



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

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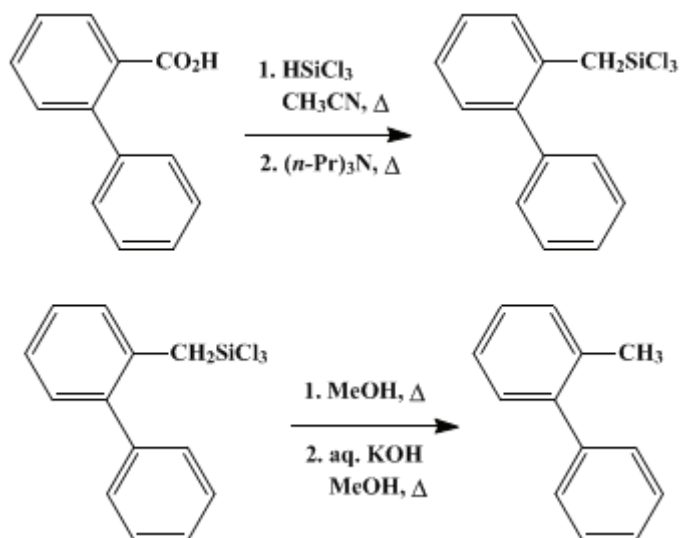
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## METHYL GROUPS BY REDUCTION OF AROMATIC CARBOXYLIC ACIDS WITH TRICHLOROSILANE - TRI-*n*-PROPYLAMINE: 2-METHYLBIPHENYL

### [1,1'-Biphenyl, 2-methyl]



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### 1. Procedure

*Caution! This procedure should be conducted in a well-ventilated hood to avoid inhalation of trichlorosilane and hydrogen chloride.*

A 300-ml., three-necked, round-bottomed flask is equipped with a magnetic stirrer, a thermometer, a glass stopper, and an efficient condenser attached to a nitrogen line with a gas bubbler (Note 1). The system is flushed with dry nitrogen, then charged with 19.8 g. (0.100 mole) of biphenyl-2-carboxylic acid (Note 2), 80 g. (60 ml., 0.59 mole) of trichlorosilane (Note 3) and (Note 4), and 80 ml. of acetonitrile (Note 5). A low nitrogen flow is maintained as the mixture is stirred and heated to reflux (40–45°) for 1 hour or until gas evolution ceases and the carboxylic acid has dissolved. The solution is then cooled in an acetone–dry ice bath to at least 0°, and the glass stopper is replaced with a 100-ml., pressure-equalizing dropping funnel charged with 37.8 g. (0.264 mole) of tri-*n*-propylamine (Note 6) and (Note 7), which is emptied rapidly into the stirred solution. The cooling bath is removed, and the flask contents are allowed to stir until the reaction ceases to be exothermic. A heating mantle is then used to maintain reflux for 16 hours (Note 8), during which time the temperature rises to 70–75°.

As soon as reflux is terminated, the solution is poured rapidly into a 1-l. Erlenmeyer flask, allowed to cool, and diluted with enough anhydrous diethyl ether (Note 9) to make the total volume about 850 ml. (Note 10). After the flask has been sealed and refrigerated for one hour, the precipitate is removed by rapid filtration (water aspirator) through a 150-ml. Büchner funnel and washed with three 50-ml. portions of anhydrous ether. The clear yellow filtrate is concentrated as follows. A 300-ml., one-necked, round-bottomed flask is fitted with a magnetic stirring bar and a 100-mm. Vigreux column topped with a distillation head. The filtrate is placed in a 1-l., pressure-equalizing dropping funnel inserted into the top of the distillation head. Approximately 100 ml. is run down through the column into the flask, which is then heated. As ether is removed by distillation, the remainder of the filtrate is dripped into the flask

at a constant rate, and in this way the solution is concentrated into a small flask in a continuous operation. Distillation is continued until most of the ether has been removed, and the resulting murky solution is heated at 40° (80 mm.), removing the remaining volatiles.

The Vigreux column, dropping funnel, and distilling head are then replaced by a 100-ml., pressure-equalizing dropping funnel charged with 100 ml. of **methanol**. With the top of the funnel left open to the atmosphere, the **methanol** is added slowly to the oily flask contents (Note 11). After vigorous boiling has ceased, the solution is heated under reflux for one hour, cooled in an ice bath, then treated slowly with a solution of 56 g. (1.0 mole) of **potassium hydroxide** in 25 ml. of water and 50 ml. of **methanol**.<sup>2</sup> The resulting mixture is heated under reflux for 19 hours (Note 8), dissolved in 600 ml. of water, and extracted three times with 100 ml. of **ether**. The extracts are combined, washed once with 50 ml. of 5 *N* **hydrochloric acid**, and dried over anhydrous **magnesium sulfate**. **Ether** is removed by distillation as described above, using a 300-ml., pressure-equalizing dropping funnel, a 50-ml., round-bottomed distilling flask, and a 100-mm. Vigreux column. Vacuum distillation of the remaining liquid gives 12.5–13.4 g. (74–80%) of **2-methylbiphenyl**, b.p. 76–78° (0.5 mm.),  $n_D^{20}$  1.5920 (Note 12) and (Note 13).

## 2. Notes

1. All glassware is thoroughly dried by flame or in an oven prior to use.
2. **Biphenyl-2-carboxylic acid** was purchased from Aldrich Chemical Company, Inc., and used without further purification.
3. The submitters used **trichlorosilane** supplied by Union Carbide Corporation. The checkers obtained **trichlorosilane** from Tokyo Chemical Industries Company, Ltd., Japan.
4. Good results may sometimes be achieved with a 4:1 or 5:1 mole ratio of **trichlorosilane** to carboxylic acid. Excess **trichlorosilane** is needed to compensate for losses of this volatile reactant over extended reflux periods.
5. The submitters used reagent grade **acetonitrile** (Mallinckrodt Chemical Works) dried prior to use by storage over Matheson Linde type 4A molecular sieves. The checkers used reagent grade **acetonitrile** obtained from Ishizu Pharmaceutical Company, Japan, dried prior to use by storage over 4A molecular sieves obtained from Nakarai Chemicals, Ltd., Japan.
6. The submitters used **tri-*n*-propylamine** obtained from Aldrich Chemical Company, Inc., and the checkers used **tri-*n*-propylamine** obtained from Wako Pure Chemical Industries, Ltd., Japan. Both groups stored the reagent over Linde type 4A molecular sieves prior to use.
7. To ensure a homogeneous reducing medium, the **tri-*n*-propylamine**: **trichlorosilane** ratio should be about 1:2.
8. Overnight reflux was chosen partly for convenience. Similar results are possible with somewhat shorter reaction times.
9. The submitters employed anhydrous **ether** obtained from Mallinckrodt Chemical Works; the checkers used anhydrous **ether** obtained from Wako Pure Chemical Industries, Ltd., Japan and distilled it from **sodium hydride** under **nitrogen** shortly prior to use.
10. The volume of ether added should be sufficient to precipitate most of the **tri-*n*-propylamine hydrochloride** in solution. The checkers diluted to a total volume of about 1 l. to precipitate the salt more efficiently.
11. Vigorous evolution of **hydrogen chloride** is observed as the **methanol** is added.
12. The literature<sup>3</sup> value for a carefully purified sample of **2-methylbiphenyl** is  $n_D^{20}$  1.5914.
13. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (multiplicity, number of protons, assignment): 2.55 (s, 3H, CH<sub>3</sub>), 7.27 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 7.33 (s, 5H, C<sub>6</sub>H<sub>5</sub>). IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 1600 medium, 1480 medium strong (aromatic), 1380 medium (CH<sub>3</sub>). GC analysis of the product (1.5 m. by 0.5 cm. glass column, KF-54 on Chromosorb W, 60–80 mesh) showed a single peak with a retention time of 2.60 minutes at 170°.

## 3. Discussion

**2-Methylbiphenyl** has been prepared by diazotization of *o*-toluidine and coupling with **benzene** (8%);<sup>4</sup> by reaction of *o*-tolylmagnesium bromide with **cyclohexanone**, followed by dehydration of the resulting alcohol and dehydrogenation (30–50%);<sup>5</sup> and by coupling *o*-tolyllithium with **chlorobenzene** in the presence of **piperidine** (51%).<sup>6</sup> The present procedure gives **2-methylbiphenyl** in much improved yield.

In a more general sense, this reduction method provides a convenient pathway for converting an aromatic carboxyl group to a methyl group (see Table I).<sup>7</sup> Previously, this transformation has been achieved by reduction of the acid to the alcohol with lithium aluminum hydride, conversion of the alcohol to the tosylate, and a second reduction either with lithium aluminum hydride, or Raney nickel and hydrogen.<sup>8</sup> Alcohols of the benzylic type have also been reduced directly with hydrogen under pressure in the presence of various catalysts,<sup>9</sup> and benzoic acids have been reduced to toluenes with rhenium-type catalysts and hydrogen at high temperatures and pressures.<sup>10</sup>

TABLE I  
REDUCTION OF AROMATIC ACIDS TO  
SUBSTITUTED BENZENES<sup>7</sup>

Starting Acid	Product (% Yield)
Benzoic	Toluene (78)
<i>m</i> -Toluic	<i>m</i> -Xylene (82)
<i>p</i> -Toluic	<i>p</i> -Xylene (74)
3,5-Dimethylbenzoic	Mesitylene (82)
4-Chlorobenzoic	<i>p</i> -Chlorotoluene (94)
4-Bromobenzoic	<i>p</i> -Bromotoluene (94)
Phthalic	<i>o</i> -Xylene (64)

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### References and Notes

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### Appendix

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

hydrogen chloride,  
hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

ether,  
diethyl ether (60-29-7)

hydrogen (1333-74-0)

acetonitrile (75-05-8)

Cyclohexanone (108-94-1)

nitrogen (7727-37-9)

nickel (7440-02-0)

chlorobenzene (108-90-7)

potassium hydroxide (1310-58-3)

toluene (108-88-3)

piperidine (110-89-4)

p-Chlorotoluene (106-43-4)

p-xylene (106-42-3)

Mesitylene (108-67-8)

magnesium sulfate (7487-88-9)

lithium aluminum hydride (16853-85-3)

sodium hydride (7646-69-7)

tri-n-propylamine (102-69-2)

biphenyl-2-carboxylic acid (947-84-2)

o-toluidine (95-53-4)

p-Bromotoluene (106-38-7)

TRICHLOROSILANE (10025-78-2)

2-Methylbiphenyl,  
1,1'-Biphenyl, 2-methyl (643-58-3)

m-xylene (108-38-3)

o-Xylene (95-47-6)

o-tolylmagnesium bromide

o-Tollythium

tri-n-propylamine hydrochloride

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