dry HMPA protected from moisture with a drying tube was added 3.45 g (25 mmol) of powdered anhydrous potassium carbonate and 4.9 ml (60 mmol) of ethyl iodide, and the mixture was stirred for 24 hr at room temperature (23–25°). The reaction mixture was then poured into 50 ml of water which was then extracted with two 40-ml portions of ether. The combined ether extract was washed with two 10-ml portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give 1.70 g of liquid. Analysis of the liquid by glpc[8] revealed that the actual yield of diethyl malonate was 91%. The infrared spectrum of the glpc-purified product was identical with that of an authentic sample.

Ethyl Triphenylacetate. To a mixture of 0.76 g (5.5 mmol) of powdered anhydrous potassium carbonate, 14 ml of dry HMPA, and 1.6 ml (20 mmol) of ethyl iodide protected from moisture with a drying tube was added 1.44 g (5.0 mmol) of triphenylacetic acid and the mixture was stirred for 24 hr at room temperature (23–25°). Work-up as described in the case of diethyl malonate gave 1.60 g (100%) of crystals, mp 116–118° (lit.[9] mp 116–117°, 120–121°). After recrystallization from ether the melting point was 117–119°. The infrared spectrum was identical with that of an authentic sample.

Reaction of 2-Ethylbutanoic Acid with Dibromomethane. To a solution of 2.32 g (20 mmol) of 2-ethylbutanoic acid in 50 ml of HMPA was added 4.8 g of an aqueous 25% sodium hydroxide solution (30 mmol of NaOH) and 5.6 ml (80 mmol) of dibromomethane. The solution was stirred for 24 hr at room temperature (23–25°). The solution was then poured into 100 ml of water which was then extracted with two 75-ml portions of ether. The combined ether extract was washed with two 25-ml portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give 2.84 g of liquid. Analysis of this liquid by glpc[8] revealed that it consisted only of diester **1** and some dibromomethane and that the actual yield of **1** was 100%. An analytical sample of **1** was obtained by glpc: $n^{26}D$ 1.4262; ir (neat) 1760 cm^{-1} (C=O); nmr (CCl_4) τ 4.28 (s, 2 H), 9.11 (t, 12 H, J = 7 Hz).

Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.85; H, 9.75.

Reaction of Benzoic Acid and Dibromomethane. To a solution of 2.44 g (20 mmol) of benzoic acid in 50 ml of HMPA was added 4.8 g of aqueous 25% sodium hydroxide solution (30 mmol of NaOH) and 5.6 ml (80 mmol) of dibromomethane. The mixture (sodium benzoate precipitated out initially) was stirred for 48 hr at room temperature. The solution was then poured into 100 ml of water which was then extracted with two 75-ml portions of ether. The combined ether extract was washed with two 25-ml portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give 2.50 g of a white solid, mp 85–88°. The 2.50-g sample was dissolved in about 50 ml of ether which was then washed with two 10-ml portions of 10% sodium hydroxide solution and two 10-ml portions of water. After drying over sodium sulfate, the ether solution was evaporated under reduced pressure to give 2.20 g (86%) of diester **2** as colorless crystals, mp 96.5–98.5° (lit.[5] mp 99°).

Methyl Ester and Ether of (+)-Podocarpic Acid. To a solution of 2.74 g (10 mmol) of (+)-podocarpic acid in 50 ml of HMPA was added 6.4 g of aqueous 25% sodium hydroxide solution (40 mmol of NaOH) and the solution was stirred for 0.5 hr at room temperature (23–25°). Then 5.0 ml (80 mmol) of methyl iodide was added and the solution was stirred for 7 hr at room temperature. The solution was then poured into 100 ml of 5% hydrochloric acid solution which was then extracted twice with 75-ml portions of ether. The combined ether extracts were washed with two 25-ml portions of water, dried over anhydrous sodium sulfate, and evaporated to give 3.04 g (100%) of **4** as yellow crystals, mp 128–129.5° (lit.[10] mp 128°). Recrystallization from ether gave white crystals but did not change the melting point.

Isopropyl Phenyl Ether. To a solution of 1.88 g (20 mmol) of phenol in 50 ml of HMPA was added 6.4 g of aqueous 25% sodium hydroxide solution (40 mmol of NaOH) and the solution was stirred for 5 min before the addition of 8.0 ml (80 mmol) of isopropyl iodide. After stirring for 2.5 hr at room temperature (23–25°), the reaction mixture was poured into 100 ml of 5% hydro-

chloric acid solution which was then extracted with two 75-ml portions of ether. The combined ether extract was washed with two 25-ml portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give 3.14 g of a liquid residue. Analysis of this liquid by glpc[8] revealed that it contained only isopropyl phenyl ether except for a little isopropyl iodide and that the yield of ether was 100%. Product purified by preparative glpc gave a refractive index of $n^{25}D$ 1.4946 (lit.[11] $n^{25}D$ 1.4944) and an infrared spectrum identical with that of an authentic sample.

Acknowledgment. We wish to thank the Research Corporation for financial support.

Registry No.—**1**, 51310-59-9; **2**, 5342-31-4; **3**, 5947-49-9; **4**, 1231-74-9; diethyl malonate, 105-53-3; malonic acid, 141-82-2; ethyl iodide, 75-03-6; ethyl triphenylacetate, 5467-22-1; triphenylacetic acid, 595-91-5; 2-ethylbutanoic acid, 88-09-5; dibromomethane, 74-95-3; benzoic acid, 65-85-0; methyl iodide, 74-88-4; isopropyl phenyl ether, 2741-16-4; phenol, 108-95-2; isopropyl iodide, 75-30-9.

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A New Method for Preparation of Alkyl and Aryl Isothiocyanates Using Amines, Butyllithium, and Carbon Disulfide

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Alkyl and aryl isothiocyanates are usually prepared in several steps from amines *via* dithiocarbamate derivatives.[1-4] We now describe a convenient alternative approach involving the amine, carbon disulfide, and butyllithium, which lead to isothiocyanates in good yields from alkyl- or arylamines which do not contain groups that react with butyllithium.

The amines are treated with an equimolar amount of butyllithium followed by carbon disulfide to give the lithium dithiocarbamate **1**. Treatment with additional butyllithium and carbon disulfide leads *via* the dilithio derivative **2** to the complex **3**. The formation of **3** is indicated by the absence of characteristic ir bands for carbon disulfide at 1520 and 2230 cm^{-1}. After the reaction mixture was for 2 hr at the temperature indicated in Table I, the inorganic lithium salt had precipitated, and the solution showed the ν_{NCS} band at about 2150 cm^{-1}. Isothiocyanate **4** was obtained in good yield by distillation of the reaction mixture, as shown in Table I.

$$\underset{\mathbf{1}}{RNHCS_2Li} \xrightarrow[-BuH]{BuLi} \underset{\mathbf{2}}{RN(Li)CS_2Li} \xrightarrow{CS_2} \underset{\mathbf{3}}{RN(CS_2Li)_2} \xrightarrow[-LiCS_3]{} \underset{\mathbf{4}}{RNCS}$$

Successive additions of butyllithium and carbon disulfide to form intermediate **3** are essential for the formation of isothiocyanate in good yield. For example, phenyl isothiocyanate was formed quantitatively in the reaction *via* the intermediate **3** (R = Ph) at 80°, while it was obtained only in 46 and 11% yields by thermal decompositions (150°) of lithium *N*-lithio-*N*-phenyldithiocarbamate, **2** (R = Ph), and of lithium *N*-phenyldithiocarbamate, **1** (R = Ph), respectively. When the reaction product formed by treatment of aniline with 2 equiv of butyllithium was allowed to react with 2 equiv of carbon disulfide for 4 hr at 70°, *N,N'*-diphenylthiourea was obtained in good yield, accompanied by the formation of a trace amount of phenyl isothiocyanate.

Experimental Section

All melting and boiling points were uncorrected. The ir and nmr spectra were determined with a JASCO Model IR-S spectrometer and a Hitachi Perkin-Elmer Model R-20 spectrometer, respectively. Solvents and amines were dried by common methods.

Standard Method for Preparation of Isothiocyanate. A. Butyl Isothiocyanate. Butylamine (4.39 g, 60 mmol) was dissolved in dry tetrahydrofuran (50 ml) under dry nitrogen in a flask equipped with a mechanical stirrer, a condenser, a dropping funnel, and a nitrogen inlet, and treated with butyllithium (66 mmol in 53 ml of petroleum ether) at 0°. After stirring for 30 min at room temperature, carbon disulfide (5.01 g, 66 mmol) in 5 ml of tetrahydrofuran was added dropwise at 0° to form the dithiocarbamate salt **1** (R = Bu). The solution of **1** thus prepared *in situ* was treated again with butyllithium (66 mmol) at 0° and was stirred for 30 min at room temperature, followed by the addition of carbon disulfide (66 mmol), to form the intermediate **3** (R = Bu). After the reaction mass was stirred for 30 min at room temperature, the inorganic lithium salt had precipitated and the characteristic band of isothiocyanate at 2170 cm^{-1} appeared in the ir spectrum of the reaction mixture. The mass was stirred for 2 hr at 60° and filtered to remove the salt. Tetrahydrofuran was evaporated *in vacuo* and butyl isothiocyanate was distilled: yield 5.5 g (80%); bp 47–48° (10 mm); ir ($CHCl_3$) ν_{NCS} 2170 cm^{-1}. The ir and nmr spectra were in good agreement with those of the authentic sample prepared by the published method.[1]

B. Other Isothiocyanates. The intermediates **3** were prepared *in situ* from the respective amines, analogously to the case of butylamine, and were heated for 2 hr at the temperature indicated in Table I. The isothiocyanates formed were isolated by distillation. Their yields and boiling points are summarized in Table I. Their ir and nmr spectra were the same as those of authentic samples prepared by the literature method.[1]

Among the isothiocyanates shown in Table I, α-naphthyl isothiocyanate was obtained by pyrolytic distillation of the reaction mixture.

Thermal Decomposition of Lithium *N*-Lithio-*N*-phenyldithiocarbamate, 2 (R = Ph). The solution of **2** (R = Ph) in tetrahydrofuran was prepared *in situ* analogously to the case of *N*-butyl dithiocarbamate, **2** (R = Bu), and was pyrolytically dis-