trile.[6] Recrystallization from 50% ethanol gave a 73% yield of a pale yellow solid, mp 170–171°.

Anal. Calcd for $C_{16}H_{11}O_2N$: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.00; H, 4.75; N, 5.72.

α-(*o*-Carboxyphenyl)cinnamic Acid (1). A. α-(*o*-Carboxyphenyl)cinnamonitrile (11.4 g) was refluxed with concentrated hydrochloric acid (300 ml) for 48 hr. The mixture upon cooling gave a pale yellow solid, mp 197–201°. Purification by dissolving the solid in 10% sodium hydroxide, decolorizing with decolorizing carbon, and acidifying with hydrochloric acid gave 8.8 g of a white solid melting at 215–216°.

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.69; H, 4.29.

B. A mixture of *o*-carboxyphenylacetic acid (36.0 g), benzaldehyde (75 ml), and acetic anhydride (28.4 ml) at 70–80° was treated dropwise with triethylamine (50 ml) over a period of 1.5 hr. Heating and stirring were continued for another 4 hr and the resulting dark brown mixture was poured into 10% hydrochloric acid (700 ml) and allowed to stand overnight at 0°. The resulting brown oil was separated and dissolved in benzene (300 ml). Extraction with 5% sodium hydroxide followed by acidification gave a resinous solid which was filtered and treated with benzene (400 ml). The resulting pale tan solid melted at 185–190° and was purified by the method used in part A. The white solid melted at 215–216°, yield 25.8 g.

α-(*o*-Carboxyphenyl)-β-phenylpropionic Acid (2). α-(*o*-Carboxyphenyl)cinnamic acid (**1**, 15.5 g) was dissolved in 10% sodium hydroxide (275 ml) and the resulting solution was treated at 90° with small amounts of nickel–aluminum alloy (Raney catalyst, 27 g) during the course of 2 hr. The mixture was heated for an additional 1 hr and filtered, and the residue was washed with hot 10% sodium hydroxide (25 ml) and hot water (50 ml). The filtrate was added dropwise with stirring to 150 ml of concentrated hydrochloric acid at a rate such that the temperature did not exceed 80–85°. The resulting acid (13.5 g) melted at 166–167°.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.79; H, 5.31.

α-(*o*-Carboxyphenyl)-β-phenylpropionic Anhydride (3). α-(*o*-Carboxyphenyl-β-phenylpropionic acid (**2**, 27.0 g) was refluxed with toluene in a flask fitted with a Dean-Stark for 24 hr or until 1.82 ml of water was formed. Removal of the toluene gave a quantitative yield of the anhydride **3**, mp 114–116°, ir (Nujol) 1780, 1740 cm^{-1} (anhydride).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.17; H, 4.79. Found: C, 75.97; H, 4.55.

Indeno[1,2-*c*]isocoumarin (4). A. A solution of α-(*o*-carboxyphenyl)-β-phenylpropronic acid anhydride (**3**, 5.0 g) in nitrobenzene (100 ml) was treated with aluminum chloride (10.7 g) and heated at 60° for 15 min. The resulting mixture was poured into dilute hydrochloric acid (300 ml) containing ice and then steam distilled to remove the nitrobenzene. The resulting solid was filtered and purified by dissolving in 10% sodium carbonate, treating the solution with decolorizing carbon, and acidifying. The crude product upon recrystallization from 70% ethanol gave 0.88 g of indeno[1,2-*c*]isocoumarin (**4**) melting at 175–176°; ir (Nujol) 1740 (C=O), 1685 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.10 (s, 2, CH_2), 7.68 (m, 8, aromatic H).

Anal. Calcd for $C_{16}H_{10}O_2$: C, 81.06; H, 4.53. Found: C, 81.16; H, 4.32.

B. α-(*o*-Carboxyphenyl)-β-phenylpropionic acid (**2**, 10 g) was added quickly with stirring to a mixture of concentrated phosphoric acid (80 g) and phosphorus pentoxide (80 g) at 160° and maintained at this temperature for 12 hr. The mixture was cooled and added to water (300 ml) and ice (300 g) and the resuling solid was extracted with ether. Removal of the ether gave a product which upon crystallization from 70% ethanol gave 5.14 g of indeno[1,2-*c*]isocoumarin (**4**), mp 175–176°.

11-Bromoindeno[1,2-*c*]isocoumarin (5). A solution of **4** (0.60 g) in carbon tetrachloride (15 ml) was treated with *N*-bromosuccinimide (0.46 g) and a trace of benzoyl peroxide and the resulting mixture was refluxed and irradiated for 6 hr. Upon cooling a pale yellow solid (0.8 g) was obtained and purified by stirring with water (20 ml) for 2 hours and recrystallizing from hexane: yield 0.49 g; mp 216–217°; ir (Nujol) 1760 (C=O), 1705 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.44 (s, 1 H, CHBr), 7.67 (m, 8, aromatic protons).

Anal. Calcd for $C_{16}H_9BrO_2$: C, 59.82; H, 3.01. Found: C, 59.71; H, 2.96.

6a,11a-Dihydro-11-ketoindeno[1,2-*c*]isocoumarin (6). A. A solution of **5** (0.25 g) in absolute ethanol (15 ml) was stirred at room temperature with 10% sodium hydroxide (1 ml) for 12 hr. Acidification with dilute hydrochloric acid gave a pale orange solid which upon recrystallization from benzene gave a pale green solid melting at 183–184°; yield 0.15 g. Two recrystallizations from ethanol gave a white solid melting at 186–187°; ir (1% in tetrahydrofuran) 3367 (OH), 1754, 1695 (very small, CO), 1639 (C=C), 1645 cm^{-1} (aromatic C=C); NMR (Me_2SO-d_6) δ 5.48 (d, 1, CH, J = 8 Hz), 5.97 (d, 1, OH, J = 8 Hz), 7.17–8.25 (m, 8, aromatic); NMR (Me_2SO-d_6 + D_2O) δ 5.45 (s, 1, CH), 7.17–8.25 (m, 8, aromatic).

Anal. Calcd for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 76.83; H, 4.23.

B. A solution of 11-ketoindeno[1,2-*c*]isocoumarin, (0.2 g) in glacial acetic (30 ml) was treated at reflux with zinc dust until the orange color of the solution disappeared. The resulting mixture was filtered into water (70 ml) and the solid formed was recrystallized from benzene, yield 0.14 g, mp 183–184°. A mixture melting point with the sample prepared in procedure A melted at the same point.

11-Ketoindeno[1,2-*c*]isocoumarin[4]. A solution of **6** in ethanol (15 ml) and 10% sodium hydroxide (1 ml) was stirred at room temperature for 7 days. Acidification with hydrochloric acid gave an orange solid which when recrystallized from benzene melted at 260–261°. A mixture melting point with an authentic sample melted at the same point.

Registry No.—**1**, 39585-13-2; **2**, 2897-88-3; **3**, 2897-89-4; **4**, 5651-52-5; **5**, 5614-25-1; **6**, 56114-26-2; α-(*o*-carboxyphenyl)cinnamonitrile, 5614-27-3; *o*-carboxyphenylacetonitrile, 6627-91-4; benzaldehyde, 100-52-7; *o*-carboxyphenylacetic acid, 89-51-0; *N*-bromosuccinimide, 128-08-5; 11-ketoindeno[1,2-*c*]isocoumarin, 5651-60-5.

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The *O*,2-Dilithio Derivative of Allyl Alcohol, a Useful Synthetic Reagent

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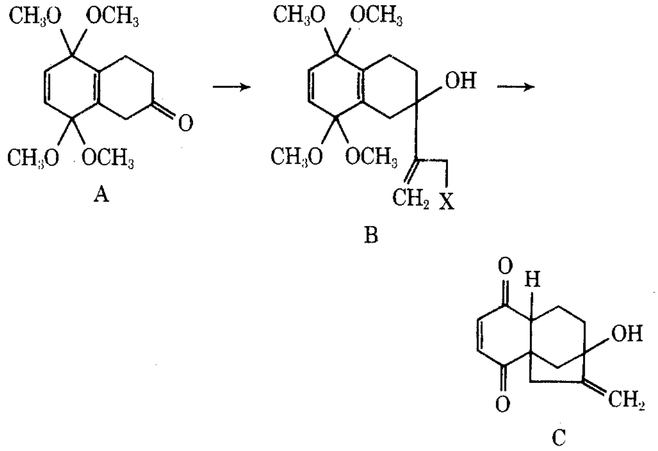
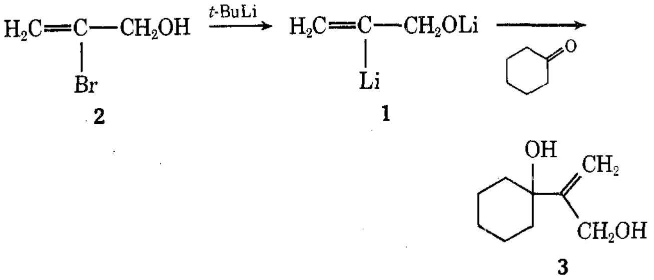
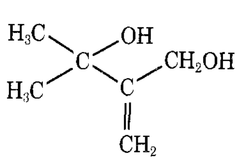
In connection with research directed toward a synthesis of gibberellic acid,[1] a reagent was required for effecting the sequence A → B → C. The ideal candidate seemed to be the previously unknown *O*,2-dilithio derivative of allyl alcohol, $H_2C{=}C(Li)CH_2O^-Li^+$ (**1**). A similar reagent,



$H_2C{=}C(Li)CH_2N(CH_3)_2$, had been generated and utilized advantageously in earlier work in these laboratories.[2] It was also known that the reaction of metals such as magnesium with ethers of 2-bromoallyl alcohol leads rapidly to allene presumably via the intermediate $H_2C{=}C(Met)CH_2OR$.[3] The generation of 1 has in fact been found to be quite straightforward. Communication of our results at this time has been prompted by the obvious practicality and usefulness of 1 and also by the appearance of a recent paper[4] dealing with two reagents of the same general type (substituted 2-oxido vinyllithium derivatives).

Treatment of the readily available[5] 2-bromoallyl alcohol (**2**) in ether with 2.5 equiv of *tert*-butyllithium[6] at −78 to 0° resulted in formation of **1** as evidenced by the isolation of the adduct **3** in 73% yield after reaction with cyclohexanone. The unsaturated diols **4** and **5** were similarly obtained from acetone and benzaldehyde in good (65–70%) yield.[7]

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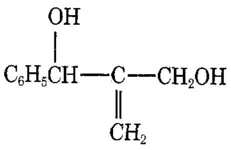
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Experimental Section

General Method. 2-(1′-Hydroxycyclohexyl)allyl Alcohol (3). To a solution of 413 mg (3.01 mmol) of 2-bromoallyl alcohol in 8 ml of ether at −78° was added slowly 7.65 ml of 0.99 *M tert*-butyllithium in pentane. The solution was quickly warmed to 0° and stirred for 4 hr. Cyclohexanone (98.5 μl, 1.0 mmol) was added to the reaction solution and stirring was continued for an additional 1 hr at 0°. The reaction was hydrolyzed with methanol and a minimal amount of water, and the aqueous phase was extracted with ether. The ethereal extracts were combined with the organic phase of the reaction, dried (brine and Na_2SO_4), and concentrated. Preparative TLC (silica gel, 1:1 benzene–ether, R_f 0.25) of the residue gave 113 mg of diol **3** as a clear, colorless oil (73%): ir (film) 3600–3100, 2930, 2855, 1640, 1030, 960, and 905 cm^{-1}; NMR ($CDCl_3$) δ 5.13 (2 H, s, =CH), 4.28 (2 H, s, $-OCH_2$), 3.03 (2 H, br, OH), and 2.1–1.4 (10 H, br s, $-CH_2-$). After recrystallization from hexane–ether, crystalline **3**, mp 48.5–50°, was obtained, mass spectrum *m/e* (% of base peak) 156 (4), 138 (19), 95 (64), 81 (64), 67 (90), 55 (100).

Spectroscopic data for **4**: ir ($CHCl_3$) 3600–3100, 2970, 1640, 1460, 1375, 1365, 1155, 1010, 915 cm^{-1}; NMR ($CDCl_3$) δ 5.15 (2 H, s, =CH), 4.32 (2 H, s, $-OCH_2-$), 3.47 (2 H, br, OH), 1.60 (6 H, s, $-CH_3$); mass spectrum *m/e* (% of base peak) 101 (69), 83 (39), 59 (100).

Spectroscopic data for **5**: ir (film) 3600–3100, 3025, 2870, 1650, 1490, 1450, 1020, 915, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.32 (5 H, s, ArH), 5.25 (1 H, s, ArCHO), 5.15 (2 H, s, =CH), 3.98 (2 H, s, OCH_2), 3.52 (2 H, br, OH); mass spectrum *m/e* (% of base peak) 164 (0.6), 146 (96), 97 (80), 79 (100), 77 (97).

Registry No.—**1**, 56030-45-6; **2**, 598-19-6; **3**, 56030-46-7; **4**, 56030-47-8; **5**, 56030-48-9; *tert*-butyllithium, 594-19-4.

References and Notes

(1) See E. J. Corey and R. L. Danheiser, *Tetrahedron Lett.*, 4477 (1973), and previous papers cited therein.

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Dehydrobromination of α-Bromo Ketones with Palladium Tetrakis(triphenylphosphine)

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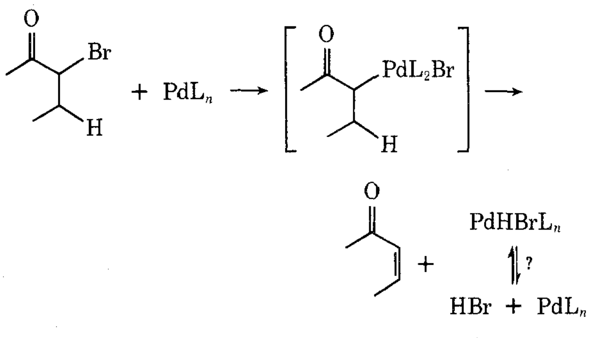
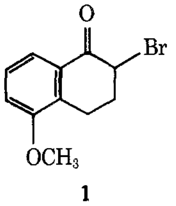
The conversion of ketones to α,β-unsaturated ketones is important in organic synthesis. The most widely used pathway for this transformation has consisted in preparation and dehydrohalogenation of intermediate α-bromo ketones. These dehydrobrominations usually require quite vigorous conditions.[1] This note reports our attempts to develop a mild method for this type of elimination using palladium tetrakis(triphenylphosphine).[2]

It was hoped that $Pd(PPh_3)_4$ would undergo facile oxidative addition with α-bromo ketones just as Pd(0) complexes do with other organic halides.[3] The resulting species, for which one possible representation is shown in eq 1,[4,5] might be expected to expel a β hydrogen along with palladium to form enone.[6] Presumably, the intermediate(s) involved would be similar to those in the direct oxidation of ketones to enones using Pd(II) salts.[7-9] The proposed method offers the potential advantage of regioselectivity in enone formation and could, in principle, be catalytic in palladium without added Cu(II) salts.[7,9]



(1)

The method works well in the case of 2-bromo-1-tetralones, where the initially formed enone can aromatize simply by tautomerization. When 5-methoxy-2-bromo-1-tetralone (**1**) is treated with 1 equiv of $Pd(PPh_3)_4$ in benzene under nitrogen, it is converted to 5-methoxy-1-naphthol (**2**)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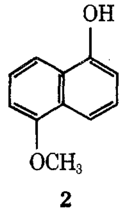
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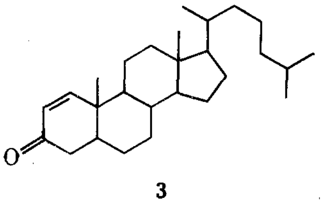
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