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 group[3] at the α position have been used for preparation of alkynes. Pyrolysis of 5-chloromethyl-1*H*-tetrazole[4] 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)benzyllithium[5] (**2**: $R^2 = C_6H_5$) afforded phenyl (methylthio)benzyl ketone **3a**, whose *p*-toluenesulfonylhydrazone **4a** was treated with methyllithium in dry Et_2O to give diphenylacetylene **5a**[6] in 65% yield.[7] Treatment of lithium 3,4-dimethoxybenzoate **1b**[8] with (methylthio)methyllithium[9] (**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 **5b**[10] 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 (Et_2O) were dried and distilled from $LiAlH_4$ 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)methyllithium[9] (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 Na_2SO_4, 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.[15]

General Procedure for Preparation of Alkynes (5). (a) To a stirred suspension of **4** (6 mmol) in Et_2O (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 Et_2O. The extract was washed with water, dried over Na_2SO_4, 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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(15) All *p*-toluenesulfonylhydrazones gave satisfactory analyses.

Conversion of Aromatic and α,β-Unsaturated Aldehydes to Dichlorides by Thionyl Chloride and Dimethylformamide[1]

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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.

$C_6H_5CHOHSO_6Na$	$C_6H_5CHClSO_2Cl$	$C_6H_5CHCl_2$
1	**2**	**3**

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 α-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 $SOCl_2$ are mixed in the cold in CH_2Cl_2 and the solvent is removed under vacuum a colorless solid, **4**, remains for which the ionic structures **4a** and **4b** have been advanced[6-8] 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 PCl_5, $COCl_2$, oxalyl chlo-

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Table I. Reactions of C_6H_5CHO and $C_6H_5CHOHSO_3Na$ with $SOCl_2$

time, min	% reaction[a] C_6H_5CHO **4a**[b]		C_6H_5CHOH-SO_3Na[d]
		5[c]	
15	76	26	16
30	85	57	31
60	88	81	58
120[e]	95	90	86

[a] The percent reaction was estimated by integration of the singlet (^1H NMR) at δ 6.60 ($C_6H_5\mathbf{CH}Cl_2$) compared to the singlet at 9.95 ($C_6H_5\mathbf{CHO}$) assuming a direct relationship between the integrated values and concentration of the species involved. [b] Reaction involving **4** (we assume structure **4a**). [c] Reaction involving **5**. [d] Reaction involving bisulfite addition compound and **4**. [e] After longer reaction times both benzaldehyde and the bisulfite addition compound gave about 90% isolated yields of **3** which showed no carbonyl hydrogen peak by ^1H NMR.

ride, and other compounds also leads to **5**,[3,9] frequently called the Vilsmeier reagent.

$$[(CH_3)_2N{=}CHOSOCl]^+Cl^- \quad [(CH_3)_2N{=}CHCl]^+SO_2Cl^-$$

4a **4b**

$$[(CH_3)_2N{=}CHCl]^+Cl^-$$

5

We prefer **4a** as the structure for **4** because the rate of reaction of benzaldehyde with the DMF·$SOCl_2$ complex which has not lost SO_2, **4**, is greater than the rate of reaction of benzaldehyde with **5** (see Table I).

Since only catalytic amounts of DMF complexes were used in experiments b and c in Table I only the rate involved in the first 15-min interval relates to comparative rates because complex **5** on reaction produces DMF. The latter then reacts with thionyl chloride to produce a complex of type **4**. Hence the reactions occurring at the later times are all with type **4** complexes.

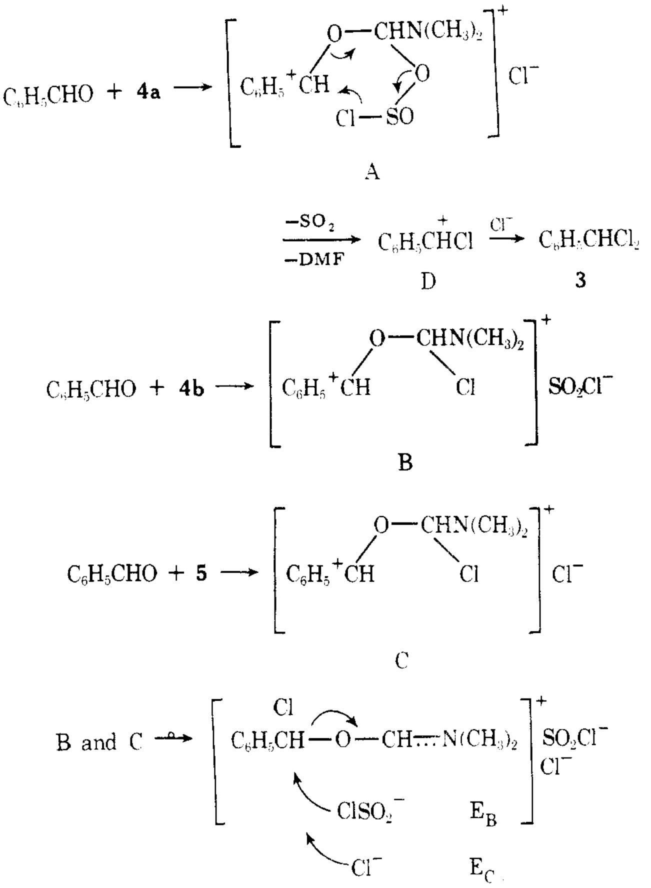
The effectiveness of DMF as a catalyst for the reaction of $SOCl_2$ with a variety of organic compounds has been discussed in terms of three intermediates, **4a, 4b,** and **5,** which may be formed by reaction of DMF with $SOCl_2$.[6] When these reagents are mixed in the cold (−10 to 0 °C) **4a** and/or **4b** are produced.[6] On warming SO_2 is lost and **5** results. The ionic form for each is preferred over a covalent form because of physical properties (e.g., insolubility in nonpolar solvents).

In most reactions involving the use of DMF and $SOCl_2$ it is not clear whether **4ab** and/or **5** was the active reagent because mixtures of DMF, $SOCl_2$, and the compound in question were heated and no measurements of the temperatures involved in the beginning were recorded. We are studying by X-ray crystallographic analysis the structure of the solid complex, **4a** or **4b**. In solution the two may be in equilibrium.

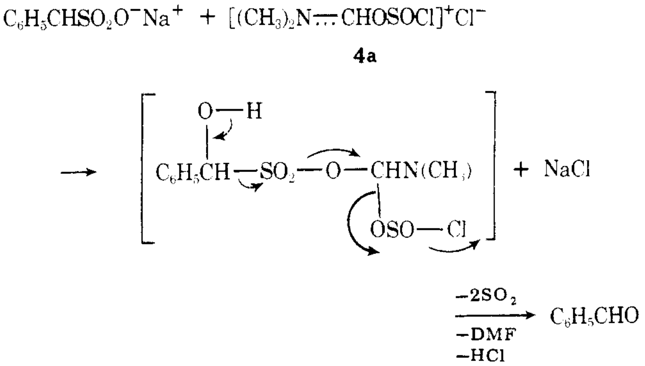
When benzaldehyde reacts with **4a, 4b,** and **5** we assume that the first step involves attack of the carbonyl oxygen at the cationic carbon to yield intermediates A, B, and C, respectively, as shown in Scheme I. Intermediate A can react by a cyclic six-atom path to yield carbonium ion D, SO_2, and DMF, followed by combination of D with a chloride ion to yield benzal chloride, **3**. Intermediates B and C, *which differ only in the nature of the negative counterion,* can undergo a chlorine shift to give intermediates E_B and E_C, respectively, which also differ only in the nature of the counterion. The reaction is then completed by attack of SO_2Cl^- or Cl^- on the benzylic carbon of E_B or E_C to yield **3** and DMF as shown.

We favor the route involving A. We see no reason why there should be an appreciable rate difference for the attack of benzaldehyde on **4b** or **5** because the intermediates, B and C, formed differ only by the negative counterion. Furthermore, there should be little difference in the rate at which B and C change to E_B and E_C prior to attack by SO_2Cl^- or Cl^- to yield **3** and DMF. Hence, if **4b** were involved we believe the rate of reaction of benzaldehyde with **4b** and **5** would be practically identical. The fact is, however, that benzaldehyde reacts much more rapidly with **4** than **5**. Because of this we believe that **4a** is involved and that the intervention of the cyclic path shown in Scheme I for A is responsible for the greater rate.

Scheme I



The generation of benzaldehyde from its bisulfite addition compound on reaction with the DMF–$SOCl_2$ complex (for example, **4a**) is undoubtedly initiated (at least in part) by attack of the bisulfite anion on the cationic carbon of **4a** followed by decomposition of the resulting complex as shown below.



With regard to diaryl ketones benzophenone has been reported to react at reflux with $SOCl_2$[10] as have xanthone and thiazanthone.[11] We believe thionyl chloride which contained a catalytically active impurity must have been used[4] since we found no reaction at reflux with any of these ketones with pure thionyl chloride. However, benzophenone does yield dichlorodiphenylmethane on long heating at reflux with $SOCl_2$ and DMF.

Experimental Section[12]

Reactions with $SOCl_2$–DMF. In typical preparative experiments 10.0 g of bisulfite addition compound, or 7.0 g of aldehyde, was added in portions to a stirred mixture of 35 mL of $SOCl_2$ (pure,[13] freshly distilled) and 0.5–1.0 mL of DMF held at −10 to −5 °C at all times during preparation. The temperature was allowed to rise slowly and the mixture was stirred for 4 h at room temperature then poured on ice and the products were collected by ether extraction in the cold. The ether layer was washed with saturated salt solution and dried over $MgSO_4$. The products (percent yield) were isolated by vacuum distillation. Benzal chloride, **3**, bp 89–90 °C (9.5 mm) (89 or 87% when an equivalent of the bisulfite addition compound was used), was characterized by its NMR spectrum.[14] Dichloro-1-naphthylmethane (91 or 86% from addition compound), bp 106–108 °C (0.5 mm) (lit.[15] bp 146–147 °C (2 mm)), was obtained from **6** and (*E*)-1,1-dichloro-3-phenyl-2-propene, mp 58.0–58.5 °C (lit[16] mp 57.5–58.5 °C), was obtained from **7.** From **8** a complex mixture of dichlorides was produced in which about 70–75% was estimated to be (*E*)-1,1-dichloro-2-methyl-3-phenyl-2-propene by integration of the NMR peak at δ 5.45 (s, 1) assigned to the $CHCl_2$ assuming the integration value as $\frac{1}{5}$ of the five ArH (m, 5, δ 7.0–7.5). Both *E* and *Z* forms were present. Because of difficulty in attempted separation and instability of the mixture no C,H analyses were attempted. However, the mass spectra of all fractions had peaks (M + 1) at 186, 188, and 190[12] indicating that two chlorine atoms were present.

Kinetic Experiments, Table I. In experiments similar to the above but on a smaller scale with benzaldehyde only the reaction mixture was poured on ice and the entire crude product, isolated as described above, was analyzed by NMR (see Table I). Reagent **5** was prepared by heating 70 mL of $SOCl_2$ and 0.5 mL of DMF at reflux for $\frac{1}{2}$ h. After cooling to −10 °C 14 g of benzaldehyde was added and aliquots were taken for analysis by the usual method described above. Similar experiments were done on the bisulfite addition compounds.

Dichlorodiphenylmethane. A solution of 4.0 g of benzophenone in 20 mL of $SOCl_2$ and 0.5 mL of DMF was held at reflux for 16 h. Vacuum distillation yielded 4.4 g (85%) of dichlorodiphenylmethane, bp 98–100 °C (0.5 mm), characterized by its IR spectrum.[14] None of this product was obtained when DMF was omitted. Xanthone and thiazanthone were recovered largely unchanged when DMF was present or absent even on heating at reflux.

Registry No.—**1**, 100-52-7; **3**, 98-87-3; **6**, 66-77-3; **7**, 104-55-2; **8**, 101-39-3; thionyl chloride, 7719-09-7; dimethylformamide, 68-12-2; (*E*)-1,1-dichloro-2-methyl-3-phenyl-2-propene, 67488-96-4; octanal, 124-13-0; cyclohexanone, 108-94-1; acetophenone, 98-86-2; $C_6H_5CHOHSO_3Na$, 4657-12-9; dichloro-1-naphthylmethane, 17180-26-6; (*E*)-1,1-dichloro-3-phenyl-2-propene, 51157-80-3; (*Z*)-1,1-dichloro-2-methyl-3-phenyl-1-propene, 67488-97-5; benzophenone, 119-61-9; dichlorodiphenylmethane 2051-90-3.

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Use of Dipolar Aprotic Solvents to Alter the Chemoselectivity of Lithium Dimethylcuprate[1]

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Although the presence of good donor solvents such as THF or HMP $[(Me_2N)_3PO]$ increases the rate of the displacement reaction at alkyl halides with lithium diorganocuprate reagents,[2,3] such donor solvents either retard or inhibit the conjugate addition of cuprate reagents to unsaturated carbonyl compounds.[4] Since the displacement reaction at an alkyl halide and the conjugate addition reaction exhibit opposite responses to added donor solvents, it seemed possible to effect either type of reaction selectively with a cuprate reagent by merely selecting the appropriate reaction solvent. To explore this idea, the bromo enone **5** was prepared by the sequence indicated in Scheme I.

Reaction of this bromo enone **5** with Me_2CuLi in Et_2O–Me_2S solution formed the typical conjugate adduct, bromo ketone **6,** in high yield. This result is not unexpected because conjugate addition reactions of cuprate reagents are typically much faster than displacement reactions at alkyl halides. Since our earlier studies[4] had indicated that stable solutions of Me_2CuLi could be formed in Et_2O–DMF and that these solutions failed to react with enones having reduction potentials more negative than 2.0 V (vs. SCE), we first examined the reaction of Me_2CuLi with the bromo enone **5** in an Et_2O–DMF mixture. Although the conjugate addition reaction was completely inhibited, the alternative displacement reaction was very slow. After 20 h at 25 °C only 22% of the displacement product **7** was isolated and 75% of the unchanged bromo enone **5** was recovered. Since it was also possible to prepare stable solutions of Me_2CuLi in mixtures of Me_2S, Et_2O, and *carefully purified* HMP, we also examined the reaction of the bromo enone **5** with Me_2CuLi in this solvent mixture. In this solvent system, the desired conversion of the bromo enone **5** to the methylated enone **7** was complete after 7–8 h at 25 °C and we found no evidence for the presence of any byproduct from conjugate addition. Thus, we conclude that by appropriate choice of reaction medium, it is possible to select only one of the two common synthetic applications of Me_2CuLi, either coupling with a halide or conjugate addition. This same solvent effect is presumably also applicable to other cuprate reagents provided that the cuprate reagents have sufficient thermal stability to allow their use in the relatively slow coupling reaction with an alkyl halide.

Experimental Section[5]

Preparation of the Dibromo Ketone 4 and the Bromo Enone 5. Previously described procedures[6] were employed to prepare the imine **1** and convert it successively to the unsaturated aldehyde **2** and the dienone **3,** bp 38 °C (22 mm), $n^{25}{}_D$ 1.4617 [lit.[6] bp 44 °C (25 mm), $n^{25}{}_D$ 1.4617]. Following a general procedure described earlier,[7] a solution of 500 mg (2.4 mmol) of the dienone **3** in 250 mL of pentane was flushed with N_2 and then a stream of anhydrous HBr was passed through the solution for 5 min while the solution was irradiated with the light from a 450-W medium-pressure Hg lamp. The pentane solution was again flushed with N_2 and then washed with aqueous $Na_2S_2O_3$, dried, and concentrated. The residual colorless liquid (850 mg) was chromatographed on silica gel with an Et_2O–hexane eluent (1:9 v/v) to separate 377 mg (44%) of the crude dibromide **4** as a white solid, mp 35–37 °C. Recrystallization from hexane separated 339 mg (40%) of the pure dibromide **4** as white needles: mp 46–47 °C; IR (CCl_4) 1710 cm^{-1} (C=O); NMR (CCl_4) δ 4.55 (1 H, d of d, J = 2 and 10 Hz, CH–Br), 3.0–3.6 (3 H, m, $BrCH_2$ and CHCO), 2.65 (1 H, d of d, J = 10 and 17 Hz, CHCO), 1.4–2.2 (4 H, m, CH_2), 1.18 (9 H, s, *t*-Bu), and 1.08 (6 H, s, CH_3); mass spectrum, *m/e* (rel intensity) 299 (9), 219

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