Methyl β-(3,5-Di-*tert*-butylphenyl)-β-hydroxypropionate (6).—A mixture of 136 g (0.625 mol) of **5**, 400 ml of benzene, and 44 g (0.705 g-atom) of activated zinc[9] was heated until 200 ml of benzene had distilled. After 200 ml of dry ether was added, 96 g (0.634 mol) of methyl bromoacetate was added during 5 hr to the refluxing mixture. After refluxing for 10 hr more, the cooled reaction mixture was treated with 1 l. of NH_4OH and the organic products were isolated as usual. A small amount of the crude residue was crystallized from Skellysolve B to yield the analytical sample of **6**, mp 66–67°. The remainder was treated as described below to yield **6a**.

Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.9; H, 9.7. Found: C, 73.9; H, 9.7.

β-(3,5-Di-*tert*-butylphenyl)-β-hydroxypropionic Acid Hydrazide (6a).—To a solution of 80.0 g of crude **6**, obtained as above, in 60 ml of ethanol was added 10.0 g of anhydrous hydrazine. The mixture was heated until a clear solution resulted. After cooling, the resulting crystalline hydrazide was recrystallized from benzene–ethanol to yield 66.7 g (82.5% from **5**) of pure **6a**, mp 143–145°.

Anal. Calcd for $C_{17}H_{28}N_2O_2$: C, 69.8; H, 9.6; N, 9.6. Found: C, 69.5; H, 9.4; N, 9.8.

5-(3,5-Di-*tert*-butylphenyl)oxazolidone (7).—To a stirred mixture of 32.0 g of **6a**, 200 ml of 6 *N* hydrochloric acid, and 50 ml of chloroform at 0–5° was added 12.0 g of sodium nitrite during 30 min. After stirring for 30 min the excess nitrous acid was destroyed with sodium sulfite. The organic product was taken into three 100-ml benzene extracts, which were washed with saturated salt solution and dried by pouring through magnesium sulfate. This benzene solution was added to 50 ml of refluxing benzene in a flask arranged so that the nitrogen evolved could be collected and measured over water. After nitrogen evolution had ceased the solvent was distilled and the residue was crystallized from Skellysolve B–ether to yield 27.1 g (90%) of **7**, mp 167.5–168.5°.

Anal. Calcd for $C_{17}H_{25}NO$: C, 74.1; H, 9.2; N, 5.1. Found: C, 74.1; H, 9.2; N, 5.1.

5-(3,5-Di-*tert*-butylphenyl)-3-nitrosooxazolidone (8).—By method B,[5] 10.5 g of **7** in 50 ml of pyridine on treatment with 5.9 g of nitrosyl chloride in 30 ml of acetic anhydride was converted into 10.8 g (93.5%) of **8**, mp 193–195° dec, after recrystallization of crude **8** from acetone.

Anal. Calcd for $C_{17}H_{24}N_2O_3$: C, 67.1; H, 8.0; N, 9.2. Found: C, 67.1; H, 7.9; N, 8.9.

3,5-Di-*tert*-butylphenylacetylene (1).—To a refluxing solution of 4.90 g (0.066 mol) of butylamine in 100 ml of chloroform was added 20.0 g (0.066 mol) of **8** during 30 min. About 95% of the theoretical nitrogen was evolved. After removal of solvent, distillation yielded 13.4 g (95%) of **1**, mp 87.0–88.5°. When a similar experiment was done in refluxing ether the yield was 78%.

Anal. Calcd for $C_{16}H_{22}$: C, 89.7; H, 10.4. Found: C, 89.7; H, 10.4.

Registry No.—**1**, 36720-94-2; **6**, 36763-76-5; **6a**, 36720-95-3; **7**, 36720-96-4; **8**, 36720-97-5.

(9) L. F. Fieser and W. S. Johnson, *J. Amer. Chem. Soc.*, **62**, 576 (1940).

Reaction of Naphthalene Dianions with Tetrahydrofuran and Ethylene[1a]

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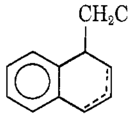
In the course of our work with reactions of arene anion radicals, a frequently observed minor product from many reactions of sodium or lithium naphthalene in THF was identified as a mixture of 1-ethyldihydronaphthalenes (I). Identity was confirmed through aromatization to the known 1-ethylnaphthalene (II) and conversion to its picrate complex. The recent work of Bates and coworkers on the cleavage of THF into ethylene and acetaldehyde enolate by strong bases[2] led us to consider this reaction as a source of the two-carbon fragment. The anion radical of naphthalene is not a particularly strong base,[3] but the dianion should be considerably stronger. The observations that the amounts of ethylidihydronaphthalene formed in THF solutions of potassium or sodium naphthalene were always very small at most, while lithium naphthalene solutions sometimes exhibited as much as 5% after standing for several days, coupled with the fact that the lithium anion radical is most prone to disproportionate to a mixture of dianion and neutral arene,[4] strongly supported this hypothesis (see Table I). Warming a solution of naphthalene in THF containing a fourfold excess of lithium yielded ethylene, easily identified through its dibromide, and similar treatment of 2-methyltetrahydrofuran yielded ethylene and propylene in a 1:15 ratio. Bates observed only propylene formation from the "α-cleavage" reaction of 2-methyltetrahydrofuran with butyllithium.[2] (The "β-cleavage reaction" reported by Bates for this substrate[2] probably also occurred in our reaction, but we did not search for the 4-penten-1-ol product.)



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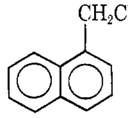

II

TABLE I

YIELDS OF 1-ETHYLDIHYDRO- AND 1-ETHYLNAPHTHALENE[a]

Solvent	Metal	Naphthalene/ metal ratio	Addend	Ethylated material, % yield[b]
THF	Li	0.22		54
Tetrahydropyran	Li	0.22		0
THF	Li	1.04		7
THF	K	0.33		~5
THF	Na	0.33		~5
1,2-Dimethoxyethane	Li	0.22		24
1,2-Dimethoxyethane	Li	0.22	750 mg of *n*-butyl vinyl ether	33
Tetrahydropyran	Li	0.29	750 mg of *n*-butyl vinyl ether	~10

[a] See Experimental Section for details. [b] Relative to original naphthalene concentration.

Noting that solutions of excess lithium and naphthalene in THF readily give rise to a large amount of naphthalene dianion at 25°,[5] we carried out the series of

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(1) (a) Supported in part by the Public Health Service (Research Grant No. RO1-AM11419 from the National Institute of Arthritis and Metabolic Diseases). (b) Alfred P. Sloan Research Fellow, 1968–1972.

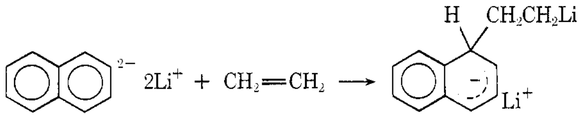
(2) R. B. Bates L. M. Kroposki, and D. E. Potter *J. Org. Chem.* **37**, 560 (1972).

(3) S. Bank and B. Bockrath *J. Amer. Chem. Soc.* **93**, 430 (1971); G. Levin, C. Sutphen and M. Szwarc, *ibid.*, **94**, 2652 (1972).

(4) M. Szwarc, *Progr. Phys. Org. Chem.*, **6**, 323 (1968).

(5) G. Henrici-Olive and S. Olive, *Z. Physik. Chem.*, **43**, 327 (1964); **42**, 145 (1964).

experiments listed in Table I. As expected, the highest yields of ethylated naphthalene derivatives were obtained under conditions where the concentration of dianion would be expected to be greatest, but surprisingly, a considerable amount of ethylation product is obtained with lithium in 1,2-dimethoxyethane (DME). This can be rationalized on the basis of the well-known formation of methoxide ion and methyl vinyl ether from DME and strong base,[6] and the report of Suga, *et al.*, that treatment of lithium naphthalene in THF with alkyl vinyl ethers affords a convenient synthesis of 1-ethylnaphthalene.[7] [Incidentally, using Suga's procedure (3:1 ratio of lithium to naphthalene in THF at 60°) we were able to produce a 30% yield of ethylated material in *the absence* of vinyl ether. Addition of butyl vinyl ether actually results in a slight decrease in yield.] Cleavage of ethers at the C–O bond by strong reducing agents is a well-known phenomenon[8] and a vinyl ether would be expected to cleave mainly between the alkyl carbon and oxygen, in analogy with phenyl alkyl ethers,[8] thus furnishing acetaldehyde enolate, one of the two-carbon fragments from THF. Considerable doubt is cast on the enolate ion as the source of the ethyl group, however, by the following experiment. A stream of ethylene was bubbled through a solution of lithium and naphthalene (3:1 ratio) in tetrahydropyran for 1 hr at 25°. A yield of 45% 1-ethyldihydronaphthalenes and 7% 1-ethylnaphthalene was realized. No ethylated material is formed in the absence of ethylene in tetrahydropyran even at 60° (see Table I). Apparently, the naphthalene dianion adds readily to ethylene, as shown in eq 1. That some sort of lithium derivative of the adduct survives for some time is clear from the fact that quenching the reaction mixture with CO_2 or methyl iodide rather than water results in a sharp diminution in yield of ethylated material. (With CO_2 there was simply a large decrease in total amount of material with retention time longer than naphthalene, presumably owing to formation of water-soluble carboxylate salts; with methyl iodide several products of longer retention than ethylnaphthalene now appeared. These were not investigated further.) Further addition of the intermediate alkyllithium to ethylene would not be expected on the basis of work by Bartlett, *et al.*, who noted that primary alkyllithiums are relatively unreactive toward ethylene.[9] Also of note is the fact that reaction of the dianion with 2-methyltetrahydrofuran produces only a trace of ethylated product and no readily identifiable products from propylene in accord with the observed sluggishness of attack of secondary and tertiary alkyllithiums upon substituted ethylenes.[10] Apparently, the lithium salt of the dianion of naphthalene (and presumably other alkali metal salts) approaches the reactivity toward ethylene of secondary and tertiary alkyllithiums. (An alternative mechanism could involve electron transfer from the dianion to ethylene, followed by combination of the resulting radical pair, but distinguishing this from carbanion addition would be difficult.)



(1)

The ethylated material from reaction of the lithium dianion in DME, and tetrahydropyran plus butyl vinyl ether, appears not to arise in some manner from acetaldehyde enolate, but most likely from ethylene derived from vinyl carbon–oxygen cleavage of vinyl ether. Thus, reaction of the dianion with butyl vinyl ether in tetrahydropyran yields a large amount (72%) of *n*-butyl alcohol, a modest amount (12%) of ethylated material, and an easily detectable amount of ethylene. Apparently, at least in these systems, the major mode of cleavage of vinyl ethers is opposite to that of phenyl alkyl ethers.[8,11] The actual manner in which such cleavage occurs and such questions as whether vinyl radicals or anions are initially produced must await further work.

Experimental Section[12]

Isolation and Identification of Ethyldihydronaphthalenes from Sodium Naphthalene in THF.—A sample (*ca.* 100 ml) of about 0.4 *M* sodium naphthalene in THF that was 3 weeks old (originally prepared using a slight excess of naphthalene over sodium) was added rapidly to 100 ml of water, and the organic material was extracted with ether and dried with magnesium sulfate. Removal of solvent at reduced pressure yielded a yellow oil, which was dissolved in ethanol and cooled to crystallize out naphthalene. After eight such repeated crystallizations the residual material showed only two peaks other than naphthalene on gas chromatography (5 ft × 0.25 in. SE-30, 150°). These two peaks were collected by preparative gc. The material from the first peak after naphthalene exhibited a complex nmr spectrum and had a mass spectrum (70 eV) of *m/e* 158, 129, and 128. Treatment of this material with DDQ (Aldrich) in CCl_4 for 30 min at 75° transformed it into material identical in retention time with that of the second, much smaller, peak after naphthalene. It was further identified as 1-ethylnaphthalene by nmr [triplet, 1.31 (3.0 H); quartet, 3.06 (2.0 H); multiplet, 7.0–8.2 (7.0 H)], mass spectrum (70 eV, *m/e* 156, 141, 115), and conversion to a picrate complex, mp 97–99° (lit.[14] mp 99°). That the first peak was initially a mixture principally of isomers of 1-ethyl-1,2- and 1-ethyl-1,4-dihydronaphthalene was confirmed by comparing its gc retention time with that of authentic material obtained by treating freshly prepared sodium naphthalene with ethyl bromide.[15]

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[6] See, for example, J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969).

[7] K. Suga, S. Watanabe, and T. Pai Pan, *Aust. J. Chem.*, **21**, 2341 (1968).

[8] J. J. Eisch, *J. Org. Chem.*, **28**, 707 (1963).

[9] P. D. Bartlett, S. J. Tauber, and W. P. Weber, *J. Amer. Chem. Soc.*, **91**, 6362 (1969).

[10] P. D. Bartlett, S. Friedman, and M. Stiles, *ibid.*, **75**, 1771 (1953).

[11] (a) Eisch did report production of a trace of phenyllithium in the cleavage of anisole with lithium biphenyl in THF,[8] and Morton and Lanpher noted that potassium sand cleaved anisole predominantly (60%) to phenylpotassium and methoxide ion.[11b] (b) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958). (c) A referee has suggested an alternative mechanism in which the dianion adds to the double bond of the vinyl ether to eventually yield a 1- or 2-(1-naphthyl)ethyl butyl ether, followed by reductive cleavage of this ether[11d] to ethylnaphthalene and butoxide. This, however, would not account for production of ethylene. (d) D. J. Cram and C. K. Dalton, *J. Amer. Chem. Soc.*, **85**, 1268 (1967).

[12] Gas chromatographic measurements were made on a Varian Model 200 (0.125-in. columns, flame ionization detector), utilizing internal standards and determining peak areas by cutting and weighing. Preparative gas chromatography was carried out with a Varian A-90 instrument. The nmr measurements were done with either a Varian A-60A or an HA-100-D modified by a Digilab FTS-3 Fourier transform system,[13] and mass spectrometric measurements were done with a AEI MS-902.

[13] We would like to thank the National Science Foundation for Grant No. GP 28061 for the purchase of this equipment.

[14] H. Cristol, R. Jacquier, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 248 (1958).

[15] J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Amer. Chem. Soc.*, **90**, 7159 (1968); G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968).

Reaction of Lithium Naphthalene Dianion with THF.—To 200 ml of dry THF was added 1.28 g (0.10 mol) of naphthalene and 2.1 g (0.30 mol) of lithium. The mixture was degassed and covered with argon, and then stirred. The solution rapidly turned green and became reddish brown after 1 hr at 25°. The solution was then refluxed for 4 hr and the effluent gases were collected for 2 hr in cooled CCl_4 and then for 2 hr in a solution of bromine in CCl_4. The solution was then cooled and quenched with water. Analysis by gc revealed 1-ethyldihydronaphthalenes, 9%, 1-ethylnaphthalene, 19%, and 72% of naphthalene and dihydronaphthalenes. Analysis by nmr of the CCl_4 solution of effluent gases showed only a sharp singlet at δ 5.3 which moved to 3.70 on addition of bromine. Authentic 1,2-dibromoethane showed an identical nmr spectrum and had a gc retention time on several columns identical with that of this material and with the material obtained by collecting the effluent gases in bromine–CCl_4.

Reaction of lithium naphthalene dianion with 2-methyltetrahydrofuran was carried out in identical fashion except that 2.8 g (0.40 mol) of lithium was used. The nmr spectrum of the material collected in bromine–CCl_4 was identical with that of 1,2-dibromopropane plus a small peak at the position of 1,2-dibromoethane. Analysis of the mixture of dibromides by gc indicated the ratio of dibromoethane to dibromopropane to be *ca.* 1:15. Quenching of the lithium naphthalene solution with water and gc analysis indicated only a very small amount of ethylation products and some even smaller peaks at longer retention time.

Effects of Solvent and Metal on Yield of Ethylated Material.—Ampoules containing 0.320 g (2.5 mmol) of naphthalene in 5.0 ml of different dry solvents and 2.5–7.5 mmol of different alkali metals plus, in some cases, 0.75 g (7.5 mmol) of butyl vinyl ether, were prepared and sealed under nitrogen. After stirring at 25° until deep colors had formed, they were heated at 65° for 13 hr. They were then cooled, opened, quenched with a small amount of water, dried with magnesium sulfate, and analyzed for 1-ethyldihydro- and 1-ethylnaphthalene by gc. The results are shown in Table I.

Reaction of lithium naphthalene dianion with butyl vinyl ether in THF was carried out according to the procedure of Suga, *et al.*[7] A mixture of 3.2 g (25 mmol) of naphthalene, 0.70 g (0.10 mol) of lithium, and 10 g (100 mmol) of butyl vinyl ether in 50 ml of THF under nitrogen was stirred for 1 hr at 25°, then heated at reflux for 3 hr. It was then cooled and quenched with methanol. Usual work-up and analysis by gc indicated ethyldihydronaphthalenes, 6%, and 1-ethylnaphthalene, 3%, relative to the original amount of naphthalene. A reaction carried out in identical fashion except for the absence of butyl vinyl ether afforded a 16% yield of ethyldihydronaphthalenes and a 14% yield of 1-ethylnaphthalene.

Reaction of Lithium and Naphthalene with Ethylene in Tetrahydropyran.—A mixture of 6.25 g (0.049 mol) of naphthalene and 1.05 g (0.15 mol) of lithium in 50 ml of dry tetrahydropyran was stirred at 25° under nitrogen for 3 hr and then ethylene was bubbled through the solution for 1 hr by means of a glass-frit inlet tube. Quenching the solution with water, drying with magnesium sulfate, and analysis by gc revealed a 45% yield of ethyldihydronaphthalenes and 7% of 1-ethylnaphthalene. A control experiment, carried out in identical fashion except for addition of ethylene, yielded no detectable amount (less than 0.1%) of ethylated product.

Reaction of Lithium, Naphthalene, and Butyl Vinyl Ether in Tetrahydropyran.—In a glass ampoule equipped with glass-covered stirring bar were sealed 0.32 g (2.5 mmol) of naphthalene, 0.080 g (11.4 mmol) of lithium, and 0.300 g (3.0 mmol) of butyl vinyl ether in 5.0 ml of dry tetrahydropyran under vacuum. The mixture was stirred for 48 hr at 25°. Analysis by gc of the gas in the ampoule indicated a modest amount of ethylene. Analysis of the water-quenched solution indicated 2.17 mmol (72%) of *n*-butyl alcohol and a 12% (relative to naphthalene) combined yield of ethyldihydro- and ethylnaphthalene.

Registry No.—THF, 109-99-9; ethylene, 74-85-1; 1-ethylnaphthalene, 1127-76-0; 1-ethyl-1,2-dihydronaphthalene, 34599-49-0; 1-ethyl-1,4-dihydronaphthalene, 36789-17-0; lithium naphthalene dianion, 34488-61-4; 2-methyltetrahydrofuran, 96-47-9; butyl vinyl ether, 111-34-2.

Synthesis of 5-Vinylcyclohexa-1,3-diene by a Nickel-Catalyzed Cooligomerization of Acetylene and Butadiene

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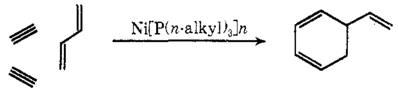
5-Vinylcyclohexa-1,3-diene is the major product formed (*ca.* 60% yield based on acetylene) when acetylene and butadiene are cooligomerized by nickel(0)–tri-*n*-alkylphosphine complexes. By-products are benzene (*ca.* 20% yield based on acetylene) and small amounts of 1,3,6-cyclooctatriene, styrene, 4-vinylcyclohexene, 1,5-cyclooctadiene, and several unidentified compounds. Isolation of 5-vinylcyclohexa-1,3-diene may be achieved by fractional distillation, under diminished pressure, of the volatile portion of the reaction mixture or by preparative glpc. This compound was previously obtained in moderate yield by pyrolysis of 1,3,5-cyclooctatriene.[1,2] As a preparative method, the synthesis described here appears more attractive.



Substituted derivatives of 5-vinylcyclohexa-1,3-diene have previously been prepared by nickel(0)-*tert*-phosphine catalyzed mixed oligomerizations of substituted acetylenes with butadiene.[3,4] However, the identities of reaction products from acetylene and butadiene were not reported, apparently because the course of the reaction was rather ill defined.[5] In yet earlier studies with $(R_3P)_2Ni(CO)_2$ complexes (R = OPh, OMe) as catalysts, acetylene and butadiene yielded small amounts of cyclooctatriene (presumably the 1,3,6 isomer) and a compound believed to be 4,5-divinylcyclohexene.[6] The principle process occurring in this study was a dimerization of butadiene.[6]

The relative simplicity of the product mixtures obtained here results largely from the choice of the *tert*-phosphine. As shown in Table I, the highest selectivity to 5-vinylcyclohexa-1,3-diene occurs with tri-*n*-alkylphosphines at R_3P:Ni mole ratios between 1:1 and 4:1. At low butadiene to acetylene mole ratios, reaction times are shortened and reaction temperatures below 25° may be used, but the selectivity to 5-vinylcyclohexa-1,3-diene suffers and the benzene yield increases.

The nickel catalyst is conveniently prepared *in situ* by treating $Ni(acac)_2$ with $AlEt_3$ at $-78°$ in the presence of the *tert*-phosphine and the monomers, although

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[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[3] P. Heimbach, K.-J. Ploner, and F. Thömel, *Angew. Chem., Int. Ed. Engl.*, **10**, 276 (1971).

[4] W. Brenner, P. Heimbach, K.-J. Ploner, and F. Thömel, *ibid.*, **8**, 753 (1969).

[5] W. Brenner, P. Heimbach, and G. Wilke, *Justus Liebigs Ann. Chem.*, **727**, 194 (1969).

[6] H. W. B. Reed, *J. Chem. Soc.*, 1931 (1954).