



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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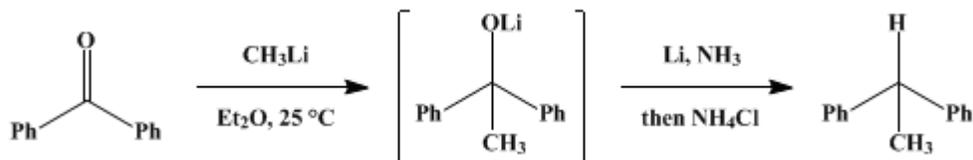
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## AROMATIC HYDROCARBONS FROM AROMATIC KETONES AND ALDEHYDES: 1,1-DIPHENYLETHANE

### [Benzene, 1-phenylethyl-]



Submitted by Sharon D. Lipsky and Stan S. Hall<sup>1</sup>.

Checked by Robert E. Ireland, Paula J. Clendening, Kathryn D. Crossland, and Alvin K. Willard.

### 1. Procedure

A 500-ml., three-necked, round-bottomed flask, equipped with a 5-cm., glass-coated, magnetic stirring bar, a Dewar condenser connected to a static argon line (Note 1), and a pressure-equalizing dropping funnel, is sealed with a rubber septum (Note 2). After flushing with argon, 30 ml. of anhydrous diethyl ether and 19.5 ml. of 1.89 *M* (0.0368 mole) methyllithium solution (Note 3) are injected through the septum into the flask (Note 4). A solution of 4.54 g. (0.0249 mole) of benzophenone (Note 5) in 35 ml. of anhydrous ether is placed in the dropping funnel and added to the reaction mixture over a 20-minute period. The mixture is allowed to stir for one half hour (Note 6). The septum is removed, and the side arm is quickly adapted with Tygon® tubing leading through a tower of solid potassium hydroxide to a tank of anhydrous ammonia. After approximately 75 ml. of ammonia is slowly distilled into the flask (Note 7), the tubing is removed, and 0.525 g. (0.0761 g.-atom, *ca.* 15 cm. added as 0.5 cm. pieces) of lithium wire (Note 8) is quickly added, and the flask is stoppered. After 15 minutes the dark blue color is discharged by the continuous addition of excess ammonium chloride (*ca.* 5 g. over a 15-minute period) (Note 9). The argon-inlet tube is disconnected, and the ammonia is allowed to evaporate. The residue is then partitioned between 100 ml. of aqueous saturated sodium chloride and 100 ml. of ether. The aqueous layer is separated and extracted with two 50-ml. portions of ether. The combined ether extracts are dried over anhydrous magnesium sulfate. Removal of the ether on a rotary evaporator yields 4.36–4.49 g. of crude product (Note 10). Filtration of the product through 60 g. of Woelm alumina (Grade III) with 150 ml. of petroleum ether affords 4.16–4.31 g. (92–95%) of 1,1-diphenylethane (Note 11), which on evaporative distillation in a Kügelrohr oven gives 4.12–4.21 g. (91–93%) of 1,1-diphenylethane, b.p. 100° (0.25 mm.),  $n_D^{28}$  1.5691 (Note 12).

### 2. Notes

1. The entire reaction sequence is performed under an argon atmosphere. A T-tube and an oil bubbler are utilized, and the system is operated at a moderate flow-rate throughout the synthesis.
2. All of the glassware is oven dried and cooled to room temperature in a large box desiccator, or the assembled glassware can be flamed dry under an argon atmosphere and allowed to cool.
3. Methyllithium in ether solution is available from Foote Mineral Company and the Aldrich Chemical Company.
4. If methyllithium of a different molarity is used, the total volume should be adjusted to 50 ml. by varying the amount of ether used.
5. Benzophenone is available from Matheson, Coleman and Bell.
6. Toward the end of this sequence 2-propanol and dry ice are added to the condenser in preparation for the reduction step.
7. To prevent splattering, the apparatus is tilted slightly to allow the condensing ammonia to run down the walls of the flask.
8. Evidently surface area is important, since when the 15 cm. of lithium wire was added as 1-cm. pieces, the reduction was incomplete. Lithium wire (0.32 cm., 0.02% sodium) available from Alpha Inorganics,

Inc., was wiped free of oil and rinsed with petroleum ether immediately prior to use.

9. Ammonium chloride is most conveniently introduced by attaching a glass tube filled with the salt to a side arm with Tygon® tubing. When the ammonium chloride is to be added, the tube is raised and tapped gently to introduce the quenching agent smoothly. Often a very vigorous reaction occurs after a considerable (10-minute) induction period. Should this step start to become violent, the addition and the vigorous stirring should be momentarily stopped to avoid eruption.

10. GC on a 200 cm. by 0.6 cm. column packed with 10% Apiezon L on Chromosorb W (AW, DMCS) using a flame-detector instrument, at a 40 ml./minute helium carrier gas flow rate, gives a trace peak at 9.9 minutes (diphenylmethane), a major peak at 11.7 minutes (1,1-diphenylethane), and a trace peak at 15.4 minutes (1,1-diphenylethanol) when the oven is held at 190° for 10 minutes and then programmed at 10°/minute to 290°.

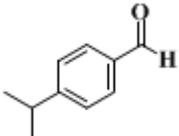
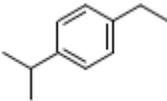
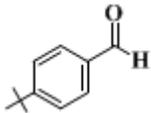
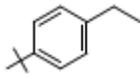
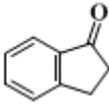
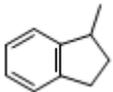
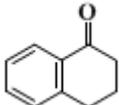
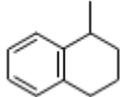
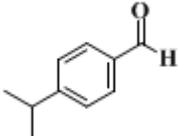
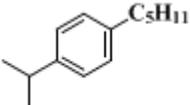
11. The sample is sufficiently pure at this point to use for most purposes. The chromatography step is an efficient means to remove any 1,1-diphenylethanol that was not reduced.

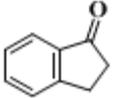
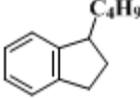
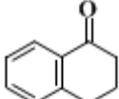
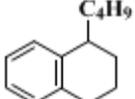
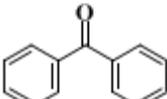
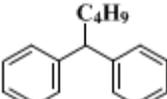
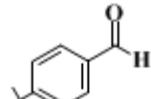
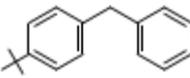
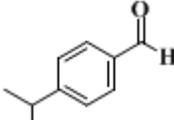
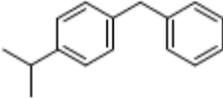
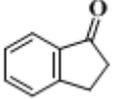
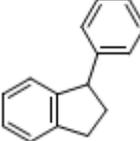
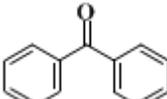
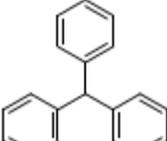
12. The spectral properties of the product are as follows; <sup>1</sup>H NMR (CCl<sub>4</sub>), δ (multiplicity, coupling constant *J* in Hz., number of protons, assignment): 1.54 (d, *J* = 7, 3H, CH<sub>3</sub>), 4.03 (q, *J* = 7, 1H, CH), 7.12 (s, 10H, 2C<sub>6</sub>H<sub>5</sub>); mass spectrum *m/e* (relative intensity): 182 (M, 32), 167 (100).

### 3. Discussion

This procedure illustrates a general method for preparing aromatic hydrocarbons by the tandem alkylation-reduction of aromatic ketones and aldehydes.<sup>2</sup> Additional examples are given in Table I. The advantages of the method are that the entire sequence is carried out in the same reaction vessel without isolation or purification of intermediates, the procedure consumes only a few hours, and in most cases the isolated yield of the aromatic hydrocarbon is excellent.

TABLE I  
AROMATIC HYDROCARBONS FROM AROMATIC KETONES AND ALDEHYDES

Aromatic Carbonyl Compound	Organolithium Reagent	Product	Yield(%)
	CH <sub>3</sub> Li		95
	CH <sub>3</sub> Li		94
	CH <sub>3</sub> Li		95
	CH <sub>3</sub> Li		78
	C <sub>4</sub> H <sub>9</sub> Li		86 <sup>a,e</sup>
	C <sub>4</sub> H <sub>9</sub> Li		89 <sup>a,e</sup>

			
	$C_4H_9Li$		76 <sup>b,e</sup>
	$C_4H_9Li$		70 <sup>a,e</sup>
	$C_6H_5Li$		93 <sup>c,e</sup>
	$C_6H_5Li$		89 <sup>d,e</sup>
	$C_6H_5Li$		97 <sup>c,e</sup>
	$C_6H_5Li$		97 <sup>d,e</sup>

<sup>a</sup>The organolithium reagent was generated *in situ* in ether from 1-bromobutane.

<sup>b</sup>Commercial butyllithium (Foote Mineral Company, ca. 15% in hexane) and six equivalents of lithium were used.

<sup>c</sup>The organolithium reagent was generated *in situ* in ether from bromobenzene.

<sup>d</sup>Commercial phenyllithium (the Aldrich Chemical Co., 2 M in cyclohexane-ether) and six equivalents of lithium were used.

<sup>e</sup>Reaction conducted on a 0.005 mole scale using as solvent 20 ml. of ether and 20 ml. of ammonia. Yield after column chromatography.

The method may be modified so that the organolithium reagent is generated *in situ* in ether from the corresponding bromide. Best results were obtained by having from the outset all of the lithium wire necessary to generate the organolithium reagent and reducing the intermediate benzyl alkoxide present.<sup>3</sup> Commercial organolithium reagents such as *n*-butyllithium in hexane or phenyllithium in cyclohexane-ether were satisfactory when twice as much lithium is used for the reduction step. In some cases, by running the alkylation step at  $-78^\circ$  to minimize competing side reactions,<sup>4</sup> higher yields than those listed in Table I can be realized. In addition to the present method, other procedures have been reported for the synthesis of 1,1-diphenylethane.<sup>5,6,7</sup>

This alkylation-reduction sequence has now been extended to benzylidene carbonyls,<sup>8</sup> complex carbonyls,<sup>9</sup> and esters and lactones;<sup>10</sup> and has been used to synthesize  $\alpha$ -cyclopropyl aromatic hydrocarbons,<sup>11</sup>  $\beta,\gamma$ -unsaturated aromatic hydrocarbons,<sup>12</sup> and 1,4-dienes from  $\alpha,\beta,\gamma,\delta$ -unsaturated

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## References and Notes

1. Department of Chemistry, Rutgers University, Newark, New Jersey 07102.
  2. S. S. Hall and S. D. Lipsky, *J. Chem. Soc. D*, 1242 (1971); *J. Org. Chem.*, **38**, 1735 (1973).
  3. The lithium wire is cut into 0.5-cm. pieces and hammered to a foil immediately prior to use.
  4. J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973).
  5. J. S. Reichert and J. A. Nieuwland, *J. Am. Chem. Soc.*, **45**, 3090 (1923).
  6. E. Späth, *Monatsh. Chem.*, **34**, 1965 (1913).
  7. J. Böeseken and M. C. Bastet, *Recl. Trav. Chim. Pays-Bas*, **32**, 184 (1913).
  8. S. S. Hall, *J. Org. Chem.*, **38**, 1738 (1973).
  9. S. S. Hall and F. J. McEnroe, *J. Org. Chem.*, **40**, 271 (1975).
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  11. S. S. Hall, C.-K. Sha, and F. Jordan, *J. Org. Chem.*, **41**, 1494 (1976).
  12. F. J. McEnroe, C.-K. Sha, and S. S. Hall, *J. Org. Chem.*, **41**, 3465 (1976).
  13. J. S. R. Zilenovski and S. S. Hall, *J. Org. Chem.*, **44**, 1159 (1979).
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## Appendix

### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alumina

petroleum ether

ammonia (7664-41-7)

ether,  
diethyl ether (60-29-7)

ammonium chloride (12125-02-9)

sodium chloride (7647-14-5)

1-bromobutane (109-65-9)

cyclohexane (110-82-7)

potassium hydroxide (1310-58-3)

Benzophenone (119-61-9)

sodium (13966-32-0)

2-propanol (67-63-0)

Diphenylmethane (101-81-5)

bromobenzene (108-86-1)

Phenyllithium (591-51-5)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

butyllithium,  
n-butyllithium (109-72-8)

hexane (110-54-3)

Methylithium (917-54-4)

argon (7440-37-1)

helium (7440-59-7)

1,1-Diphenylethane,  
Benzene, 1-phenylethyl- (612-00-0)

1,1-diphenylethanol (599-67-7)