Table III. Trapping the *tert*-Butyl Radical from the Ag-Catalyzed Reaction of EtMgBr and *tert*-BuBr[a]

[Ag], 10^4 *M*	[Styrene], *M*	Rates of formation of products[b] ΣEt[c]	Σ*tert*-Bu[d]	Σ*tert*-Bu/ ΣEt
2.9	0	212	207	0.98
2.9	0.415	162	53	0.33
2.9	2.08	122	41	0.33
8.9	0.415	397	262	0.66

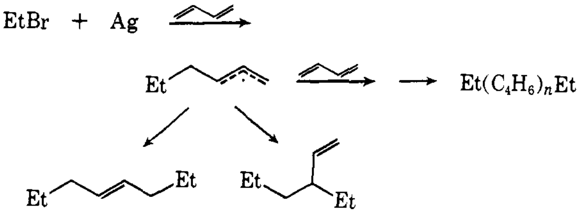
[a] In THF solution containing 0.18 *M* EtMgBr and 0.30 *M tert*-BuBr at 2°. [b] Initial rate given as 3.6 × 10^6 *M*/sec. [c] $C_2H_4 + C_2H_6 + 2C_4H_{10} + CH_3CH_2C(CH_3)_3$. [d] $i\text{-}C_4H_8 + i\text{-}C_4H_{10} + 2\text{-}[(CH_3)_3C]_2 + CH_3CH_2C(CH_3)_3$.

decreased to 25% of its value in the absence of styrene. It is clear that styrene was able to trap most of the *tert*-butyl radicals[10] formed as intermediates in eq 6′.

$$tert\text{-BuBr} + \text{Ag} \longrightarrow tert\text{-Bu}\cdot + \text{AgBr} \qquad (6')$$

$$tert\text{-Bu}\cdot + \text{PhCH}{=}\text{CH}_2 \longrightarrow \text{Ph}\dot{\text{C}}\text{HCH}_2\text{-}tert\text{-Bu, etc.} \qquad (9)$$

In a similar experiment a mixture of telomeric adducts (eq 10) was isolated from the catalytic reaction of ethylmagnesium bromide and ethyl bromide in the presence of butadiene as scavenger.



(10)

The catalytic reaction of *cis*-propenylmagnesium bromide with methyl bromide yielded *cis*-butene-2 (>94%), in agreement with the work of Whitesides and Casey,[11] who showed that the coupling of vinylsilver(I) complexes occurred stereoselectively. On the other hand, *cis*-propenyl bromide and methylmagnesium bromide were catalytically converted to a mixture of *cis*-butene-2 (70%) and *trans*-butene-2 (30%). The latter resulted from the inversion of configuration of the 1-propenyl radical.

Finally, we wish to comment on the formation of alkyl dimers according to eq 5. Previous studies[11] showed that the decomposition of 1-alkenylsilver(I) did not occur *via* dimerization of vinylic radicals[3b] and are supported by the observation (Table I) that styrene has no effect on the decomposition of alkylsilver(I). Furthermore, our results obtained from catalytic studies are also consistent with a concerted bimolecular mechanism since the rate of the coupling process relative to disproportionation increased with the bulk concentration of the silver catalyst.[12,13]

Acknowledgment. We wish to thank the National Science Foundation for granting financial support and R. A. Bailey for preliminary studies.

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(10) (a) The *tert*-butyl adducts to styrene showed characteristic bands at 1357 and 1385 cm^{-1} in the infrared spectrum but were not analyzed quantitatively since high molecular weight polymers were also formed. (b) The *tert*-butyl radicals were not completely trapped even at higher styrene concentrations. They may have been directly trapped by another silver, particularly if the latter is aggregated, *e.g.*

$$\text{R–X} + (\text{Ag})_n \longrightarrow \text{RAg} + \text{AgX} + (\text{Ag})_{n-2}$$

(11) G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

(12) (a) This assumes that alkane and alkene are formed by processes first order in organosilver(I) [*cf.* G. M. Whitesides, *et al.*, *ibid.*, **92**, 1426 (1970)]. (b) It is not clear whether di- and polynuclear alkylsilver(I) species are also important intermediates.[6] The degree of aggregation would also influence the relative rates on dilution since coupling may also occur in the aggregate.

(13) The mechanism of the coupling of aryl Grignard reagents with alkyl halides is unique. Thus, phenylsilver(I) is significantly more stable than alkylsilver(I) and could be readily isolated under our conditions. It reacted with alkyl Grignard reagents to yield only *dialkyl*, and with ethyl bromide only on heating (60°) to produce biphenyl and Ag, exclusively. Cross coupling was observed with the allyl bromide. The catalyzed reaction of ethylmagnesium bromide and bromobenzene was complicated by the exchange reaction.

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Alkylcopper(I) in the Coupling of Grignard Reagents with Alkyl Halides

Sir:

Copper complexes have been used as catalysts in the reaction of Grignard reagents with alkyl halides in ethereal solutions.[1] The mechanism of the catalysis, however, has been obscured by the occurrence of several simultaneous homolytic and heterolytic processes. In this report the various competing reactions have been clearly differentiated by the use of tetrahydrofuran (THF) as solvent in which the key organocopper(I) intermediates are more stable. Further, we wish to show that catalysis of the coupling reaction by silver[2] and copper, despite their similarity, occurs by fundamentally different mechanisms.

Alkylcopper(I) species were readily formed at temperatures less than −10° in THF by metathesis between copper(I) salts and Grignard reagents.[3,4] The same alkylcopper(I) was also produced from copper(II)

$$\text{RMgX} + \text{Cu}^{\text{I}}\text{Y} \longrightarrow \text{RCu}^{\text{I}} + \text{MgXY} \qquad (1)$$

salts at temperatures as low as −78°, accompanied spontaneously by 0.5 mol of dialkyl.

$$2\text{RMgX} + \text{Cu}^{\text{II}}\text{Y}_2 \longrightarrow \text{RCu}^{\text{I}} + 2\text{MgXY} + 0.5\text{R}_2 \qquad (2)$$

Solutions of alkylcopper(I) showed varying stability and underwent autocatalytic disproportionation according to eq 3[4,5] (Table I) in sharp contrast to the

$$2\text{RCu}^{\text{I}} \longrightarrow \text{RH} + \text{R}(-\text{H}) + 2\text{Cu} \qquad (3)$$

behavior of alkylsilver(I).[2] The disproportionation reaction (3) was unaffected by radical traps such as styrene in accord with Whitesides' observation[6] of the

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(1) V. D. Parker, L. H. Piette, R. M. Salinger, and C. R. Noller, *J. Amer. Chem. Soc.*, **86**, 1110 (1964); V. D. Parker and C. R. Noller, *ibid.*, **86**, 1112 (1964).

(2) M. Tamura and J. Kochi, *ibid.*, **93**, 1483 (1971).

(3) (a) H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas.*, **55**, 821 (1936); (b) see also K. H. Thiele and J. Kohler, *J. Organometal. Chem.*, **12**, 225 (1968); G. Costa, G. Alti, and L. Stefani, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **31**, 267 (1961); C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, 3926, 4162 (1960).

(4) K. Wada, M. Tamura, and J. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970).

(5) It was also possible to carry out the decomposition of Grignard reagents (eq 1 or 2 and 3) with less than stoichiometric amounts of copper if lithium nitrate or NO_2 was used as a mild oxidant to reconvert copper to copper(I,II). Some of the copper remained in solution as a metastable species (λ ≈ 575 nm) which quantitatively precipitated copper metal on standing or on treatment with dilute sulfuric acid [*cf.* silver, ref 2].

(6) (a) G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966); (b) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *ibid.*, **91**, 6542 (1969); **92**, 1426 (1970).

Table I. Decomposition of Alkylcopper(I) in THF at 2° [a]

Alkylcopper(I)		Products[b]					
C_2H_5Cu	C_3H_7Cu	C_2H_6	C_2H_4	C_3H_8	C_3H_6	D_{Et}[c]	D_{Pr}[d]
CH_3CH_2Cu		0.48	0.49			−0.01	
	$CH_3CH_2CH_2Cu$			0.49	0.51		−0.02
	$(CH_3)_2CHCu$			0.49	0.54		−0.05
CH_3CH_2Cu	$CH_3CH_2CH_2Cu$	0.31	0.20	0.18	0.31	+0.11	−0.13
CH_3CH_2Cu	$(CH_3)_2CHCu$	0.15	0.33	0.34	0.18	−0.18	+0.16

[a] From the reaction of ethyl and propylmagnesium bromides with copper(I) or copper(II) chloride (after correction for reaction 2). [b] Millimoles per millimole of copper. [c] $(C_2H_6–C_2H_4)$. [d] $(C_3H_8–C_3H_6) \equiv -(C_2H_6–C_2H_4)$.

unimportance of a homolytic pathway. A mixture of ethylcopper(I) and propylcopper(I) afforded ethane, ethylene, propane, and propylene by homo- and cross-disproportionation. The latter occurred in two ways given in eq 4, the relative amounts of which can be computed simply by taking the difference (D_{Et}) between the yield of ethane and ethylene (or alternatively, propylene and propane, $-D_{Pr}$).[7]

$$C_2H_5Cu^I, C_3H_7Cu^I \begin{array}{ll} \nearrow C_2H_6 + C_3H_6 + 2Cu & (4a) \\ \searrow C_2H_4 + C_3H_8 + 2Cu & (4b) \end{array}$$

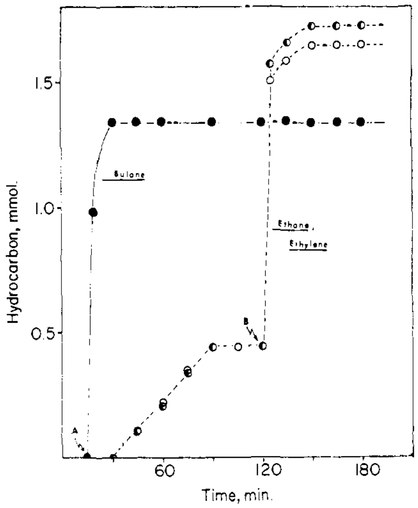

Figure 1. The Cu^I and Cu catalyzed reaction of ethylmagnesium bromide and ethyl bromide: A, addition of 1.35 mmol of ethyl bromide to a solution of 6.0 mmol of ethylmagnesium bromide and 1.0 mmol of Cu^I; B, addition of 1.35 mmol of ethyl bromide to a suspension of 1.0 mmol of Cu and 4.65 mmol of ethylmagnesium bromide (●, *n*-butane; ◐, ethylene; ○, ethane).

The results in Table I indicate that cross-disproportionation of ethylcopper(I) and *n*-propylcopper(I) favors path 4a, whereas 4b predominates with ethylcopper(I) and isopropylcopper(I). The copper hydride mechanism[6b] by itself does not appear to be sufficient to account for this conclusion, since isopropylcopper is expected to undergo elimination much more readily than *n*-propylcopper(I).[8] We suggest that an additional mechanism involving two alkylcopper(I) species in a direct dismutation should also be considered.[9]

The stability of p-alkylcopper(I) allowed us to examine directly the coupling reaction with alkyl halides. For example, stoichiometric amounts of ethylcopper(I) reacted immediately with ethyl bromide at 2° to form butane quantitatively according to eq 5.[10] The facility

$$EtCu^I + EtBr \longrightarrow EtEt + Cu^IBr \tag{5}$$

of this reaction enabled catalytic amounts ($<10^{-4}$ *M*) of copper halides to be used effectively in the coupling of ethylmagnesium bromide and ethyl bromide. Ethyl

$$EtMgBr + EtBr \xrightarrow{Cu^I} EtEt + MgBr_2 \tag{6}$$

radicals were not involved since the rate was unaffected by 0.4 *M* styrene. The rate of formation of butane was determined by systematically varying the concentrations of each component and could be approximated (using the initial slope method) by the following expression[11]

$$\frac{d[C_4H_{10}]}{dt} = k[Cu]^{1.0}[EtMgBr]^{0.8}[EtBr]^{0.7} \tag{7}$$

The rates of catalytic coupling of various Grignard reagents with alkyl halides are given in Table II. The effects of structural variations on the rate, as well as the reaction kinetics, suggest a rate-limiting step involving nucleophilic displacement of halide. We propose the following catalytic process for the coupling

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(7) (a) The total yields of alkane were comparable to alkene in all cases examined at these temperatures. (b) Taking the difference allows for syn proportionation of each alkylcopper(I) and is a direct measure of the predominance of reaction 4a over 4b. (c) Rapid exchange between alkyl groups prior to disproportionation was indicated since this *difference* was insensitive to the (relative) concentrations of the Grignard reagents and the order of mixing.

(8) (a) The α,β elimination of metal hydrides from various main group and transition metal alkyls generally follows the trend t > s ≫ p [G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, Methuen and Co., Ltd., London (1967), pp 298 ff; R. P. A. Sneeden and H. H. Zeiss, private communication]. The role of copper during autocatalytic elimination[4] may obscure this order. (b) However, these results do not perforce obviate the copper hydride mechanism, nor is such intended, since in the formulation of the latter the distribution of products in Table I also depends on a number of other factors including the rates of subsequent protonolysis of the alkylcopper as well as the concentrations and states of aggregation of the relevant alkyl and hydrido copper species, among others. We wish to thank Dr. G. M. Whitesides for a discussion of these points. Further delineation of the mechanism would be aided by a complete kinetic study. A distinction between the modes of decomposition of alkylsilver[2] and alkylcopper would also be desirable.

(9) Such a disproportionation does not necessarily have to be bimolecular and could well proceed from an alkylcopper cluster of the type recently shown for arylcoppers: A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 247 (1971); A. Cairncross and H. Omura, and W. A. Sheppard, *ibid.*, **93**, 248 (1971).

(10) In the presence of excess EtMgBr, the active ethylcopper(I) species in solution is probably a complex[1a] with EtMgBr, although not necessarily as a dialkylcuprate [see H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966)].

(11) (a) The exponents in this empirical rate expression are applicable to within 10%. Rigorous kinetics cannot be established in this system since a number of side reactions of varying importance are involved (*vide infra*) and the state of aggregation of the organometallic species is unknown. (b) The yields of ethane and ethylene as minor side products in the catalytic coupling were relatively invariant with the concentrations of the copper catalyst and ethyl bromide, but increased at low concentrations of ethylmagnesium bromide and at higher temperatures. (c) H. Schäfer and H. Kuntzel, *Tetrahedron Lett.*, 3313 (1970).

Table II. Relative Rates of Coupling of Grignard Reagents and Alkyl Halides Catalyzed by Copper(I) Halides[a]

		Rel rate[b]
	RMgX + EtBr	
EtMgBr	EtBr	1.0
n-PrMgBr	EtBr	1.3
i-PrMgBr	EtBr	25
tert-BuMgBr	EtBr	4.0
	EtMgBr + R–X	
EtMgBr	*n*-PrCl	<0.01
EtMgBr	*n*-PrBr	0.42
EtMgBr	*n*-PrI	4.1[c]
EtMgBr	*i*-PrBr	<0.01
EtMgBr	*tert*-BuBr	<0.01

[a] Reaction of 0.18 *M* RMgX, 0.16 *M* R'Br, and 5.8 × 10^{-4} *M* copper at 2°. [b] Based on less than 10% reaction to form REt. [c] Complications from alkyl exchange and the Wurtz reaction.

reaction

$$\mathrm{RMgBr + Cu^IBr \longrightarrow RCu^I + MgBr_2} \qquad (1')$$

$$\mathrm{RCu^I + R'Br \xrightarrow{slow} RR' + Cu^IBr,\ etc.} \qquad (5')$$

Thus, coupling is catalyzed by copper(I) and long kinetic chains are only observed with primary alkyl halides which can be used in synthetic procedures for alkyl coupling.[12] Disproportionation of the alkylcopper intermediates (eq 3) represents a chain termination step and increases in importance with *sec*- and *tert*-alkyl derivatives (*vide infra*). Reinitiation is possible by reoxidation of the soluble copper by alkyl halide (*e.g.*, eq 9).

The catalytic reaction of secondary and tertiary alkyl halides with Grignard reagents was slow (Table II), due to the unfavorable displacement step (eq 5'). At higher copper concentrations, disproportionation was observed and it was also the favored process when stoichiometric amounts of ethylcopper(I) reacted with isopropyl bromide.

$$\mathrm{EtCu^I} + i\text{-}\mathrm{PrBr} \begin{cases} \xrightarrow{59\%} \mathrm{C_2H_4 + C_3H_8 + Cu^IBr} & (8a) \\ \xrightarrow{38\%} \mathrm{C_2H_6 + C_3H_6 + Cu^IBr} & (8b) \end{cases}$$

Catalytic disproportionation can also be induced by copper. Thus, treatment of a mixture of 0.2 *M* ethylmagnesium bromide and 0.3 *M* *tert*-butyl bromide with small amounts (2 × 10^{-3} *M*) of soluble copper[5] at 2° produced only ethane, ethylene, isobutane, and isobutylene. The reaction sequence below (eq 9–11 and 1) is consistent with this disproportionation, since styrene (as a radical trap) selectively scavenged only the *tert*-butyl moiety. Analogously, ethylmagnesium bromide and ethyl bromide under similar conditions yielded ethane (25%) and ethylene (25%) as well as butane (50%). Coupling also observed in the latter case is, no doubt, attributable to the more facile displacement reaction 5 shown by ethyl bromide compared to *tert*-butyl bromide (*vide supra*).

$$tert\text{-}\mathrm{BuBr + Cu \xrightarrow{slow}} tert\text{-}\mathrm{Bu\cdot + Cu^IBr} \qquad (9)^{13}$$

$$tert\text{-}\mathrm{Bu\cdot + Cu \longrightarrow} tert\text{-}\mathrm{BuCu^I} \qquad (10)$$

$$tert\text{-}\mathrm{BuCu^I, EtCu^I \longrightarrow [C_2H_6, C_2H_4,}\ i\text{-}\mathrm{C_4H_{10}},\ i\text{-}\mathrm{C_4H_8] + 2Cu} \qquad (11)$$

Coupling and disproportionation of Grignard reagents with alkyl halides can be clearly differentiated by a simple experiment carried out serially in which ethyl bromide was added at point A to a solution of ethylcopper(I) in the presence of excess ethylmagnesium bromide at 2°. Figure 1 shows that butane was formed quantitatively according to eq 5. The resulting solution of ethylcopper(I) slowly evolved equimolar amounts of ethane and ethylene (dotted lines) quantitatively until copper was reduced (*i.e.*, mostly precipitated, eq 3, R = C_2H_5), and the addition of ethyl bromide at this point B produced only ethane and ethylene according to eq 12.[13b]

$$\mathrm{EtMgBr + EtBr \xrightarrow[metal]{Cu} C_2H_6 + C_2H_4 + MgBr_2} \qquad (12)$$

Acknowledgment. We wish to thank the National Science Foundation for their financial support, the Dow Chemical Co. for a gift of a billet of triply sublimed magnesium, and the du Pont Co. for generous quantities of THF.

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(12) (a) Reactions 5 and 5' are, thus, mechanistically analogous to the reactions of the more stable lithium dialkylcuprates with alkyl halides; (b) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **90**, 5615 (1968); (c) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *ibid.*, **91**, 4871 (1969); (d) for use of Grignard reagents see M. Tamura and J. Kochi, *Synthesis*, in press.

(13) (a) Copper, either in the soluble form or as a copper metal, reacted with alkyl halides only when activated by excess Grignard reagent, and probably exists as a Grignard–Cu complex. Even in the soluble form copper may be aggregated. (b) Only ethane and ethylene (in equimolar amounts) were observed if copper metal was used as a catalyst. Under these conditions ethylcopper(I) can only be formed on the copper surface and the autocatalytic disproportionation by copper is presumably more facile[4] than coupling with ethyl bromide.

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Vinylation of Grignard Reagents. Catalysis by Iron

Sir:

Iron is representative of one of the most effective metal catalysts for the promotion of the reactions between Grignard reagents and organic halides.[1] Metathesis of Grignard reagents and iron(II,III) chlorides occurred readily at 2° in tetrahydrofuran solutions, and the alkyliron intermediates afforded a reduced form of soluble iron, together with alkane and alkene.[2]

The reaction between a variety of Grignard reagents and organic halides was catalyzed effectively by the soluble iron species at concentrations less than 10^{-5} *M*. For example, the reaction between 0.15 *M* ethyl bromide and 0.16 *M* ethylmagnesium bromide occurred smoothly at 2° in the presence of 1.2 × 10^{-5} *M* soluble iron to produce an equimolar mixture of ethylene and ethane. Less than 0.1% *n*-butane was formed.[3] The

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(1) M. Tamura and J. Kochi, submitted for publication.

(2) As yet the soluble iron species is not fully characterized, but our evidence points to an iron species which is readily aggregated and complexed with the Grignard reagent. Compare the preparation and characterization of the analogous cobalt species generated in a similar manner by M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 1, 497 (1968), and G. Costa, G. Mestroni, and G. Boscarato, *Ric. Sci., Parte 1*, 315 (1964).

(3) (a) Coupling dimers were only observed when the alkyl group contained no β-hydrogens (*e.g.*, methyl and neopentyl). The reaction of methylmagnesium bromide and ethyl bromide at 25° afforded only