Registry No.--Fe(acac)₃, 14024-18-1; 1-bromooctane, 111-83-1; hexadecane, 544-76-3; octane, 111-65-9; octene, 111-66-0.

References and Notes

- For previous work see: J. Org. Chem., 41, 719 (1976).
 Abstracted in part from the Ph.D. Thesis of J.L.H., Montana State University, 1976.
- The term promoter is used here to refer to a positive catalyst which en-(3)hances the rate of a given reaction. An inhibitor would be referred to as a negative catalyst.
- A review by H. Lehmkuhl, *Synthesis*, 377 (1973). The term "nachtem Nichel" is used extensively by G. Wilke [*Justus Liebigs Ann. Chem.*, **727**, 183 (1969)] to describe the metallic species generated (5) by Et₂AlOEt reduction of Ni(acac)₂. Lehmkuhl proposes that the same species can be generated electrochemically (p 379 of ref 4).
- In this earlier work electrochemical reactions were conducted under (6) conditions of constant applied potential. The present work uses poten-tiostatic control of the working electrode with a Cd (Hg) reference electrode. See J. L. Hall and P. W. Jennings, *Anal. Chem.*, **48**, 2026 (1976), for details of the reference electrode.
- The electrochemical cell components consisted of two 6061-T6 aluminum electrochemical cell components consisted of two 6061-T6 aluminum electroches ($45 \times 45 \times 0.9$ mm) separated by 6–8 mm, 60 mL of dried DMF, 4.4 g (12.46 mmol) of Fe(acac)₃, 1.5 g (5.66 mmol) of Ph₃P, 0.802 g (3.81 mmol) of Et₄NBr, and 8.6 mL (49.78 mmol) of 1-bromooctane. The refer-ence electrode was placed on the opposite side of the working electrode from the counter electrode. The same experiment conducted at a potential of =0.90 V ws. CdHzb in the shearpe of Ev(acac), for three times the length of -0.90 V vs. Cd(Hg) in the absence of Fe(acac)₃ for three times the length of time does not yield any of the organic products shown in the table. This is not surprising since the reduction potential of 1-bromooctane is 900 mV
- is not surprising since the reduction potential of 1-bromooctane is 900 mV more cathodic of the controlled potential.
 (a) M. S. Kharasch, J. K. Hambling, and T. P. Rudy, J. Org. Chem., 24, 303 (1959). This particular paper dealt with cobalt rather than iron but is analogous as shown later by Kochi (see ref 8b). (b) M. Tamura and J. Kochi, J. Organometal. Chem., 31, 289 (1971); (c) M. Tamura and J. K. Kochi, Bull. Chem. Soc. Jpn., 44, 3063 (1971).
 (a) The other component to which the alkyl group couples is a vinyl or allyl halide; (b) M. Tamura and J. K. Kochi, J. Org. Chem., 40, 599 (1975); (d) R. S. Smith and J. K. Kochi, J. Org. Chem., 40, 599 (1975); (d) R. S. Smith and J. K. Kochi, J. Org. Chem., 41, 502 (1976); (e) C. L. Kwan and J. K. Kochi, J. Am. Chem. Soc., 98, 4903 (1976).
 Y. Ohbe and T. Matsuda, Tetrahedron, 29, 2989 (1973). (9)
- X-ray fluorescence investigations have shown that there are two different types of iron material coated on the aluminum electrode. More detail on (11)this aspect of the problem will be reported later. (12) By 24 h the current had decreased from 200 mA to less than 5 mA
- (13) The trace of products formed could be due to the small amount of cathode
- deposit which flakes off and remains suspended in the solution. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 4395 (1970). (14)
- Kochi determined the k_0/k_c rate ratios from product yields assuming that (15) alkene formed only by disproportionation.

New Synthetic Design for Formation of Carbon-**Carbon Triple Bonds**

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Alkynes serve as key starting materials of versatile intermediates in organic synthesis, providing access to a wide va-



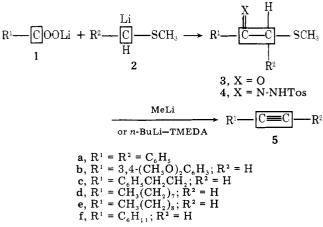


Table I. Preparation of Alkynes from Lithium Carboxylates through $lpha$ -Sulfenylated Ketones (3) and p -Toluenesulfonylhydrazones (4)	p-toluenesulfonyl-	¹ H NMR hydrazone $(4)^{15}$ alkyne (5)	compd registry yield,	COCHS no. no. % mp, °C no. no. %	5.35 4a 67489-14-9 85 157-160 5a ⁶ 501-65-5	67489-15-0 90		2.97 4c 67489-16-1 85 125-128 5c ¹¹ 16520-62-0 73		3.03 4d 67489-17-2 95 81-83 5d ¹¹ 764-93-2 70		3.02 4e 67489-18-3 95 91–93 5e ¹² 2243-98-3 66		3.10 4f $67489-19-4$ 90 $105-108$ 5f ¹³ 931-48-6 77
	α -sulfenylated ketone (3)	H	yield, m/e (CCl ₄), ppm	% (M ⁺) SCH ₃ COCHS	70 242 1.93	95 226 2.05		90 194 1.90		95 202 2.02		95 216 2.02		90 172 2.03
	α -sulfenylat		registry	no.	32368-19-7 7			67489-11-6 9		67489-12-7 9		67489-13-8 9		39195-70-5
			compd	no.	3a			3c		3d		3e		3f
		(1)	egistry	no.	553-54-8	67489-09-2		15082-45-8		63710-31-6		20336-95-2		16090 - 10 - 1
	lithium	carboxylate (1)	compd	no.	1a. CeHeCOOLi	1b , 3,4-(CH ₃ O) ₂ -	C ₆ H ₃ COOLi	1c, C ₆ H ₅ CH ₂ CH ₂ -	COOLi	1d, CH ₃ (CH ₂) ₇ -	COOLi	1e, CH ₃ (CH ₂) ₈ -	C00Li	1f, C ₆ H ₁₁ -COOLi
			run	no.	-	5		ŝ		4		5		9

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riety of functional groups.¹ Alkynes are most often prepared by dehydrogenation of vic- and gem-dihalogeno compounds and halogeno vinyl derivatives with strong base.¹ The decomposition of *p*-toluenesulfonylhydrazones of carbonyl compounds possessing a leaving group such as mesyloxy, acetoxyl, halogene,² and epoxy group³ at the α position have been used for preparation of alkynes. Pyrolysis of 5-chloromethyl-1H-tetrazole⁴ was also treated as a unique method for synthesis of alkynes. We have investigated a new synthetic design for formation of carbon-carbon triple bond by the use of carboxylic acid and (methylthio)methyllithium derivatives as two carbon units of the triple bond as outlined in Scheme I. We describe the results of the study in this paper.

Reaction of benzoic acid with 2.5 equiv of (methylthio)benzyllithium⁵ (2: $R^2 = C_6H_5$) afforded phenyl (methylthio)benzyl ketone 3a, whose p-toluenesulfonylhydrazone 4a was treated with methyllithium in dry Et₂O to give diphenylacetylene 5a⁶ in 65% yield.⁷ Treatment of lithium 3,4-dimethoxybenzoate $1b^8$ with (methylthio)methyllithium⁹ (2, R^2 = H) in dry THF gave 3,4-dimethoxyphenyl (methylthio)methyl ketone 3b in 93% yield. p-Toluenesulfonylhydrazone 4b, derived from 3b, was treated with methyllithium in dry Et_2O with stirring to afford 3,4-dimethoxyphenylacetylene 5b¹⁰ in 95% yield. In this way, lithium phenylpropionate 1c, lithium n-nonanoate 1d, lithium n-decanoate 1e and lithium cyclohexylcarboxylate 1f were converted to 4-phenyl-1-butyne 5c,¹¹ 1-decyne 5d,¹¹ 1-undecyne 5e,¹² and cyclohexylacetylene **5f**.¹³ Furthermore, n-butyllithium was also found to be useful for synthesis of alkynes from *p*-toluenesulfonylhydrazone of α -methylsulfenylated ketones. *p*-Toluenesulfonylhydrazone 4e was treated with *n*-butyllithium in dry THF in the presence of TMEDA to give 1-undecyne in 80% yield.¹⁴

This new method for preparation of alkynes starting from carboxylic acid should be applicable for formation of a variety of alkynes.

Experimental Section

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were dried and distilled from LiAlH₄ before use. Nuclear magnetic resonance spectra were recorded on a Varian T-60 instrument and mass spectra were determined on a Hitachi RMU-7L instrument.

General Procedure for Preparation of α -Methylsulfenylated Ketones (3) from Lithium Carboxylate (1). To a suspension of lithium carboxylate 1 (13.7 mmol), prepared from the carboxylic acid and an equimolar amount of n-BuLi in THF at 0 °C, was added a solution of (methylthio)methyllithium⁹ (20.5 mmol) in THF at 0 °C. After stirring at 0 °C for 0.5 h and then at room temperature for 14 h, the mixture was poured into water and extracted with benzene. The extract was washed with water, dried over Na2SO4, and evaporated to leave 3 in 90–95% yield. For the preparation of 3a, benzoic acid was treated with (methylthio)benzyllithium (2.5 equiv) in THF at -78°C under stirring. The mixture was maintained at the same temperature for 0.5 h and then at room temperature for 14 h. The mixture was worked up as above to give 3a in 70% yield. The crude ketones thus obtained were used for preparation of *p*-toluenesulfonylhydrazones 4 without purification.

General Procedure for Preparation of p-Toluenesulfonylhydrazones (4). A mixture of 3, an equimolar amount of p-toluenesulfonylhydrazide, and EtOH was refluxed for 3 h except in the case of 3a and 3b. For the preparation of 4a and 4b, the mixture was heated for 30 h under reflux. Evaporation of the solvent gave 4 as colorless needles in 85-95% yield.18

General Procedure for Preparation of Alkynes (5). (a) To a stirred suspension of 4 (6 mmol) in Et₂O (40 mL) was added an ethereal solution of MeLi (36 mmol) at 0 °C. After 0.5 h at 0 °C and then 30 h at room temperature with stirring, the mixture was poured into water and extracted with Et₂O. The extract was washed with water, dried over Na₂SO₄, and evaporated to leave 5. (b) To a stirred suspension of 4 (6.5 mmol) in THF (40 mL) containing TMEDA (19.5 mmol) was added n-BuLi (hexane solution, 19.5 mmol) at -78 °C. After stirring had been continued at 0 °C for 0.5 h and then at room temperature for 24 h, the mixture was worked up as above to give 5. By this method 1-undecyne (5e) was obtained in 80% yield.

Registry No.—*p*•Toluenesulfonyl hydrazide, 1576-35-8.

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- Yields were based in analytically pure materials. Lithium carboxylates were prepared from carboxylic acids by treatment with n-BuLi (hexane solution, 1 equiv) in THF at 0 °C. (8)

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- The reaction of lithium n-decanoate with (phenylthio)methyllithium was (14)also examined. Although the corresponding $\alpha\text{-phenyl thicketone was obtained in 60\% yield, the decomposition of p-toluenesulfonylhydrazone with$ n-BuLI-TMEDA gave 1-undecyne in much lower yield (20%).
- (15) All p-toluenesulfonvlhvdrazones gave satisfactory analyses.

Conversion of Aromatic and α,β -Unsaturated Aldehydes to Dichlorides by Thionyl Chloride and Dimethylformamide¹

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In an attempt to convert the bisulfite addition product of benzaldehyde 1 to the corresponding dichloro compound, 2, by treatment with thionyl chloride in the presence of dimethylformamide $(DMF)^3$ we found that benzal chloride, 3, was formed in high yield. This reaction was studied because it was hoped to be of value in converting substituted benz[a]anthracenes into corresponding dichlorides.

$$\begin{array}{ccc} \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CHOHSO}_{6}\mathrm{Na} & \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CHClSO}_{2}\mathrm{Cl} & \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CHCl}_{2} \\ 1 & 2 & 3 \end{array}$$

Further study revealed that treatment of benzaldehyde with thionyl chloride in the presence of a catalytic amount of DMF yielded 3 almost quantitatively at room temperature. Without DMF no reaction occurred.^{4,5} The generality of this reaction with aromatic and α,β -unsaturated aldehydes was demonstrated with 1-naphthaldehyde 6 (91% yield), cinnamaldehyde 7 (90%), and $\alpha\text{-methylcinnamaldehyde}$ 8 (85% only about 75% of which was (E)-1,1-dichloro-2-methyl-3-phenyl-2-propene). Slightly smaller yields were obtained with the corresponding bisulfite addition compounds of 6, 7, and 8. However, since aldehydes are often isolated and/or purified by means of their bisulfite addition compounds, the conversion of the latter to the dichloro compounds could save a step without overall loss of yield. In the case of *n*-octanal, cyclohexanone, and acetophenone, such mixtures of products were obtained that this reaction was of no utility.

When equal moles of DMF and SOCl₂ are mixed in the cold in CH₂Cl₂ and the solvent is removed under vacuum a colorless solid, 4, remains for which the ionic structures 4a and 4b have been advanced⁶⁻⁸ largely because of the slight solubility in nonpolar solvents. If this complex is heated SO_2 is lost and 5 is formed. Heating of DMF with PCl₅, COCl₂, oxalyl chlo-

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