

pyrone⁴ in 180 ml of dry THF was placed in a photochemical reaction vessel immersed in an ice bath and irradiated for 22 hr under nitrogen with a Hanovia 450-W high-pressure mercury lamp fitted with a Pyrex filter. By this time, the pyrone had disappeared as indicated by ir spectroscopy. Iron pentacarbonyl (2.55 g, 13.0 mmol) was then added, and irradiation was continued for 1 hr. The reaction mixture was concentrated on a rotary evaporator at reduced pressure at room temperature,⁵ and the residue was washed through a 4.5-in. × 1.5-in. wet-packed column of alumina with methylene chloride (400–500-ml total volume). Crude ester **1c** was obtained by collection and evaporation of the first colored band eluted. This material was immediately mixed with a solution of 0.80 g of 85% potassium hydroxide in 1 ml of water and 5 ml of methanol and stirred for 2 hr. The resulting mixture was combined with 50 ml of water, washed with 50 ml of methylene chloride, acidified with concentrated hydrochloric acid, and extracted with 2 × 50 ml of ether. The ether extracts were dried over magnesium sulfate and evaporated, and the residue was recrystallized from carbon tetrachloride to give 325 mg (21%) of **1b**, mp 147–149° (lit.^{2b} mp 151–152°), the ir and nmr spectra of which were identical with those reported by Fitzpatrick.^{2b}

Tricarbonyl[methyl 1,2,3,4-η-1,3-cyclobutadienecarboxylate]iron (1c). The crude ester obtained in the preceding experiment was purified by preparative tlc (20 cm × 20 cm silica gel plate, development with CHCl₃) followed by evaporative distillation [bath temperature 34–38° (1.2 mm)] to give **1c** as a yellow oil: ir (CHCl₃) 2068, 1988, and 1709 cm⁻¹; nmr (CDCl₃) δ 3.67 (s, 3 H, OCH₃), 4.28 (s, 1 H, para proton), and 4.51 (s, 2 H, ortho protons).

Anal. Calcd for C₉H₆FeO₅: C, 43.24; H, 2.42; Fe, 22.34. Found: C, 43.11; H, 2.47; Fe, 22.10.

Registry No.—**1b**, 52571-39-8; **1c**, 52571-40-1; **2**, 25991-27-9; iron pentacarbonyl, 13463-40-6.

References and Notes

- (1) This work was supported by Public Health Service Research Grant No. CA-12008 from the National Cancer Institute.
- (2) (a) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3254 (1965); (b) J. D. Fitzpatrick, Ph.D. Thesis, University of Texas, Austin, 1966.
- (3) M. Rosenblum and C. Gatsonis, *J. Amer. Chem. Soc.*, **89**, 5074 (1967).
- (4) E. J. Corey and D. S. Watt, *J. Amer. Chem. Soc.*, **95**, 2303 (1973).
- (5) Because **1c** is sensitive to prolonged exposure to light, it was kept in the dark as much as possible during this and subsequent manipulations.

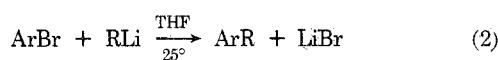
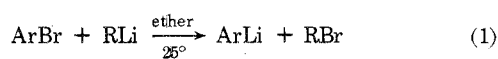
Tetrahydrofuran-Promoted Aryl-Alkyl Coupling Involving Organolithium Reagents

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The reaction of aryl halides with organolithium compounds in diethyl ether or other less polar solvents is dominated by the halogen-metal interconversion¹ (eq 1). The coupling of the aryl and alkyl groups in these solvents generally takes place very slowly.¹ We have noted that the coupling reaction (eq 2) is markedly promoted by tetrahydrofuran (THF),² producing cleanly the cross-coupled products in many cases.²



For example, the reaction of 1-bromonaphthalene with *n*-butyllithium in a 1:5 mixture of hexane and THF produces 1-*n*-butylnaphthalene (**1**) in 72% yield within 1 hr at room temperature, whereas the corresponding reaction in a

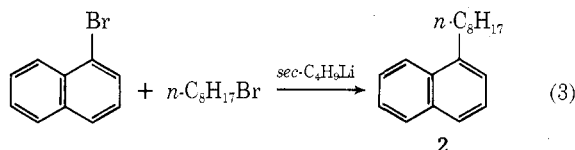
Table I
Tetrahydrofuran-Promoted Aryl-Alkyl Coupling

Aryl reagent	Registry no.	(ArX)	Alkyl reagent	Registry no.	(RY)	Procedure ^a	Product ^b	Registry no.	Yield, % ^c
<i>o</i> -Tolyl	95-46-2	Br	<i>n</i> -Butyl	109-72-8	Li	I	<i>o</i> - <i>n</i> -Butyltoluene ^d	1595-11-5	65
<i>m</i> -Tolyl	521-17-3	Br	<i>n</i> -Butyl		Li	I	<i>m</i> - <i>n</i> -Butyltoluene ^e	1595-04-6	63
<i>p</i> -Tolyl	106-38-7	Br	<i>n</i> -Butyl		Li	I	<i>p</i> - <i>n</i> -Butyltoluene ^f	1595-05-7	69
1-Naphthyl	90-11-9	Br	<i>n</i> -Butyl		Li	I	1- <i>n</i> -Butylnaphthalene ^g	1634-09-9	66 (72)
1-Naphthyl		Br	<i>sec</i> -Butyl	598-30-1	Li	I	1- <i>sec</i> -Butylnaphthalene	1680-58-6	(<1)
1-Naphthyl		Br	<i>t</i> -Butyl	594-19-4	Li	I	1- <i>tert</i> -Butylnaphthalene	17085-91-5	(<1)
4-Methyl-1-naphthyl	6627-78-7	Br	<i>n</i> -Butyl		Li	I	1- <i>n</i> -Butyl-4-methyl-naphthalene ^h	52718-76-0	52
4-Methyl-1-naphthyl		Br	Ethyl	811-49-4	Li	I	1-Ethyl-4-methyl-naphthalene ⁱ	27424-87-9	60
2-Methyl-1-naphthyl	2586-62-1	Br	Ethyl		Li	I	1-Ethyl-2-methyl-naphthalene ^j	17057-93-1	66
Phenyl	591-51-5	Li	<i>n</i> -Octyl	111-83-1	Br	II	<i>n</i> -Octylbenzene ^k	2189-60-8	82 (87)
Phenyl	108-86-1	Br	<i>n</i> -Octyl		Br	III	<i>n</i> -Octylbenzene		70 (76)
1-Naphthyl		Br	<i>n</i> -Octyl		Br	III	1- <i>n</i> -Octylnaphthalene ^l	2876-51-9	60 (74)

^a For definition of procedures I, II, and III, see the Experimental Section. ^b All isolated products yielded satisfactory pmr and ir data, and 1-*n*-butyl-4-methylnaphthalene gave the correct analytical data. ^c By isolation. The numbers in parentheses are yields by glpc (SE-30). ^d *n*^{25b} 1.4933 (lit. ⁷ *n*^{20b} 1.4960). ^e *n*^{25b} 1.4892 (lit. ⁷ *n*^{20b} 1.4910). ^f *n*^{25b} 1.4886 (lit. ⁷ *n*^{20b} 1.4916). ^g For physical constants, see the Experimental Section. ^h Bp 91–94° (0.04 mm); *n*^{25b} 1.5729; ⁱ Bp 83–86° (0.25 mm); *n*^{25b} 1.5976 [lit. ⁶ bp 122° (40 mm)]. ^j Bp 76–79° (0.15 mm); *n*^{25b} 1.5974 [lit. bp 133–134° (15 mm) from R. B. Carlin and K. P. Sivaramakrishnan, *J. Org. Chem.*, **35**, 3368 (1970)].

1:5 mixture of hexane and diethyl ether yields only 3% of 1 over the same period at the same temperature.

As summarized in Table I, a wide variety of aryl halides react readily with primary alkylolithiums to produce the cross-coupled products in high yields. On the other hand, secondary and tertiary alkylolithiums do not give the cross-coupled products in any appreciable yields under the comparable conditions. These results suggest that the actual coupling step involves the interaction of aryllithiums with alkyl halides formed by the halogen-metal exchange reaction. Indeed, phenyllithium prepared from bromobenzene and lithium metal reacted with *n*-octyl bromide in the presence of THF to produce *n*-octylbenzene in 87% yield within 2 hr at room temperature. Based on these results we have developed the following convenient procedure involving the use of a hindered alkylolithium, *i.e.*, *sec*-butyllithium. 1-Bromonaphthalene was treated sequentially with equimolar quantities of *sec*-butyllithium and *n*-octyl bromide to provide 1-*n*-octylnaphthalene (2) in 74% yield (eq 3). Only trace quantities of 1-*sec*-butylnaphthalene and 3-



methylundecane were present. The benzyne mechanism⁴ does not appear significant, since no 2-naphthyl derivatives were detected.

It should be noted that any of the three procedures described here provides a convenient alternative to the Wurtz-Fittig route for the coupling of aryl halides with alkyl halides.

Experimental Section

The following examples are representative of the three procedures discussed in this report.⁵

Preparation of 1-*n*-Butylnaphthalene by the Reaction of 1-Bromonaphthalene with *n*-Butyllithium (Procedure I). To a dry 100-ml flask equipped with a magnetic stirring bar, a septum inlet, and an outlet connected to a mercury bubbler were introduced sequentially 20 ml of THF, 2.07 g (1.41 ml, 10 mmol) of 1-bromonaphthalene, and 4.30 ml (11 mmol) of 2.56 *M* *n*-butyllithium in hexane while controlling the reaction temperature at $25 \pm 5^\circ$. After stirring the mixture for 2 hr, it was washed with water and aqueous sodium chloride. The combined aqueous layer was extracted with chloroform and the combined organic layer was dried over magnesium sulfate, evaporated, and distilled to yield 1.21 g (66% yield) of 1-*n*-butylnaphthalene: bp $78-80^\circ$ (0.05 mm); n_{25}^{25D} 1.5807 [lit.⁶ bp 289° ; n_{20}^{20D} 1.5819]; pmr (CCl₄, TMS) δ 0.8-2.0 (m, 7 H), 3.00 (t, 2 H, $J = 7.5$ Hz), 7.2-8.1 (m, 7 H) ppm; ir (neat) 797, 785 (sh), 775 cm^{-1} .

Preparation of *n*-Octylbenzene by the Reaction of Phenyllithium with *n*-Octyl Bromide (Procedure II). In a setup similar to that described above 5.56 ml (10 mmol) of 1.80 *M* phenyllithium in a 70:30 mixture of benzene and diethyl ether and 2.12 g (1.89 ml, 11 mmol) of *n*-octyl bromide in 20 ml of THF were reacted at $25 \pm 5^\circ$ for 2 hr. The mixture was worked up in a manner analogous to that described above to give 1.56 g (82%) of *n*-octylbenzene: bp $82-85^\circ$ (0.5 mm); n_{25}^{25D} 1.4832 [lit.⁷ bp $131-134^\circ$ (12 mm); n_{20}^{20D} 1.4851]; pmr (CCl₄, TMS) δ 0.7-1.9 (m, 15 H), 2.58 (t, 2 H, $J = 7.5$ Hz), 7.12 (s, 5 H) ppm; ir (neat) 745, 695 cm^{-1} .

Preparation of 1-*n*-Octylnaphthalene by the Coupling of 1-Bromonaphthalene and *n*-Octyl Bromide under the Influence of *sec*-Butyllithium (Procedure III). In a setup similar to that described above 2.07 g (1.41 ml, 10 mmol) of 1-bromonaphthalene in 10 ml of diethyl ether was treated at room temperature with 13.7 ml (11 mmol) of 0.80 *M* *sec*-butyllithium in hexane. After stirring the mixture for 10 min 2.12 g (1.89 ml, 11 mmol) of *n*-octyl bromide and 10 ml of THF were added in this order at $25 \pm 5^\circ$. The mixture was stirred for 3 hr and then worked up as described above to yield 1.59 g (66%) of 1-*n*-octylnaphthalene: bp $120-123^\circ$ (0.05 mm); n_{24}^{24D} 1.5515 [lit.⁸ bp 144.5° (0.2 mm); n_{20}^{20D} 1.5533]; pmr (CCl₄, TMS) δ 0.7-2.0 (m, 15 H), 3.01 (t, 2 H, $J = 7.5$ Hz), 7.2-8.1 (m, 7 H) ppm; ir (neat) 797, 788, 776 cm^{-1} .

Acknowledgment. We thank Research Corporation and Syracuse University for financial support.

References and Notes

- (1) R. G. Jones and H. Gilman, *Org. React.*, **6**, 339 (1951).
- (2) The marked rate-accelerating effect of THF in the aryl-alkyl coupling reaction producing the cross-coupled products in high yields does not appear to have been clearly documented.^{1,3}
- (3) A rate-accelerating effect of THF in certain aryl-aryl coupling reactions has been reported: H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 447 (1957). These reactions almost certainly proceed *via* the benzyne mechanism. In a report describing the reaction of alkyl or aryl halides with lithium metal in THF, the same authors [H. Gilman and B. J. Zai, *J. Org. Chem.*, **22**, 1165 (1957)] made the following observations: (1) the yields of alkyl- or aryllithiums decrease in the order $\text{Cl} > \text{Br} > \text{I}$, (2) the higher the reaction temperature, the lower the yields were. These results were rationalized in terms of the rate-accelerating effect of THF in the alkyl-alkyl or aryl-aryl coupling. However, no product study was made.
- (4) See, for example, G. Wittig, *Angew. Chem., Int. Ed. Engl.*, **4**, 731 (1965).
- (5) All reactions were carried out under a nitrogen atmosphere with precautions to exclude air and moisture. Diethyl ether and THF were purified by distillation from lithium aluminum hydride. The pmr spectra were obtained using a Varian A-60 nmr spectrometer.
- (6) G. Harris, J. R. A. Pollock, and R. Stevens Ed., "Dictionary of Organic Compounds," Oxford University Press, New York, N.Y., 1965.
- (7) R. C. Weast Ed., "Handbook of Chemistry and Physics," 52nd ed, The Chemical Rubber Co., Cleveland, Ohio, 1971.
- (8) B. Barrowsmith, G. H. Jeffery, and A. I. Vogel, *J. Chem. Soc.*, 2072 (1965).
- (9) R. B. Carlin and K. P. Sivaramakrishnan, *J. Org. Chem.*, **35**, 3368 (1970).

Regeneration of Ketones from Tosylhydrazones

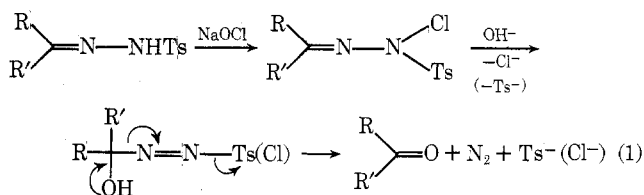
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Tosylhydrazones serve as intermediates for the synthesis of olefins¹ and the creation of carbenes.² Those derived from α,β -epoxy ketones undergo fragmentation readily to afford acetylenic carbonyl compounds.³ Generally, tosylhydrazones are highly crystalline, therefore they should be valuable for the characterization and purification of carbonyl substances. However, this last potential utility and also their applicability as protective device have been virtually completely ignored, presumably owing to their high hydrolytic stability.

Thus the recovery of carbonyl compounds from tosylhydrazones represents a pragmatic problem yet to be resolved. During the regenerative process, a hydroxyl group is to be attached to the imino carbon, and, to augment the electrophilicity of this center toward water or hydroxide ion, an additional electron-withdrawing, good leaving group has to be temporarily introduced to the tosyl-bearing nitrogen. According to our plan, such an operation is in fact mandatory, because a combination of an $\text{SN}2'$ displacement and then a fragmentation is required for the ultimate generation of the carbonyl and the release of molecular nitrogen. Further elaboration of this scheme indicated that the most elegant and convenient way to effect the overall transformation would be the reaction with alkali hypochlorite (eq 1). This reagent furnishes both Cl^+ for N-chlorina-



tion and OH^- for deprotonation and the nucleophilic attack.