though some ring closure during this separation was noted. Samples were stored under nitrogen in the freezer but rapidly absorbed oxygen and formed polymer when exposed to air at room temperature. A purified sample had the following properties: NMR (CCl_4) δ 1.86 (d of d, 3 H, J = 7, 1 Hz), 5.55–6.80 (m, 6 H) 7.05–7.44 (m, 5 H); IR (CCl_4) 1690, 1652, 1622, 1500, 1450, 1378, 960 cm^{-1} UV max (cyclohexane) 304 nm (ϵ 35 000), 317 (40 500), 327 (28 800).

(*Z,Z,E*)-1-Phenyl-1,3,5-heptatriene (6). A sample of **5** was purified by thick-layer chromatography on silica gel with petroleum ether as the eluant. The purified **5** (104 mg) was hydrogenated over 50 mg of Lindlar catalyst in 15 mL of cyclohexane until 1 equiv of hydrogen had been absorbed. The light yellow oily product was chromatographed ($^1/_4$ in. × 4 ft column, 2.5% SE-30 at 155 °C), and the major product (54%) was isolated from the column: NMR (CCl_4) δ 1.84 (d, 3 H, J = 7 Hz), 5.48–6.68 (m, 6 H), 7.16 (s, 5 H); IR (neat) 1639, 1601, 1498, 1450, 945, 770, 695 cm^{-1}; UV max (cyclohexane) 297 nm (ϵ 40 000); mass spectrum, m/e (relative intensity) 170 (93), 155 (100), 141 (36), 138 (41), 115 (51), 91 (75); calcd for $C_{13}H_{14}$ m/e 170.110, found 170.110.

(*E,Z,Z*)-1-Phenyl-1,3,5-heptatriene (4). A freshly purified sample (2.11 g) of **3** was hydrogenated over 0.40 g of Lindlar catalyst in 25 mL of cyclohexane. The desired product was isolated by GLC ($^1/_4$ in. × 8 ft column, 9% SE-30, 165 °C) as the major fraction (85%): NMR (CCl_4) δ 1.90 (d of d, 3 H, J = 7, 1 Hz), 5.4–7.04 (m, 6 H), 7.1–7.4 (m, 5 H); IR (CCl_4) 1495, 1420, 1380, 1240, 965 cm^{-1}; UV max (cyclohexane 307 nm (sh), 318 (ϵ 43 000), 331 (sh).

***cis*-5-Phenyl-6-methyl-1,3-cyclohexadiene (7).** A sample of (*E,Z,E*)-1-phenyl-1,3,5-heptatriene was purified by preparative GLC (9% SE-30 on Chromosorb W at 115 °C or 3% SF-96 at 100 °C), and a 4% solution in spectral grade cyclohexane was degassed and sealed in a Pyrex tube which had been washed with ammonium hydroxide and then with distilled water before drying. The solution was heated in an oil bath for 3 h at 135 °C. An ultraviolet spectrum showed a maximum at 265 nm and residual absorption between 300 and 336 nm. The product was not isolated.

***cis* (and *trans*)-1-Phenyl-2-methylcyclohexane (8 and 9).** The solution from the thermolysis above was hydrogenated at atmospheric pressure over platinum oxide until hydrogen uptake ceased. The product was separated by GLC ($^1/_8$ in. × 14 ft column, 15% Carbowax 20M at 165 °C) into three products. In the order of elution these were 1-phenylheptane [20%; NMR (CCl_4) δ 0.90 (br t, 3 H), 1.3 (br s), 1.45–1.7 (m), 2.59 (t, 2 H, J = 7 Hz), 7.0–7.3 (m, 5 H)], *trans*-1-phenyl-2-methylcyclohexane (0.14%, identified by internal comparison with an authentic sample), and *cis*-1-phenyl-2-methylcyclohexane [80%; NMR (CCl_4) δ 0.66 (d, 3 H, J = 7.0 Hz), 1.2–2.2 (br m, 9 H)8 2.79 (d of t, 1 H, J = 11, 3.5 Hz), 7.0–7.3 (m, 5 H)], a spectrum which matches the literature[20] spectrum. Repeated integrations established the ratio of cis to trans isomers at 550:1.

1-Phenyl-6-methyl-1,3-cyclohexadiene (10). A sample of **6** was separated from overreduced products by thick-layer chromatography on silica gel with petroleum ether as the eluant. A 5% solution of this purified material in spectral grade cyclohexane was degassed and sealed as described above for **7**. The solution was heated in an oil bath for 50 h at 150 °C. Analysis by GLC (2.5% SE-30 on Chromosorb W, 155 °C) indicated the presence of two materials, unchanged starting material (46%) and a new compund (54%). The product was isolated by preparative GLC: UV max 304 nm; NMR (CCl_4) δ 1.04 (d, 3 H, J = 7 Hz), 1.68–2.00 (m), 5.5–6.1 (br m), 7.20 (br s, 5 H); IR (neat) 1600, 1490, 1450, 750, 690 cm^{-1}; mass spectrum, m/e (relative intensity) 170 (100), 155 (98), 129 (27), 128 (32), 115 (31), 91 (53).

***cis*- and *trans*-1-Phenyl-2-methylcyclohexane.** The **10** from thermolysis of **6** was hydrogenated in cyclohexane over platinum oxide until no further hydrogen was absorbed. The product had a UV maximum at 268 nm. Analysis by GLC as above showed the presence of 1-phenylheptane (16%), **9** (6%), and **8** (78%). Under these conditions reduction of the diene gives 93% **8** and 7% **9**.

From 1-Phenyl-2-(and 6-)methylcyclohexenes. A mixture of 1-phenyl-2-(and 6-)methylcyclohexenes was prepared from 2-methylcyclohexanone by the procedure of Pines, Sih, and Lewicki.[20] This mixture (987 mg) was purified by treatment over Raney nickel at atmospheric pressure. The Raney nickel was removed, and 30 mg of platinum oxide was added, and hydrogenation continued until 1.03 equiv of hydrogen had been added. Analysis by GLC as above gave 90% **8** and 10% **9**. The cis isomer was isolated by preparative GLC and had an NMR spectrum identical with the literature[20] spectrum.

Kinetic Studies. All kinetics studies were made in sealed ampules which were washed in concentrated hydroxide, rinsed in distilled water, and dried at 120 °C under nitrogen.

(*E,Z,E*)-1-Phenyl-1,3,5-heptatriene. A sample purified from overhydrogenated products by GLC was made up to a 0.002 M solution in spectral grade cyclohexane. Sealed ampules were heated in an oil bath thermostated to ±0.01 °C. Samples were removed at intervals and analyzed by UV spectrometry at 320 nm. Infinity measures indicated the presence of an unreactive impurity having a strong absorption in that region. This was assumed from its UV spectrum to be (*E,E,E*-1-phenyl-1,3,5-heptatriene [lit.[9] UV max 310 nm (ϵ 38 000), 324 (40 000), 340 (28 100)]. The results were as follows: 113.6 °C, k = 2.24 ± 0.13 × 10^{-5} s^{-1}, 123.5 °C, k = 8.14 ± 0.11 × 10^{-5} s^{-1}; 134.4 °C, k = 2.10 ± 0.05 × 10^{-4} s^{-1}; 143.6 °C, k = 4.26 × 0.04 × 10^{-4} s^{-1}.

(*E,Z,Z*)-1-Phenyl-1,3,5-heptatriene. A GLC-purified sample was made up to 0.01 M in spectral grade cyclohexane containing acenaphthalene (0.005 M) as an internal standard. Sealed ampules were heated in the thermostated oil bath as above, and the products were analyzed by GLC (3% XF-1150 on Chromosorb W at 130 °C). Results were as follows: 177.5 °C, k = 2.34 ± 0.20 × 10^{-5} s^{-1}; 191.4 °C, k = 5.49 ± 0.71 × 10^{-5} s^{-1}.

(*Z,Z,E*)-1-Phenyl-1,3,5-heptatriene. A sample purified by thick-layer chromatography was made up to 0.004 M in spectral grade cyclohexane. Sealed ampules were heated in the thermostated oil bath, and samples were analyzed by GLC (2.5% SE-30 on Chromosorb W at 155 °C). At 150 °C samples were removed at 6, 12, 21, 28, and 36 h and gave k = 4.2 × 10^{-6} s^{-1}.

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Registry No. **1**, 87764-03-2; **2**, 3893-05-8; **3**, 87764-04-3; **4**, 87764-06-5; **5**, 87764-05-4; **6**, 87764-07-6; **7**, 87764-08-7; **10**, 59581-49-6; (*E*)-PhCH=CHBr, 588-72-7; (*Z*)-PhCH=CHBr, 588-73-8; (*E*)-MeCH=CHC≡CH, 2004-69-5; (*Z*)-MeCH=CHC≡CH, 1574-40-9; 2-methylcyclohexanone, 583-60-8.

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A Simple Preparation of a β-Iodo Acetal and a β-Iodo Ketal

John C. Stowell,* Barry T. King, and Henry F. Hauck, Jr.

Department of Chemistry, University of New Orleans, Lakefront, New Orleans, Louisiana 70148

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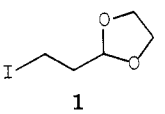
In recent years the ethylene acetal of 3-iodopropanal (**1**)[1] and ketals of 4-iodo-2-butanone[2] have seen frequent use



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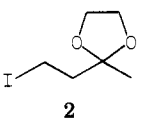

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as electrophiles with carbanions. We have found that they may be made directly from acrolein or methyl vinyl ketone and concentrated aqueous hydriodic acid, followed by ethylene glycol.

Previously, **1** was prepared from the corresponding chloro[1b] or bromo[1a] compounds, which were in turn made by using the gaseous hydrogen halides. The commonly used preparation[2g] of **2** begins with the $AlCl_3$-catalyzed reaction of acetyl chloride with gaseous ethylene. The resulting chloro ketone was treated with sodium iodide and finally ketalized in 56% overall yield. Another alternative[2h] begins with ketalization (neopentanediol) of ethyl acetoacetate followed by lithium aluminum hydride reduction, tosylation, and iodide displacement.

Anhydrous hydrogen chloride and hydrogen bromide have been added to α,β-unsaturated carbonyl compounds while trimethylsilyl iodide[3] was preferred for generating the iodo compounds via the silyl enol ethers. Although aqueous hydrobromic acid is little suited for this process,[4] we have found that concentrated aqueous hydriodic acid gives a rapid high yield of the β-iodo compound. This may then be used without purification in the reaction with ethylene glycol. By this means we have prepared **1** in 60% yield and **2** in 56–58% yield. Although boiling points are reported for these compounds, we recommend using alumina chromatography for purification since we have found that **1** decomposes with some violence upon distillation at 55 °C and 1.2 mm.

Experimental Section

2-(2-Iodoethyl)-1,3-dioxolane (1). A solution of 5.60 g (0.100 mol) of acrolein in 100 mL of CH_2Cl_2 was vigorously stirred with 24.7 g (0.110 mol) of 57% aqueous hydriodic acid in an Enlenmeyer flask for 10 h. Ethylene glycol (12.4 g, 0.200 mol) was added, and the mixture was stirred for an additional 8 h at room temperature. Excess acid was neutralized cautiously with solid Na_2CO_3, and the CH_2Cl_2 solution was washed with three portions of dilute aqueous $NaHCO_3$ and dried with $MgSO_4$. Rotary evaporation gave an oil which was purified by being passed through a column of alumina (2 × 16 cm), eluting with hexane. This gave 13.7 g (60%) of very pale yellow oil: ^1H NMR ($CDCl_3$) δ 2.17 (dt, 2 H), 3.17 (t, 2 H) 3.86 (m, 4 H), 4.84 (t, 1 H).[1b]

2-Methyl-2-(2-iodoethyl)-1,3-dioxolane (2). A solution of methyl vinyl ketone (7.00 g, 0.100 mol) in 100 mL of benzene was vigorously stirred with 45.0 g (0.200 mol) of 57% aqueous hydriodic acid for 2 h. During the first hour the reaction was slightly exothermal. The benzene solution was separated, washed with three portions of aqueous $NaHCO_3$ and one of aqueous NaCl, and dried with $MgSO_4$. Ethylene glycol (6.20 g, 0.100 mol) and *p*-toluenesulfonic acid monohydrate (0.5 g) were added to the dried solution. Azeotropic distillation for 2 h removed the product water, and then the solution was washed with saturated aqueous $NaHCO_3$, dried with $MgSO_4$, and rotary evaporated. The remaining oil was purified by being passed through a 2 × 14 cm column of neutral alumina, eluting with hexane, to afford 13.6 g (56%) of pale yellow oil. The ^1H NMR showed pure product with values identical with those reported.[2g]

The benzene solution of the unstable intermediate iodo ketone gave the following ^1H NMR values: δ 1.56 (s, 3 H), 2.33 (t, 2 H), 2.91 (t, 2 H). In CCl_4 the values were the same as those reported.[2g]

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Registry No. 1, 83665-55-8; 2, 53750-51-9; acrolein, 107-02-8; methyl vinyl ketone, 78-94-4.

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Anionically Activated Alumina in the Carboxyalkylation of Benzyl Halides

Robert A. Sawicki

Texaco Research Center Beacon, Beacon, New York 12508

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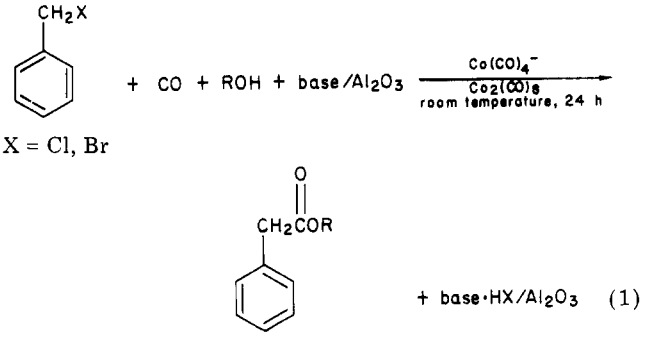
The ability of alumina to assist in various chemical transformations is well documented.[1] The combination of alumina and base, known as anionically activated or basic alumina, has been used successfully in promoting alkylation,[2] condensation,[3] and hydrolysis[4] reactions. We report the use of anionically activated alumina in the carboxyalkylation of benzyl halides using the cobalt tetracarbonyl anion catalyst. This extends the use of basic alumina to include the important area of organometallic anion chemistry.

Early work[5] on the carboxyalkylation of alkyl halides catalyzed by the cobalt tetracarbonyl anion required the use of sodium amalgam to generate the anion from the cobalt dimer. With the advent of phase-transfer catalysis,[6] the carbonylation of benzyl halides to the corresponding acid derivatives with the cobalt anion was accomplished by using sodium hydroxide and a two-phase organic–aqueous solvent system.[7,8] While this technique works well for the preparation of the carboxylic acids, the direct synthesis of the ester derivatives[9] using an alcohol solvent and an organic base has proven difficult.[5,10] Our approach (eq 1) takes advantage of the reactivity of basic alumina[11] in a carboxyalkylation scheme.



1, R = CH_3
2, R = $CH_2CH(CH_3)_2$

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