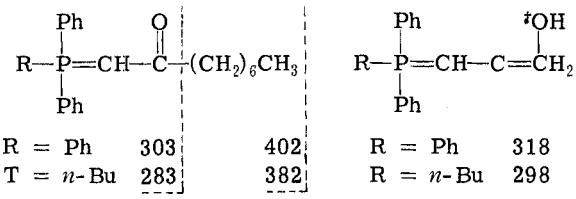
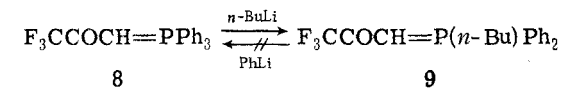
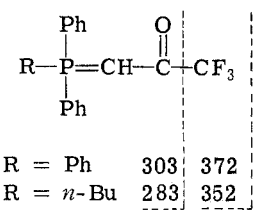
Methylenetriphenylphosphorane used in this reaction had to be generated with phenyllithium. If *n*-butyllithium was used, significant amounts of *n*-butyldiphenylphosphorane (**7**) were formed, drastically decreasing the yield of crystalline **6**. Although **7** could not be isolated in a pure state and was an oil, *m/e* 382 (molecular ion), 298, and strong 283 peaks afforded convincing evidence for structure **7**. A few precedents for similar alkyl–aryl exchange have been recorded in the literature. Seyferth,[7] for instance, showed that benzene (26%) was formed when methyltriphenylphosphonium bromide was treated with methyllithium.



Trifluoroacetylmethylenetriphenylphosphorane (**8**) was obtained accompanied by trifluoroacetylmethylene-*n*-butyldiphenylphosphorane (**9**) when ethyl trifluoroacetate was treated with methylenetriphenylphosphorane generated by *n*-butyllithium. When **8** was treated with an equimolecular amount of *n*-butyllithium in ether at 25°, approximately 70% of **8** was converted into **9** within 30 min. On the other



hand, treatment of **9** with phenyllithium did not afford any recognizable (by TLC) amount of **8**.



Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and were not corrected.

Acyl chlorides were prepared from the corresponding acids by thionyl chloride in hexane or benzene and were purified by distillation.

General Procedure for Preparation of Alkanoylmethylenetriphenylphosphorane (3). A solution of imidazole (0.2 mol) in 250 ml of tetrahydrofuran–ether (50:50) was stirred at 5° under nitrogen as an ethereal solution of acyl chloride (0.1 mol) was slowly added over 15 min. The resulting slurry was stirred for an additional 30 min and filtered under a nitrogen atmosphere. The cake of imidazole hydrochloride was washed with ether. A slurry of methyltriphenylphosphonium bromide (0.1 mol) in 1 l. of ether was treated with 0.1 mol of phenyllithium in benzene–ether (Ventron) at 25° for 1.5 hr. The ethereal acyl imidazolide solution was added to the methylenetriphenylphosphorane solution at −70° over 30 min. The mixture was allowed to warm to 25°, poured into 2 l. of dilute hydrochloric acid, and shaken with 1 l. of ether. The aqueous phase containing a heavy oil which was soluble in neither phase separated. The insoluble oily substance was the hydrochloride of **3** and often crystallized during the work-up. The aqueous phase was made alkaline (pH 10) with potassium carbonate and the oil which separated was extracted with toluene or benzene. The organic extract was washed[8] and evaporated in vacuo. The residue was recrystallized from hexane or ether–hexane.

Isolation and Identification of Pentadecan-8-one (5) as Byproduct. The preparation of **6** was carried out according to the general procedure except that methylenetriphenylphosphorane was generated with *n*-butyllithium. The ethereal phase was separated from the aqueous hydrochloric acid layer and concentrated. The residue was dissolved in benzene, washed,[8] and concentrated. The residue was recrystallized from hexane to give **5**: mp 43° (lit.[9] mp 43°); ir ($CHCl_3$) 1715 cm^{-1}; mass spectrum (70 eV) *m/e* 127 [$CH_3(CH_2)_6C(OH)=CH_2$].

Anal. Calcd for $C_{15}H_{30}O$: C, 79.59; H, 13,36. Found: C, 79.30; H, 13.39.

The aqueous phase containing the heavy oil gave **6** and **7**.

Trifluoroacetylmethylenetriphenylphosphorane (8) and Trifluoracetylmethylene-*n*-butyldiphenylphosphorane (9). To a solution of methylenetriphenylphosphorane (prepared from 0.22 mol of methyltriphenylphosphonium bromide and 0.2 mol of *n*-butyllithium) in 1 l. of ether was added 0.2 mol of ethyl trifluoroacetate at −70° under nitrogen. The reaction mixture was stirred at −70° for 1 hr, brought to 25°, then stirred with 1.5 l. of 2% hydrochloric acid and filtered to collect a colorless precipitate (A). The ethereal phase was worked up in the usual manner[8] (B). The aqueous acidic layer was made alkaline with potassium carbonate and extracted with methylene chloride[8] (C). The crystalline precipitate (A) was dissolved in methylene chloride, washed, and dried[8] (D). Extracts B and D gave totally 30.3 g of crude **8** whereas extract C gave 42.3 g of a mixture of **8** and **9**. Pure **8** of mp 233° was obtained (~30 g) by recrystallization from benzene: ir ($CHCl_3$) 1590 (C=O), 1575 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.27 (d, 1, J = 20 Hz).

Anal. Calcd for $C_{21}H_{16}OF_3P$: C, 67.74; H, 4.33. Found: C, 67.81; H, 4.49.

Pure **9** (~15 g) was obtained by chromatography of a mixture of **8** and **9** on silica gel using 1% ethyl acetate–methylene chloride and recrystallization from ethyl acetate: mp 138°; ir ($CHCl_3$) 1587 (C=O), 1572 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.07 (d, 1, J = 19 Hz), 2.73 (m, 2), 1.47 (m, 4), 0.90 (m, 3).

Note Added in Proof. A preparation of benzoylmethylene triphenylphosphorane from benzoylimidazole and 2 mol of methylenetriphenylphosphorane was recorded in the literature, but no example of an imidazolide having an α H was given: H. J. Bestmann, N. Sommer, and H. A. Staab, *Angew. Chem.*, **74**, 293 (1962).

Registry No.—**5**, 818-23-5; **8**, 55759-55-2; **9**, 55759-56-3; methyltriphenylphosphonium bromide, 1779-49-3; phenyllithium, 591-51-5; methylenetriphenylphosphorane, 3487-44-3; ethyl trifluoroacetate, 383-63-1.

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Metal–Hexamethylphosphoramide Reduction. IV. Birch-Like Reduction of 2,6- and 2,7-Dimethoxynaphthalenes[1]

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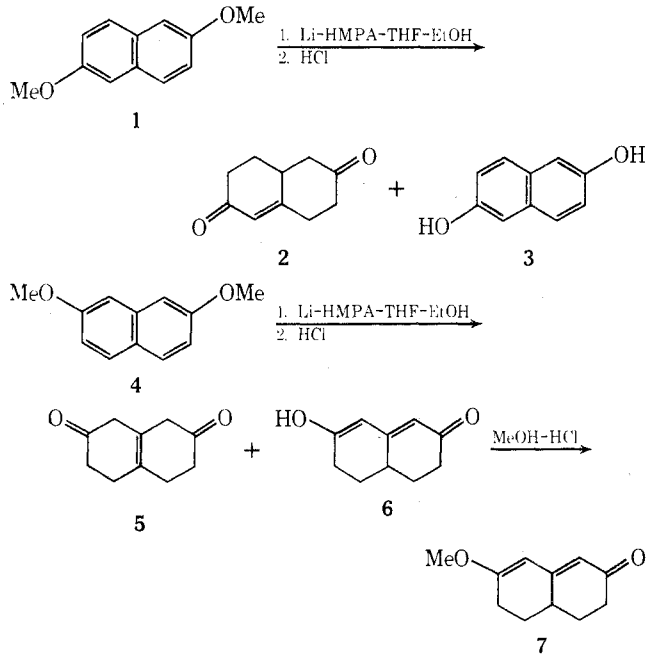
Recently we reported[2] preliminary results on the reduction of β-substituted dimethoxynaphthalenes with lithium in hexamethylphosphoramide (HMPA)–tetrahydrofuran (THF) with or without a proton donor (ethanol). We demonstrated that in the absence of an alcohol reductive cleavage of the type naphth–OMe and naphthO–Me is the major reaction pathway. In the presence of ethanol reduction of

the ring prevails; however, it can be preceded by attack of an electron at one or both methoxyl groups, which in consequence may give phenolic products without or with partial reduction of the aromatic rings. Therefore the product mixture differed distinctly from that obtained from the standard Birch reduction with sodium in liquid ammonia.

For that reason we decided to study this reaction in detail to find conditions that would give results analogous to those obtained by Birch reduction. The first experiments successful in this regard were achieved with 6-methoxytetralin and with estradiol 3-methyl ether.[3] In both cases we obtained the desired α,β-unsaturated ketones in good yield (~80%) after acid hydrolysis.

The present paper describes the successful reduction of 2,6-dimethoxynaphthalene (1) and 2,7-dimethoxynaphthalene (4) under the conditions of our new procedure leading to α,β-unsaturated ketones as major products. This procedure consists of slow addition of a 4:1 HMPA–THF lithium solution at −40° to a solution of the aryl ether in a HMPA–THF–EtOH mixture, followed by acid hydrolysis. In both cases we obtained the same products as those obtained by Birch reduction[4] in good yield (60–70%), along with some unreacted dimethoxynaphthalene and, especially in the case of 1 small amounts (<10%) of the related dihydroxynaphthalene.



The structural assignment of the purified reaction products was made by comparison of physical (melting point, mixture melting point, TLC retention time) and spectral (uv, ir) data with samples prepared by sodium–liquid ammonia reduction of 1 and 4. In the case of 7-hydroxy-2,3,4,5,6,10-hexahydronaphthalen-2-one (6), additional confirmation was made by conversion of it to 7-methoxy-2,3,4,5,6,10-hexahydronaphthalen-2-one (7) and its comparison with an authentic sample.

The above experiments describe for the first time an efficient, Birch-like conversion of naphthalenic diethers into bicyclic ketones by means of alkali metals dissolved in HMPA.

Experimental Section

Melting points were determined on a Boetius melting point apparatus and are uncorrected. Ir spectra were taken in chloroform with a Zeiss Model UR-20 spectrophotometer in absolute methanol. Thin layer chromatography was performed on microscopic slides coated with silica gel G (E. Merck) using benzene or benzene–ethyl acetate(4:1) solvent system for developing. Compounds were detected by iodine vapor. All solvents were made absolute according to standard procedure immediately before use. The lithium, cut into small pieces, was washed free of oil with hexane immediately before addition to the reaction mixture. Compounds 1 and 4 were prepared as described by Fisher and Kern[5]: 1, mp 149.5° from EtOH (lit.[6] mp 150°), and 4, mp 138° from EtOH (lit.[5] mp 138°).

Preparation of 2,6-Diketo-1,2,3,4,6,7,8,9-octahydronaphthalene (2). To a mixture of anhydrous and freshly distilled HMPA (60 ml) and THF (15 ml) placed into a dry three-neck round-bottom flask, equipped with a mechanical stirrer, a thermometer, and a calcium chloride tube, 150 mg (8 g-atoms) of lithium cut into small pieces was added under stirring. The blue coloration of the metal solution developed after a few minutes and the temperature rose to 25–28°. The solution was then cooled to 0° and the stirring was continued for about 1.5 hr until almost all lithium was dissolved.

Simultaneously, a similarly equipped flask containing a solution of 1 (0.5 g) in HMPA (20 ml), THF (20 ml), and EtOH (3 ml) was cooled to −45° with a Dry Ice–acetone bath. The lithium solution prepared as above was now added slowly in small portions so that the temperature of the mixture did not exceed −30°. After addition of THF (40 ml) the complete reaction mixture was stirred until decolored (usually after about 5 hr). The solution was then acidified with 2 *N* hydrochloric acid, allowed to stand for 30 min, and extracted with three 50-ml portions of ether. Usual work-up of the combined ether extracts led after evaporation of the ether to a crude product which was dissolved in 20 ml of THF–EtOH (2:1) mixture and 5 ml of 2 *N* HCl and refluxed for 30 min. After this time the mixture was treated with a saturated ammonium sulfate solution and extracted three times with ether. The combined ether layers were washed ten times with 2 *N* HCl, then with a saturated ammonium sulfate solution, and dried over anhydrous magnesium sulfate. After filtration and evaporation of ether 2 was isolated by column chromatography on silica gel (E. Merck) using benzene and benzene–ethyl acetate (4:1) as eluents. Recrystallization from ethyl acetate afforded 0.26 g (60.5%) of colorless needles: mp 93–93.5° (lit.[4a] mp 93–94°); uv λ_{max} 235 nm (ϵ 26,000); ir ν_{max} 1615, 1680, 1725 cm^{-1}. Preparation of the 2,4-dinitrophenylhydrazone in the usual manner provides red prisms, mp 274° (lit.[4a] mp 275°), after recrystallization from ethyl acetate.

Reduction of 2,7-Dimethoxynaphthalene (4) in a manner completely analogous to that described above for 1 afforded from 0.5 g of 4 after column chromatography on silica gel using the same eluent 0.056 g of 5 and 0.214 g of 6 (total yield 63%). 5: colorless needles; mp 65° (lit.[4d] mp 62.5–63.5°) after recrystallization from benzene–petroleum ether (bp >80°); ir ν_{max} 1718 cm^{-1}. 6: fine pale yellow crystals; mp 176° (lit.[4d] mp 179–179.5°) after recrystallization from benzene–petroleum ether; uv λ_{max} 321 nm (ϵ 17,700); ir ν_{max} 1560, 1608, 3250–3350 cm^{-1}.

Preparation of 7-Methoxy-2,3,4,5,6,10-hexahydronaphthalen-2-one (7). A solution of 0.2 g of 6 in 20 ml of MeOH saturated with HCl was heated under reflux for 1 hr. Then the cooled solution was diluted with ether and extracted with water, 1 *N* NaOH, and three times with water. The ethereal solution was dried over anhydrous magnesium sulfate. After filtration, evaporation of ether, and recrystallization from ethyl ether–petroleum ether (bp 60–80°), 7 was obtained as colorless needles: mp 97° (lit.[4f] mp 93–94°); uv λ_{max} 310 nm (ϵ 22,500); ir ν_{max} 1260, 1560, 1608 cm^{-1}.

Registry No.—1, 5486-55-5; 2, 54440-32-3; 4, 3469-26-9; 5, 3468-56-2; 6, 1614-83-1; 7, 1614-84-2; lithium, 7439-93-2.

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