

KI in one portion. The mixture was stirred for 22 h at room temperature and then at reflux for 2 h. The cooled solution was poured into 200 mL of 10% HCl overlaid with 200 mL of ether. The aqueous layer was separated and washed with ether. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to give 1.41 g of material. This material consisted of starting Hagemann's ester, the desired α -alkylated product, and some γ -alkylated material as shown by ^1H NMR. The mixture was stirred with 20 mL of 15% KOH in 95% ethanol for 12 h at 0 °C. The reaction was poured into 50 mL of water overlaid with 50 mL of ether. The separated aqueous layer was extracted twice with ether to remove unhydrolyzed material (primarily the γ -alkylated ester). The aqueous layer was acidified and extracted with ether until no color remained. The combined ether extracts were washed with brine, dried (Na_2SO_4), concentrated, and evaporatively distilled (130 °C (6.2 mm)) to give 710 mg (59% yield) of ketone 1: IR (film) 1670 (C=O), 3100, 1625, 990, and 925 cm^{-1} (C=C); ^1H NMR (100 MHz, CDCl_3) δ 1.95 (bs, 3 H, CH_3) and 4.8–6.05 (m, 3 H, $\text{CH}=\text{CH}_2$); ^{13}C NMR (CDCl_3) δ 21.1 (C-3 methyl), 22.4, 24.8, 28.3 (C-2'), 32.9, 33.9 (C-3'), 37.9, 114.3 (C-4'), 135.6 (C-2), 138.7 (C-5'), 154.9 (C-3), and 198.3 (C-1). The ^{13}C spectrum and VPC analysis (OV-101, 130 °C) indicated a purity >95%. MS m/e calcd for $\text{C}_{12}\text{H}_{18}\text{O}$, 178.135760; found, 178.135076.

Cyclization of Enone 1. To 380 mg (2.1 mmol) of enone 1 was added 10 mL of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride. The mixture was stirred for 2 h at room temperature. The TFA and TFAA were removed by concentration and the residue was distilled (115 °C (0.2 mm)) to give 650 mg of product: IR (film) 1780 cm^{-1} (trifluoroacetate C=O); ^1H NMR (60 MHz, CCl_4) δ 1.2 (angular methyl). This material was treated at room temperature with 20 mL of 10% KOH in methanol. After 20 min, the methanol was removed by concentration. Methylene chloride was added and salts were removed by filtration. The solution was dried (Na_2SO_4), concentrated, and distilled (125 °C (0.15 mm)) to give 310 mg (75% yield) of crystalline diol 2b which was recrystallized from hexane: mp 133–135 °C; IR (KBr) 3400 and 1050 cm^{-1} (OH); ^1H NMR (100 MHz, CDCl_3) δ 0.94 (s, angular methyl); ^{13}C NMR (benzene- d_6) δ 18.6, 19.4, 20.5 (CH_3), 25.8, 30.3, 33.9, 34.0, 34.3, 39.6 (>C-H), 40.7 (>C<), 78.4 (>C-O-), and 78.8 (>C-O-); MS m/e calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2$, 196.146320; found, 196.145711.

2-(4-Pentynyl)-3-methyl-2-cyclohexen-1-one (5). This material was prepared in a manner similar to that of enone 1 using 3.7 g (20 mmol) of Hagemann's ester and 3 g (20 mmol) of 5-bromo-1-pentyne.¹¹ In this case the crude alkylation product (3 g) was chromatographed on a silica gel column using methylene chloride to obtain 900 mg of starting ester and 2.0 g (52% yield based on recovered starting material) of pure α -alkylated product. Hydrolysis gave 1.3 g (91% yield) of enone 5: IR (film) 3300 and 2150 (C \equiv CH), 1650 and 1630 cm^{-1} (C=CC=O); ^1H NMR (100 MHz, CDCl_3) δ 1.94 (s, 3 H, CH_3), 1.92 (t, $J = 2$ Hz, C \equiv CH); ^{13}C NMR (CDCl_3) δ 18.4 (C-3'), 21.2 (C-3 methyl), 22.3, 24.4, 27.9 (C-2'), 32.9, 37.8, 68.4 (C-5'), 84.5 (C-4'), 134.8 (C-2), 155.8 (C-3), and 198.4 (C-1). Analysis by VPC (OV-101, 130 °C) showed only one peak. MS m/e calcd for $\text{C}_{12}\text{H}_{16}\text{O}$, 176.120110; found, 176.119792.

Cyclization of Enone 5. A mixture of 10 mL of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride was added to 650 mg (3.7 mmol) of enone 5. The mixture was stirred at room temperature for 2.5 h. The TFAA and TFA were removed by concentration and the residue was distilled (115 °C (0.1 mm)) to give 1.23 g (86% yield) of bis(enoltrifluoroacetate) 7: IR (film) 1785 (trifluoroacetate C=O) and 1680 (C=C); ^1H NMR (100 MHz, CCl_4) δ 1.29 (s, angular methyl), 5.24 (bs, C=CH). This ester was treated with 25 mL of saturated sodium bicarbonate in methanol for 20 min at room temperature. The methanol was removed by concentration and methylene chloride and MgSO_4 were added. The solution obtained after filtration was concentrated and distilled (125 °C (0.15 mm)) to give 600 mg (85% overall yield) of diketone 8 as a 6:1 mixture of cis and trans isomers: IR (film) 1725 cm^{-1} (C=O); ^1H NMR (100 MHz, CDCl_3) δ 1.07 (s, cis angular methyl) and 0.78 (s, trans angular methyl); ^{13}C NMR (CDCl_3) (major isomer) δ 20.9, 21.3, 26.6, 27.4 (C-1 methyl), 37.6, 39.0 (C-1), 39.5, 43.3, 53.3 (C-2), 60.4 (C-7), 212.0 (C-3 or C-8), 212.6 (C-3 or C-8). Analysis by VPC (Carbowax, 200 °C) showed one major peak with a shoulder for the trans isomer. MS m/e calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$, 194.130670; found, 194.130136.

Hydrolysis of bis(enoltrifluoroacetate) 7 under more vigorous conditions or treatment of diketone 8 with methanolic hydroxide led to a tricyclic aldol product. A 220-mg sample of diketone 8 was treated with 10 mL of 15% KOH in methanol at room temperature for 1 h. The mixture was poured into water and extracted with ether. The combined ether extracts were washed with brine, dried (Na_2SO_4), concentrated, and distilled (130 °C (0.2 mm)) to give 200 mg (90% yield)

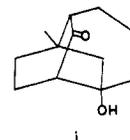
of a solid keto alcohol assigned structure 9: mp 146–148 °C (from hexane); IR (CCl_4) 1715 (C=O) and 3450 cm^{-1} (OH); ^1H NMR (100 MHz, CDCl_3) δ 1.00 (s, angular methyl); ^{13}C NMR (CDCl_3) δ 19.9 (C-10), 22.7, 27.2 (C-1 methyl), 27.4, 34.5, 37.0 (C-1), 39.6, 46.2 (C-2), 52.4 (C-7), 60.9 (C-4), 81.1 (C-8), and 214.2 (C-3).¹¹

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Registry No.—1, 67425-72-3; 2a, 67425-73-4; 2b, 67425-74-5; 5, 67425-75-6; 7, 67425-76-7; cis-8, 67425-77-8; trans-8, 67425-78-9; 9, 67463-82-5; Hagemann's ester, 487-51-4; 5-bromo-1-pentene, 1119-51-3; trifluoroacetic acid, 76-05-1; 5-bromo-1-pentyne, 28077-72-7.

References and Notes

- (1) For the previous paper in this series see: K. E. Harding, P. M. Puckett, and J. L. Cooper, *Bioorg. Chem.* **7**, 221 (1978).
- (2) (a) R. J. Ferrier and J. M. Tedder, *J. Chem. Soc.*, 1435 (1957); (b) P. E. Peterson and R. J. Kamat, *J. Am. Chem. Soc.*, **88**, 3152 (1966); (c) *ibid.*, **91**, 4521 (1969); (d) K. Hummel and M. Hanack, *Justus Liebig's Ann. Chem.*, **746**, 211 (1971); (e) G. Ohloff, F. Näf, R. Decorzant, W. Thommen, and E. Sundt, *Helv. Chim. Acta*, **56**, 1414 (1973); (f) M. Hanack, T. Dehesch, K. Hummel, and A. Nierth, *Org. Synth.*, **54**, 84 (1974); (g) R. E. Ireland, C. A. Lipinski, C. J. Kowalski, J. W. Tilly, and D. M. Walba, *J. Am. Chem. Soc.*, **96**, 3333 (1974); (h) S. W. Baldwin and J. C. Tomesch, *Synth. Commun.*, **5**, 445 (1975); (i) S. W. Baldwin and J. C. Tomesch, *Tetrahedron Lett.*, 1055 (1975); (j) J. Dijkink, H. E. Shoemaker, and W. N. Speckamp, *ibid.*, 4043 (1975); (k) T. J. Boer-Terpstra, J. Dijkink, H. E. Shoemaker, and W. N. Speckamp, *ibid.*, 939 (1977); (l) P. T. Lansbury and A. K. Serelis, *ibid.*, 1909 (1978).
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- (5) Other examples of intramolecular cyclization to tricyclic products by bicyclic fused ring cations generated from cationic π cyclization are known: (a) G. Stork and P. A. Grieco, *J. Am. Chem. Soc.*, **91**, 2407 (1969); (b) R. A. Volkmann, G. C. Andrews, and W. S. Johnson, *ibid.*, **97**, 4777 (1975); (c) W. S. Johnson, H. T. Hall, and R. A. Volkmann, unpublished observations, see ref 5b and H. T. Hall, Ph.D. dissertation, Stanford University, 1973.
- (6) See A. van der Gen, K. Wiedhaup, J. J. Swoboda, H. C. Dunathan, and W. S. Johnson, *J. Am. Chem. Soc.*, **95**, 2656 (1973); M. J. T. Robinson, *Tetrahedron Lett.*, 1685 (1965).
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clo[5.4.0.0^{3,9}]undecane.

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- (9) It should be noted that the differences observed are a result of the different allowable geometries for the bicyclic cationic intermediates in these two cyclizations and are not necessarily applicable to all alkyne cyclizations. In particular, tricyclic products have been observed in cases involving an internal alkyne as the π participant.^{5b,5c}
- (10) Prepared from 4-pentyn-1-ol using PBr_3 in pyridine.
- (11) This ^{13}C NMR spectrum correlates well with the spectrum of an isomeric tricyclic alcohol, 8-methyltricyclo[5.4.0.0^{4,8}]undecan-3-on-1-ol: K. E. Harding and J. L. Cooper, unpublished results.

Carbon-Carbon Bond Formation. 6.¹ Alkyl Halide Coupling from an Electrochemically Generated Iron Promoter

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The use of transition metal complexes to promote organic reactions has been well-established. However, the nature of

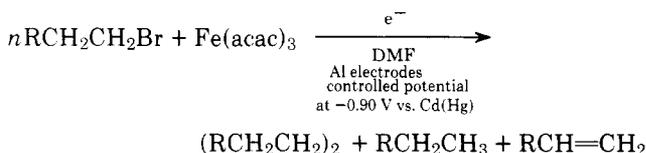
Table I

	A ^a	B	C
base electrolyte	TEAB	TEAB	TEAB
working electrode	Al	Al	Al
counter electrode	Al	Al	Al
E_{ref} , V, vs. Cd(Hg)	-0.90	-0.90	-0.90
$C_{16}H_{34}$, %	59.0 ^b	48.8	none
C_8H_{18} , %	23.8	27.0	<0.04 mmol
C_8H_{16} , %	10.9	8.4	<0.06 mmol
reaction, %	57.5	37.0	

^a There is no organic product formed in this type of experiment in the absence of $Fe(acac)_3$. ^b Percent yields were based on the amount of 1-bromooctane used.

the actual metallic promoters³ and the methods of their generation are not as well-established. In this note, we wish to provide evidence for the heterogeneous character of an iron promoter which has been generated by the electrochemical reduction of iron acetylacetonate, $Fe(acac)_3$.

In 1973, Lehmkuhl reported⁴ that transition metal promoters could be generated in nonaqueous solvents by the electrochemical reduction of metal acetylacetonates. These promoters were characterized as "naked" homogeneous catalysts⁵ which could be either trapped as an organometallic complex or used to promote organic reactions on the organic components in situ. The released ligand, acetylacetonate, is complexed by aluminum ions generated from the sacrificial anode. In a previous article, we reported¹ our preliminary findings⁶ on the use of promoters generated from nickel acetylacetonate to couple benzylic or aryl halides, and $Fe(acac)_3$ to couple alkyl halides. More details of the latter reaction which is shown below are now presented.



Experiment A of Table I is an example of the results obtained from a standard, controlled potential, cathodic reduction of $Fe(acac)_3$ in the presence of the substrate 1-bromooctane⁷ at aluminum electrodes. The yield of coupled product is surprisingly high in light of the fact that other iron-promoted coupling reactions such as the Kharasch reaction give poor yields of the symmetrically coupled alkane product. Particularly low yields of the symmetrically coupled product are obtained in the Kharasch reaction if a proton exists on the β carbon of the alkyl halide.⁸ Presumably, the presence of this proton facilitates the well-known elimination of metal hydride and alkene formation. Kochi⁹ and Ohbe¹⁰ have circumvented this problem by introducing the labile alkyl group into the Kharasch reaction as the Grignard component. As a result they have achieved 50–83% yields of cross-coupled product.^{9a} Thus, it is apparent that the iron promoter in our electrolytic reaction is somewhat different from those previously reported. Inspection of our reaction electrodes revealed the aluminum cathode to be coated with a black material which was subsequently shown to contain iron¹¹ and promote coupling of alkyl halides (experiment B).

The results of experiments B and C show that the mechanism for coupled and disproportionated product formation must have a heterogeneous iron component. These two experiments were conducted in the following manner. An electrochemical cell was charged with all the components mentioned for experiment A except for 1-bromooctane. Controlled potential electrolysis was conducted for 24 h¹² at a potential of -0.9 V vs. Cd(Hg). The black deposit on the cathode

formed as usual. This electrode assembly was subsequently removed from the original solution and placed into a new cell containing all the components including 1-bromooctane, but no $Fe(acac)_3$ was added. Experiment B was started by electrolyzing this last solution at -0.9 V vs. Cd(Hg). The current rose immediately to an instrument limited current of 200 mA followed shortly by an exponential decay to 5 mA. The products obtained therefrom were the same as those obtained in a standard reaction represented as experiment A.

The original solution, from which the electrodes for experiment B were removed, was charged with 1-bromooctane and equipped with a set of new aluminum electrodes. Continued electrolysis of this solution, experiment C, failed to generate a significant yield of products.¹³

The results of experiments A, B, and C clearly demonstrate that the iron-containing material deposited on the cathode is directly involved in the reactions noted above for alkyl halides.

These results are significant in two ways. First, they demonstrate that an iron promoter may be prepared and reacted with alkyl halides resulting in carbon-carbon bond formation *even in the presence of protons on the β carbon*. Second, they demonstrate that a metallic component is first deposited on the aluminum cathode followed by reaction with the alkyl halide. This is in contrast to Lehmkuhl's report in which the metal is reduced to a homogeneous "naked" metallic state which subsequently interacts with the organic substrate. Thus, our work suggests that in some cases the soluble organometallic compound alluded to by Lehmkuhl may be formed by interaction of the organic substrate with a deposited metal. At least, in the case of $Fe(acac)_3$ reduction in DMF at -0.9 V vs. Cd(Hg) using an aluminum cathode, a totally homogeneous reaction cannot be assumed.

Details of the reaction pathway are not fully understood at this time, but there are indications that free-radical intermediates may account for the product distribution. For example, Kochi¹⁴ reported in 1970 that the relative rate ratio (k_d/k_c) of disproportionated to dimeric or combined products was 0.12–0.15 for primary radicals. The same ratios for experiments A and B are 0.18 and 0.17, respectively.¹⁵

Experimental Section

Preparation of TEAB and $Fe(acac)_3$ has been reported previously.¹

Dimethylformamide (DMF). "Baker Analyzed" reagent grade DMF was distilled under atmospheric conditions. The fraction boiling at 144 °C was collected and stored in an amber colored bottle over Linde 4A molecular sieves. The solvent was used within 14 days after distillation.

1-Bromooctane. This reagent was used as it was received from Aldrich Chemical Co. as was the *n*-decane (Gold Label) which was used for the internal standard in quantitating the organic reaction products.

Electrolysis Cell. The cell was composed of a rubber stoppered beaker¹ containing two 6061-T6 aluminum electrodes (45 × 45 × 0.9 mm) separated by 6–8 mm, 60 mL of DMF, 4.4 g (12.46 mmol) of $Fe(acac)_3$, 1.5 g (5.66 mmol) of Ph_3P , 0.802 g (3.81 mmol) of Et_4NBr , and 8.6 mL (49.78 mmol) of 1-bromooctane. The Cd(Hg) reference electrode⁶ was positioned on the opposite side of the working electrode from the counter electrode.

Isolation and Analysis of Organic Products. Octane and octene were removed from the original reaction mixture by vacuum distillation and analyzed by GC using *n*-decane as a standard. The remaining reaction mixture was treated with 100 mL of H_2O containing 2 mL of concentrated HCl. Extraction of this solution with ether, drying, and concentration followed by alumina chromatography resulted in the isolation of hexadecane and unused 1-bromooctane. These products were also analyzed by GC using *n*-decane as a standard. The GC column was 8 ft × 1/8 in. copper tubing packed with 20% Carbowax 20 M on 80–100 mesh Chromosorb W.

Acknowledgment. We thank Montana State University for support of this research.

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

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- (2) Abstracted in part from the Ph.D. Thesis of J.L.H., Montana State University, 1976.
- (3) The term promoter is used here to refer to a positive catalyst which enhances the rate of a given reaction. An inhibitor would be referred to as a negative catalyst.
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- (5) The term "nachtem Nickel" is used extensively by G. Wilke [*Justus Liebig's Ann. Chem.*, **727**, 183 (1969)] to describe the metallic species generated by Et₂AlOEt reduction of Ni(acac)₂. Lehmkuhl proposes that the same species can be generated electrochemically (p 379 of ref 4).
- (6) In this earlier work electrochemical reactions were conducted under conditions of constant applied potential. The present work uses potentiostatic 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.
- (7) The electrochemical cell components consisted of two 6061-T6 aluminum electrodes (45 × 45 × 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 reference 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 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 more cathodic of the controlled potential.
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- (10) Y. Ohbe and T. Matsuda, *Tetrahedron*, **29**, 2989 (1973).
- (11) X-ray fluorescence investigations have shown that there are two different types of iron material coated on the aluminum electrode. More detail on 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.
- (14) Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 4395 (1970).
- (15) Kochi determined the *k_d/k_c* rate ratios from product yields assuming that alkene formed only by disproportionation.

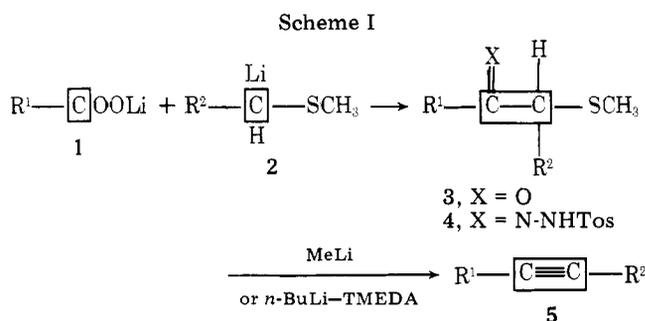
New Synthetic Design for Formation of Carbon-Carbon Triple Bonds

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



- a, R¹ = R² = C₆H₅
 b, R¹ = 3,4-(CH₃O)₂C₆H₃; R² = H
 c, R¹ = C₆H₅CH₂CH₂; R² = H
 d, R¹ = CH₃(CH₂)₇; R² = H
 e, R¹ = CH₃(CH₂)₈; R² = H
 f, R¹ = C₆H₁₁; R² = H

Table I. Preparation of Alkynes from Lithium Carboxylates through α -Sulfenylated Ketones (3) and *p*-Toluenesulfonylhydrazones (4)

run no.	lithium carboxylate (1)		α -sulfenylated ketone (3)		¹ H NMR (CCL ₄), ppm		<i>p</i> -toluenesulfonylhydrazone (4) ¹⁵		alkyne (5)			
	compd no.	registry no.	yield, %	<i>m/e</i> (M ⁺)	(CCL ₄), ppm	registry no.	yield, %	mp, °C	compd no.	registry no.	yield, %	
1	1a, C ₆ H ₅ COOLi	553-54-8	70	242	1.93	5.35	67489-14-9	85	157-160	5a ⁶	501-65-5	65
2	1b, 3,4-(CH ₃ O) ₂ C ₆ H ₃ COOLi	67489-09-2	95	226	2.05	3.58	67489-15-0	90	169-172	5b ¹⁰	4302-52-7	93
3	1c, C ₆ H ₅ CH ₂ CH ₂ COOLi	15082-45-8	90	194	1.90	2.97	67489-16-1	85	125-128	5c ¹¹	16520-62-0	73
4	1d, CH ₃ (CH ₂) ₇ COOLi	63710-31-6	95	202	2.02	3.03	67489-17-2	95	81-83	5d ¹¹	764-93-2	70
5	1e, CH ₃ (CH ₂) ₈ COOLi	20336-95-2	95	216	2.02	3.02	67489-18-3	95	91-93	5e ¹²	2243-98-3	66
6	1f, C ₆ H ₁₁ COOLi	16090-10-1	90	172	2.03	3.10	67489-19-4	90	105-108	5f ¹³	931-48-6	77