For bis-(*p*-methoxybenzoyl)diazine (**1c**, 96%): mp 133–134 °C (lit.[11] 132 °C).

Preparation of 1,2-Diazetidines 2a–c. A solution of 4.6 g (50.0 mmol) of quadricyclane and 16.8 mmol of the appropriate diaroyldiazine **1a–c** in 200 mL of acetonitrile was refluxed for the following periods of time: 1.5 h for **1a**, 3 h for **1b**, and 24 h for **1c**. Removal of solvent and excess quadricyclane at reduced pressure afforded crude 1,2-diazetidines **2a–c** in yields in excess of 90%. Recrystallization from carbon tetrachloride afforded analytically pure 1,2-diazetidines in 90, 65, and 60% yields for **2a**, **2b**, and **2c**, respectively.

For 3,4-bis[*p*-(trifluoromethyl)benzoyl]-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene (**2a**): mp 220–221 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 4 H, $J = 9$ Hz), 7.37 (d, 4 H, $J = 9$ Hz), 5.95 (broad s, 2 H), 4.42 (s, 2 H), 2.98 (broad s, 2 H), 2.25 (d, 1 H, $J = 9$ Hz), 1.77 (d, 1 H, $J = 9$ Hz); ^{19}F NMR ($CDCl_3$) ϕ 36.81 (s); IR (KBr) 1685 cm^{-1} (C=O), no NH. Anal. Calcd for $C_{23}H_{16}F_6N_2O_2$: C, 59.23; H, 3.46; N, 6.01. Found: C, 59.28; H, 3.24; N, 5.90.

For 3,4-dibenzoyl-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene (**2b**): mp 211–212 °C; ^{1}H NMR ($CDCl_3$) δ 7.57–8.09 (m, 10 H), 6.10 (broad s, 2 H), 4.49 (s, 2 H), 3.08 (broad s, 2 H), 2.38 (d, 1 H, $J = 11$ Hz), 1.78 (d, 1 H, $J = 11$ Hz); IR (KBr) 1680 cm^{-1} (C=O), no NH. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.01; H, 5.22; N, 8.16.

For 3,4-bis(*p*-methoxybenzoyl)-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene (**2c**): mp 190–191 °C; ^{1}H NMR ($CDCl_3$ (δ 7.97 (d, 4 H, $J = 9$ Hz), 7.05 (d, 4 H, $J = 9$ Hz), 6.10 (broad s, 2 H), 4.47 (s, 2 H), 3.95 (s, 6 H), 2.38 (d, 1 H, $J = 10$ Hz), 1.85 (d, 1 H, $J = 10$ Hz); IR (KBr) 1670 cm^{-1} (C=O), no NH. Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.71. Found: C, 70.52; H, 5.56; N, 7.53.

Kinetic Measurements. Solutions of 0.01 M in **1a–c** and 0.1 M in quadricyclane in acetonitrile or carbon tetrachloride were tightly stoppered in round-bottom flasks and heated at 60 ± 1 °C in a thermostatically controlled water bath. Aliquots were withdrawn at various intervals and immediately quenched at −78 °C. Analyses for unreacted **1a–c** were performed by visible spectroscopy on a Cary-14 ultraviolet–visible spectrometer at the wavelengths shown in Table I. Pseudo-first-order rate constants were determined graphically over at least three half-lives for the disappearance of **1a–c**. Second-order rate constants k (shown in Table I) were determined by dividing the observed pseudo-first-order rate constants by initial quadricyclane concentration and represent the average of at least two runs. First-order rate constants at 60 °C for the unimolecular decomposition of **1a–c** in the absence of quadricyclane account for less than 5% of the observed pseudo-first-order rate constant in the presence of the hydrocarbon.

Acknowledgment. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Research and Projects at Southern Illinois University at Edwardsville for support of this research.

Registry No.—**1a**, 69780-57-0; **1b**, 959-31-9; **1c**, 38192-16-4; **2a**, 69780-58-1; **2b**, 69780-59-2; **2c**, 69780-60-5; **3a**, 69780-61-6; **3b**, 787-84-8; **3c**, 849-82-1; *p*-(trifluoromethyl)benzoyl chloride, 329-15-7; benzoyl chloride, 98-88-4; *p*-methoxybenzoyl chloride, 100-07-2; hydrazine, 302-01-2; quadricyclane, 278-06-8.

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2,3-Dimethylenebutadiene Dianion: Convenient Procedure for Allylic Metalation of Conjugated Dienes

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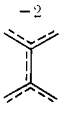
While 2,3-dimethylenebutadiene dianion (**1**) has been formally present as a ligand of iron in a complex,[1] efforts to prepare alkali metal salts of it by metalation of 2,3-dimethylbutadiene with base–solvent systems such as *n*-butyllithium–tetramethylethylenediamine have failed due to faster addition to its conjugated diene system. This rapid addition to 1,3-dienes has made the much less accessible 1,4-dienes the usual precursors of pentadienyl carbanions,[2] though 1,3-dienes can be used with KNH_2/NH_3 with its temperature and pressure limitations.[3] We wish to report that Lochmann's base mixture *n*-butyllithium–KO-*t*-Bu[4] metalates 2,3-dimethylbutadiene smoothly to dianion **1** and in addition gives pentadienyl anions **2** and **3** in good yield from the corresponding 1,3-dienes.



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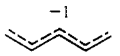

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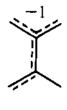

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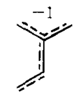

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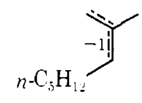

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After efforts to prepare **1** by dimetalation/ring opening of isopropenylcyclopropane failed,[5] direct dimetalation of 2,3-dimethylbutadiene using Lochmann's base was found to work well. The dianion salt dissolved in tetrahydrofuran (THF) to give a ^{1}H NMR spectrum consisting of a broad singlet at δ 1.05. It reacted with D_2O to give a 73% yield of dideuterio-2,3-dimethylbutadiene and with diethyl sulfate to give a 71% yield of 2,3-dipropyl-1,3-butadiene.

This same metalation procedure gave a quantitative yield of pentadienyl anion (**2**, ^{1}H NMR in THF-d_8,[6] expected products from D_2O quench[2]) from a mixture of (*Z*)- and (*E*)-piperylenes but went to a mixture of di- and trianion[7] from 1,3-cycloheptadiene. Monanion **3**[8] was prepared virtually free of di- and trianion using 1 equiv each of KO-*t*-Bu and *n*-butyllithium and *inverse* addition.

As monoanion **4** is no doubt an intermediate in the above metalation which produces dianion **1**, it was expected that isoprene could be metalated by this system to the elusive 2-vinylallyl anion **5**,[9] isomeric with **2**. However, in this case addition of *n*-butyllithium to give allyl anion **6** predominates (H_2O quench products: 2-methyl-1-octene and 2-methyl-2-octene). The formation of an allyl anion with a primary and a *secondary* charge-bearing carbon in the latter case (primary and *tertiary* in the 2,3-dimethylbutadiene case) presumably tips the balance in favor of addition.

This metalating system can no doubt be used for the preparation of many new anions other than **1–3** from conjugated dienes. We are investigating this and also further reactions of new dianion **1**.

Experimental Section

Melting points were determined on a Kofler hot-stage and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Gas chromatography (GC) was performed with a Varian Aerograph, Model 700, equipped with a 6 ft × 0.25 in. column packed with 10% UCON LB550X on Chromosorb W.

Dianion 1. To a mixture of 2.24 g (20 mmol) of KO-*t*-Bu, 20 mL of pentane, and 9.6 mL (20 mmol) of 2.2 M *n*-BuLi in hexane (ALFA Division, Ventron Corp.) in an argon-filled round-bottom flask was added dropwise via dropping funnel over 5 min with stirring 1.15 mL of 2,3-dimethyl-1,3-butadiene in 20 mL of pentane. After being stirred 10 min more, the orange dianion 1 salt was allowed to settle, the supernatant was removed via syringe, and the solid was blown dry with argon. For reactions, it was suspended in 20 mL of dry THF; a saturated solution in THF-d_8 gave a ^{1}H NMR spectrum consisting of a single broad peak at δ 1.05. This dianion preparation proceeds in 70–80% yield as judged by the yields of quench products given below.

Anion 2. The same metalation procedure quantitatively converted a mixture of (*Z*)- and (*E*)-piperylenes to pentadienyl anion, as indicated by its ^{1}H NMR spectrum.[6] The outer C–C rotation barriers in the carbanion prepared in this way are noticeably higher than those of the earlier preparation.

Anion 3. To a mixture of 0.58 g (5.1 mmol) of KO-*t*-Bu, 15 mL of pentane and 0.57 g (5.1 mmol) of 1,3-cycloheptadiene in an argon-filled round-bottom flask was added dropwise via syringe 2.0 mL (5.2 mmol) of 2.6 M *n*-BuLi in hexane over 5 min with stirring. After being stirred for 10 min more, the green monoanion **3** salt was allowed to settle, the supernatant was removed via syringe, and the solid was blown dry with argon. For reactions, it was dissolved in 20 mL of ether. This anion preparation proceeds in 50–60% yield.

Reaction of Dianion 1 with D_2O and Diethyl Sulfate. To an argon-filled, septum-capped, 250-mL, round-bottom flask equipped with magnetic stirring bar at −78 °C were added 30 mL of dry THF and 2 equiv of D_2O or diethyl sulfate. The reaction was conducted with rapid stirring by dropwise addition of dianion suspension via syringe through the septum cap. After being stirred for 30 min, the reaction mixture was quenched with 1 mL of H_2O. For the D_2O quench, 20 mL of pentane was added, and the solution was extracted 5× with water to remove THF and inorganic salts. The pentane solution was dried over magnesium sulfate, and the product was purified by distillation. For the diethyl sulfate quench, 20 mL of 10% KOH in 80% ethanol was added to the THF solution to hydrolyze any remaining diethyl sulfate. After 3 h of reflux, the solution was extracted with pentane and dried over magnesium sulfate, and the pentane was removed by rotary evaporation. The product was purified by GC at 90 °C. The yield of dideuterio-2,3-dimethylbutadiene (MS, *m/e* 84; ^{1}H NMR (4H) δ 1.7) was 73%. The yield of 2,3-dipropyl-1,3-butadiene was 71%.

Reaction of Anion 3 with D_2O. One equivalent of D_2O was added quickly to the ether solution of **3**. The solution was extracted with saturated ammonium chloride, and the ether was removed by distillation. A Kugelrohr distillation was performed at 130 °C, and the distillate was purified by preparative GC. The yield of 5-deuterio-1,3-heptadiene (MS, *m/e* 95; ^{1}H NMR (3 H) δ 2.0) was 52%.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No.—**1**, 69780-62-7; **2**, 35731-42-1; **3**, 35731-46-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; (*Z*)-piperylene, 1574-41-0; (*E*)-piperylene, 2004-70-8; 1,3-cycloheptadiene, 4054-38-0; dideuterio-2,3-dimethylbutadiene, 52221-66-6; 2,3-dipropyl-1,3-butadiene, 16356-06-2; 5-deuterio-1,3-heptadiene, 69780-63-8; D_2O, 7789-20-0; diethyl sulfate, 64-67-5.

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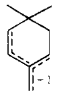
(9) 2-Vinylallyl anion i is an unisolated intermediate in the KO-*t*-Bu–*t*-BuOH catalyzed isomerization of ii to iii (Allen S. Roth, M.S. Thesis, University of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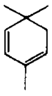
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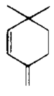
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Arizona, 1972); however, all of our efforts to produce **5** or a simple derivative in high concentration have failed.

One-Step Method for Converting Esters to Acyl Chlorides

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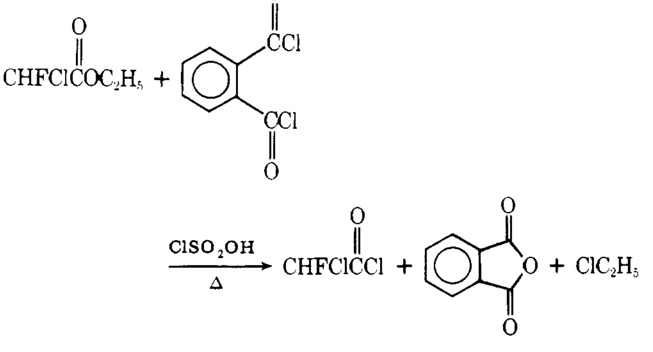
Acyl chlorides are usually prepared from the parent carboxylic acids or their salts. This is true even when the corresponding ester is more accessible because there is no general method for a one-step conversion of esters to acyl chlorides.

Our research required a large sample of chlorofluoroacetyl chloride. The ethyl ester of chlorofluoroacetic acid is readily available,[1] but the free acid is difficult to prepare in good yield because of its volatility and extreme water solubility.[2] The sodium salt also presents difficulties because it is thermally unstable. To overcome these problems, we developed a one-step method for the conversion of esters to the corresponding acyl chlorides by using a mixture of phthaloyl chloride and chlorosulfonic acid.

Chlorofluoroacetyl chloride was prepared in 50% yield by heating an equimolar mixture of ethyl chlorofluoroacetate and chlorosulfonic acid and distilling out the chloride as it was formed. The yield was improved to 88% when an equimolar amount of phthaloyl chloride was added to the reaction mixture. Some gases, particularly ethyl chloride, were also formed, so the product was collected in an efficiently cooled receiver.



Bromofluoroacetyl chloride and chloroacetyl chloride were also prepared in good yields by this same method from their corresponding esters. In addition, acetyl chloride was formed from ethyl acetate, but in this case the yield was only 52%. The

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