Experimental Section

Infrared spectra were determined as 10% carbon disulfide solutions on a Beckman IR-5A instrument; boiling points are uncorrected.

Materials.—Butadiene was Phillips research grade, 99.88% pure. Treatment of all other solvents and gases has been described previously.[12]

Reference Compounds.—3,4-Dichloro-1-butene (I) and *trans*-1,4-dichloro-2-butene (II) were obtained from Columbia Organic Chemicals; the latter was seriously contaminated with I and IV. *cis*-1,4-Dichloro-2-butene (IV) was prepared from the corresponding diol obtained by catalytic reduction of 2-butyn-1,4-diol according to the method of Mislow and Hellman[11] except that Lindlar's catalyst[29] was substituted for Raney nickel. 2-Chlorobutadiene in xylene solution was obtained from K & K Laboratories and served to established its retention time. Dichloride II was gradually heated with solid potassium hydroxide until a volatile product distilled off; the distillate was collected in toluene; and this solution served to establish the retention time of 1-chlorobutadiene (V).[2] Chlorocyclohexane and toluene are commercially available.

Product Isolation.—Butadiene (40 ml, 0.5 mole) was collected at −9° under a Dry Ice condenser and diluted with 200 ml of carbon tetrachloride. The mixture was flushed with nitrogen and 8.1 ml (0.17 mole) of liquid chlorine, condensed in a calibrated trap, was swept into the stirred mixture in 30 min in the absence of light at −9°. Glpc analysis showed I and II as the only significant volatile products with (II)/(I + II) = 0.71. Solvent was removed on a rotary evaporator and the residue distilled through an 18-in. spinning-band column. After a forerun, in which a minor amount of I was lost, the following fractions were collected: (1) 1.62 g, bp 44–47° (50 mm); (2) 9.03 g, bp 75–79° (50 mm); and (3) 5.91 g of liquid residue. Fraction 1 had an infrared spectrum consistent with that of commercial 3,4-dichloro-1-butene (I) and glpc analysis showed it to be >95% I. Fraction 2 had an infrared spectrum generally consistent with that reported[11] for *trans*-1,4-dichloro-2-butene (II); however, glpc analysis revealed 10% of I. The (II)/(I + II) ratio in recovered material is thus 0.77; this increase probably represents some loss of I during distillation since the individual isomers are thermally stable under the distillation and the glpc analysis conditions. Analysis of residue 3 showed C, 29.94; H, 3.77; Cl, 66.29. $(C_4H_6Cl_3)_x$ requires C, 30.08; H, 3.92; Cl, 66.05. This residue may well be a mixture of tetrachlorides and telomeric material.

Quantitative Chlorination Runs.—The general procedure and equipment have been described.[12] Butadiene was introduced as a gas and condensed by use of a Dry Ice condenser; 1,1,2-trichlorotrifluoroethane and cyclohexane were added as liquids. Initial concentrations, as well as final product ratios, wer edetermined by glpc analysis of a 1-μl aliquot (Micro-Tek snap sampler) on a Micro-Tek 2500-R instrument equipped with 2-m Perkin-Elmer "R" columns (polypropylene glycol) by use of a flame ionization detector.

Retention times in minutes at 92° and a helium flow of *ca.* 200 ml/min follow: V, 1.85; 2-chlorobutadiene, 2.1; toluene, 5.2; I, 8.0; chlorocyclohexane, 11.0; IV, 20.6; and II, 24.8. Areas and area calibration factors were determined as before.[12] Yields of (I + II) were calculated by addition of a known amount of toluene after reaction as an internal standard; comparison of the areas of I, II, and toluene with the amount of chlorine introduced (calibrated liquid trap) gave the yield. The relative reactivity of butadiene compared with cyclohexane was determined from the expression

$$\left[\frac{12(\mathrm{I} + \mathrm{II})}{(C_6H_{11}Cl)}\right]\left[\frac{(C_6H_{12})_0}{(C_4H_6)_0}\right]$$

where $C_6H_{11}Cl$ is chlorocyclohexane and $(C_6H_{12})_0$ and $(C_4H_6)_0$ are the initial concentrations of cyclohexane and butadiene. Under purely radical conditions at low conversion, this value becomes equal to k_a/k_t, where k_a is the relative rate of addition of chlorine atom to butadiene as a whole and $k_t \equiv 1.00$ for abstraction of a single cyclohexane hydrogen by chlorine atom.[12]

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(29) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

Coordination Effects in Organic Reactions. I. A Novel Preparation of *t*-Alkyl Isocyanide Complexes by N-Alkylation of Hydrogen Cyanide

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Reaction of isobutene with hydrogen cyanide in the presence of a cuprous halide was found unexpectedly to give *t*-butyl isocyanide cuprous complexes, $[(CH_3)_3CNC]_3CuX$ and $(CH_3)_3CNC \cdot CuCN$. Isocyanide ligands can be liberated from the cuprous complexes by aqueous potassium cyanide. A reaction scheme is proposed to explain the formation of these cuprous complexes. Scope of the novel alkylation reactions was studied and physical properties of a number of new *t*-alkyl isocyanides thus obtained were recorded.

In most metal cyanide complexes neutron-diffraction measurements indicate that CN^- is bonded to metal by carbon.[2-3] The fact that alkylation of cyanide gives corresponding alkyl isocyanide complexes supports this observation.[4-8] In the parent acid, hydrogen cyanide, it is likely that both of the two σ lone pairs on the carbon and nitrogen of the anion projecting outward along the CN axis are utilized for bonding with hydrogen, since the acid is hydrogen bonded and a weak acid in water (pK = 9.21).[9] Further, hydrogen cyanide is known to be a Lewis base toward acidic metal halides, *e.g.*, B_2Cl_4[10a] or $SbCl_5$.[10b] Thus it would be of interest to see whether coordination of hydrogen cyanide to certain metals occurs through carbon or nitrogen.

During a course of study on the catalytic syntheses of nitriles from olefins an addition reaction was observed between isobutene and hydrogen cyanide when cuprous bromide was used. The reaction products were apparently cuprous complexes containing organic ligands, but not of alkyl nitriles. This unexpected finding stimulated us to elucidate the structure of the complex products in order to provide an answer to the above question. The purpose of this paper then is to present

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(1) Osaka University.

(2) W. H. Jones, *J. Chem. Phys.*, **26**, 1578 (1957); **27**, 468 (1957).

(3) N. A. Curry and W. A. Runciman, *Acta Cryst.*, **12**, 674 (1959).

(4) M. Freund, *Ber.*, **21**, 931 (1888).

(5) E. G. J. Hartley and H. M. Powell, *J. Chem. Soc.*, 250 (1927).

(6) H. Irving and M. Jonason, *ibid.*, 2095 (1960).

(7) W. Z. Heldt, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 99.

(8) S. C. Malhotra, *J. Inorg. Nucl. Chem.*, **25**, 971 (1963).

(9) K. P. Ang., *J. Chem. Soc.*, 3822 (1959).

(10) (a) A. K. Holliday, F. J. Marsden, and A. G. Massey, *ibid.*, 3348 (1961); (b) E. Allenstein and A. Schmidt, *Chem. Ber.*, **97**, 1863 (1964).

TABLE I

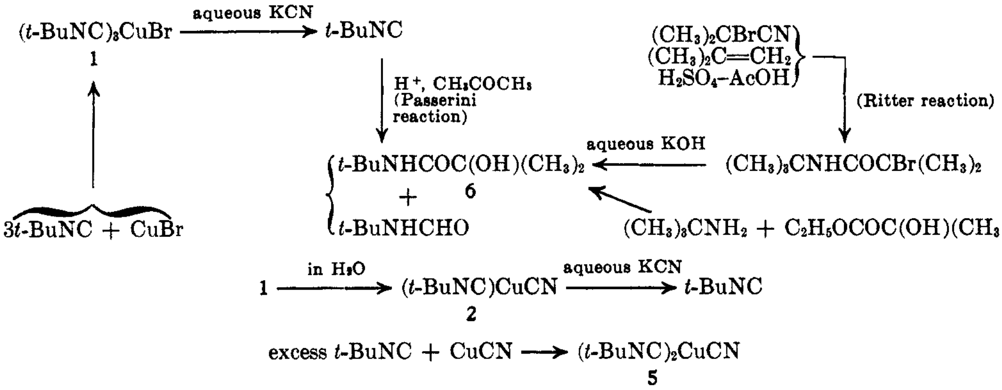
CUPROUS COMPLEXES OBTAINED FROM ALKYLATION WITH ISOBUTENE[a]

Formula	$[(CH_3)_3CNC]_3CuBr$				$(CH_3)_3CNC \cdot CuCN$			
Form	Colorless needles (from C_6H_6)				Colorless prism (from CH_3CN)			
Mp, °C	151–153				196–198			
Solubility	Soluble in most organic solvents				Slightly soluble in CH_3CN; insoluble in hydrocarbons, alcohols, and ether			
Infrared,[b] cm^{-1}	2182 ($\nu_{N\equiv C}$ of isonitrile)[c]				2182 ($\nu_{N\equiv C}$ of isonitrile), 2140 ($\nu_{C\equiv N}$ of metal cyanide)[d]			
Mol wt	Calcd, 393. Found,[e] 391 and 387							
	Cu	C	H	N	Cu	C	H	N
Calcd, %	16.17	45.85	6.92	10.69	36.79	41.73	5.25	16.22
Found, %	16.36	46.11	7.07	10.42	36.72	41.80	5.51	16.24

[a] For reaction conditions see the Experimental Section. [b] Nujol mull. [c] $\nu_{N\equiv C}$ of authentic *t*-butyl isocyanide and $\nu_{C\equiv N}$ of authentic pivalonitrile are seen at 2143 (strong) and 2232 cm^{-1} (strong), respectively. [d] $\nu_{C\equiv N}$ of cuprous cyanide is seen at 2172 cm^{-1}. [e] Cryoscopically in $C_6H_5NO_2$.

CHART I

STRUCTURE PROOF FOR THE CUPROUS COMPLEXES 1 AND 2 FORMED BY THE ALKYLATION REACTION



a general picture of the new alkylation reaction of hydrogen cyanide with iso olefins in the presence of cuprous halides.

Results and Discussion

Formation of *t*-Butyl Isocyanide Complexes.—When a mixture of hydrogen cyanide, isobutene, and cuprous bromide in a mole ratio of >3:>3:1 was heated at above room temperature under autogenous pressure, the cuprous salt gradually dissolved, resulting in a water-clear homogeneous solution. Two cuprous complexes were isolated from the reaction mixture: one was a monomeric bromo complex (**1**) readily soluble in ethanol and the other was a polymeric cyano complex (**2**) insoluble in cold ethanol. Treatment of the complex **1** with aqueous potassium cyanide solution yielded an oily layer. The infrared spectrum involving an isocyanide stretching absorption band at 2143 cm^{-1} was identical with that of authentic *t*-butyl isocyanide (Table I). There was no indication of the presence of alkylnitrile in the organic layer. This finding was surprising, since isocyanide formation has never been noted in the literature dealing with the addition reaction of hydrogen cyanide to carbon–carbon double bonds. For example, nucleophilic addition of cyanide anion to give nitriles has been accomplished with olefins whose double bond is activated by negative groups.[11] Branched-chain olefins, such as isobutene and trimethylethylene, or α-olefins like propene yield nitriles by contact reaction with hydrogen cyanide over alumina,[12] cobalt cyanide on alumina, or cobalt on alumina.[13] Liquid phase reaction of ethylene, propene, and higher α-olefins with hydrogen cyanide using dicobalt octacarbonyl as a catalyst[14] also produced nitriles. Thus, formation of nitriles has been observed invariably, irrespective of the types of olefins, catalysts, and reaction phases.[15] It was felt necessary, therefore, to obtain further evidence that **1** contains *t*-butyl isocyanide as a ligand.

An aqueous acetone solution of **1** was heated in the presence of hydrogen bromide; the reaction produced colorless, readily sublimable crystals (**6**), mp 96–97°, together with a small amount of N-*t*-butylformamide, bp 103° (18 mm). *t*-Butyl isocyanide prepared separately was treated with aqueous acetone–hydrobromic acid (modified Passerini reaction[16]) to give a crystalline compound, mp 96–97°, whose infrared spectrum was found to be identical with that of **6**. Neither product did show melting point depression with an authentic sample of N-*t*-butyl-2-hydroxy-2-methylpropionamide prepared according to the known routes (Chart I). In addition to these facts, elemental analysis and molecular weight measurements (Table I) led us to infer that **1** is monobromotris(*t*-butyl isocyanide)-

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(11) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p 219.

(12) C. R. Harris and W. W. Deatley, U. S. Patent 2,455,995 (Dec 14, 1948).

(13) T. G. O'Neiland and F. W. Kirkbride, British Patent 678,014 (Feb 4, 1953).

(14) P. Arthur, Jr., D. C. England, B. C. Pratt, and G. M. Whitman, *J. Am. Chem. Soc.*, **76**, 5364 (1954).

(15) For review articles, see, for example, D. T. Mowry, *Chem. Rev.*, **42**, 222 (1948); P. Kurtz, "Methoden der organishen Chemie," Vol. VIII, G. Thieme Verlag, Stuttgart, Germany, 1952, p 247.

(16) I. Hagedorn and U. Eholzer, *Angew. Chem.*, **76**, 538 (1964); *Chem. Ber.*, **98**, 936 (1965).

copper(I). This was confirmed by an independent synthesis of the complex **1** from a known sample of the isocyanide and cuprous bromide.

t-Butyl isocyanide was also liberated when the cyano complex **2** was treated with aqueous potassium cyanide solution. Data collected in Table I indicated that **2** is cyano(*t*-butyl isocyanide)copper(I) and the identification was confirmed by synthesis of **2** from cyanobis(*t*-butyl isocyanide)copper(I) (**5**), readily preparable from cuprous cyanide and excess *t*-butyl isocyanide.

The ratio of **1** to **2** in the alkylation products depends upon the reaction variables, being especially sensitive to the nature of solvent (Table II). While the reaction carried out in aqueous medium produced **2** as a major product, the reaction in ethanol gave mainly **1**. In accord with this solvent effect, treatment with hot water of the bromo complex **2** produces the cyano complex **1** quantitatively, as will be described later. The medium effects for the reaction path appear to be difficult to interpret because of the complex reaction steps involved (Chart II). It may be noted that catalytic hydration of isobutene to *t*-butyl alcohol occurred to a considerable extent as a side reaction in aqueous medium (Table II), presumably owing to the presence of such a Brønsted acid as H[CuBrCN], analogous to a strong complex acid, $H[Cu(CN)_2]$ ($K_a = 1.22 \times 10^{-5}$).[17]

TABLE II

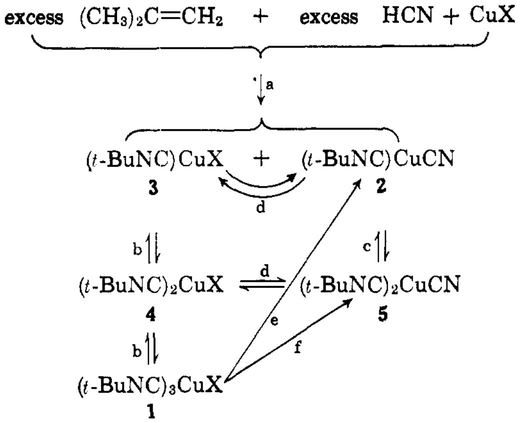
SOLVENT EFFECTS ON THE TYPE OF CUPROUS COMPLEXES FORMED BY THE ALKYLATION REACTION

	Products,[a] g				
			Other products		
Solvents	Complex 1	Complex 2	*t*-BuOH	*t*-BuBr	*t*-BuNH$_2$·HBr
None	5.3	0.7	...	Trace	
Water	Trace	2.8	10	*ca.* 0.3 g	0.15
Ethyl alcohol	4.7	Trace	...	A small amount	Trace
Tetrahydrofuran	2.8	2.7	...	...	...
Benzene	2.8	2.0	...	...	...

[a] Products obtained from the reaction of 14 g (0.25 mole) of isobutene, 6.8 g (0.25 mole) of hydrogen cyanide, and 3.6 g (0.025 mole) of cuprous bromide at 50° for 24 hr in 20 ml of solvent.

CHART II

ALKYLATION SCHEME



A reaction scheme for the new alkylation reaction proposed in Chart II is based on the experimental observations that follow. The complexes **1**, **2**, and **4** have been detected in the reaction. The predominant formation of **1** or **2** and the failure to detect **3** and **5** may be understood in terms of the equilibrium constants, K_b and K_c for steps b and c, respectively. The over-all formation constant K_b or K_c for isocyanide complexes, $(RNC)_nCuX$ (n = 1–4) apparently depends on nature of the anion X. There are qualitative indications that K_c should be very small and $K_b \gg K_c$. For example, tetrakis(isocyanide) complexes $(RNC)_4CuX$ are readily formed from CuX and excess isocyanide, provided X is halogen anion, but are not isolable for $X{=}CN^-$. Even the cyano tris(isocyanide) complex was too unstable to isolate in an analytically pure state. The cyano bis(isocyanide) complex **5** prepared separately was transformed readily into the more stable complex **2** upon treatment with hot organic solvents or water. Similar equilibrium reactions are involved in the formation of chloro complexes, $(ArNC)_nCuCl$ (n = 1–3).[18] Thus, these formation constants seem to account for the predominant formation of **1** or **2** among the bromo or cyano isocyanide complexes.

Conversion of bromo complexes into cyano complex was observed. The bromo complex **1** was converted quantitatively into **2** (route e or c–f) by heating the aqueous suspension of **1**; the conversion in benzene required prolonged heating and resulted in a lower yield. In the latter case a small amount of the bis(isocyanide) complex was found (route f).

Scope and Mechanism of the Reaction.—At temperatures up to 100° ethylene, propene, 1- and 2-butene, and butadiene failed to alkylate hydrogen cyanide in the presence of cuprous halides. Isoprene gave a mixture of unsaturated nitriles in addition to the isoprene polymers; the main component among the unsaturated nitriles was 2-methyl-4-cyano-2-butene. 2,3-Dimethylbutadiene gave a number of isocyanide and nitriles; no attempt was made to isolate and identify these products. It was soon realized that olefins must have a disubstituted olefinic carbon, RR′C= for the N-alkylation reaction. Table III lists olefins which gave corresponding isocyanide by this reaction.

The structural requirement for the olefin suggests a carbonium ion mechanism, *i.e.*, attack of a tertiary carbonium ion on the lone-pair electrons of the nitrogen of the coordinated cyanide. The formation of *t*-butyl bromide, and *t*-butylamine hydrogen bromide, and the catalytic hydration of isobutene observed in the alkylation reaction carried out in aqueous medium are consistent with carbonium ion mechanism. In an acid-catalyzed N-alkylation of hydrogen cyanide by olefins, which produce N-formylamines, an alkylcarbonium ion has been assumed as an intermediate.[19] The following is a tentative mechanism to explain the formation of isocyanide complexes.

$$\mathrm{HCN} + \mathrm{CuBr} \longrightarrow \underset{\mathbf{7}}{\mathrm{H^+[NC\cdot CuBr]^-}} \xrightarrow{\mathrm{C_4H_8}} t\text{-}\mathrm{Bu^+[NC\cdot CuBr]^-}$$

$$\underset{\mathbf{3}}{t\text{-}\mathrm{BuNC\cdot CuBr}} \xrightarrow{\mathrm{HCN}} \underset{\mathbf{8}}{\mathrm{H^+}[t\text{-}\mathrm{BuNC\cdot CuBrCN}]^-} \xrightarrow{\mathrm{C_4H_8}} \cdots \text{etc}$$

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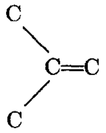
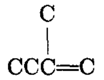
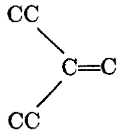
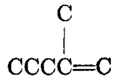
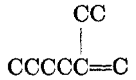
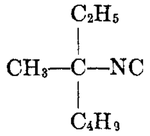
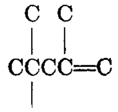
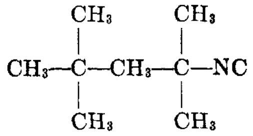
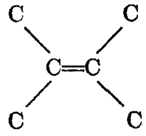
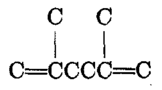
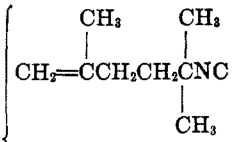
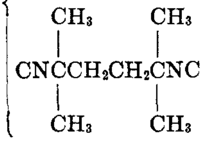
[17] M. G. Vladimisov and I. A. Kakousky, *Zh. Prikl. Khim.*, **23**, 580 (1950).

[18] F. Klages, K. Monkemeyer, and R. Heinle, *Chem. Ber.*, **85**, 109 (1952).

[19] L. Schuster, *Tetrahedron Letters*, **29**, 2001 (1963).

TABLE III

OLEFINS AND ALKYLISOCYANIDES OBTAINED BY THE NEW ALKYLATION REACTION

Olefin	Isocyanide	Yield, (moles/g-atom of Cu)	Bp (mm), °C	$n^{20}D$	Anal, %					
					C		H		N	
					Calcd	Found	Calcd	Found	Calcd	Found
	$(CH_3)_3CNC$	1.2	60–63 (314)	1.3749						
	$(CH_3)_2(C_2H_5)CNC$	1.6	68–69 (153)	1.3938	74.17	74.09	11.41	11.59	14.42	14.27
	$(CH_3)(C_2H_5)_2CNC$	1.5	80–81 (100)	1.4079	75.61	75.73	11.79	11.91	12.60	12.67
	$(CH_3)_2(C_3H_7)CNC$	1.2	74–75 (92)	1.4012	75.61	74.90	11.79	12.15	12.60	12.45
	 $CH_3{-}\overset{C_2H_5}{\underset{C_4H_9}{C}}{-}NC$	1.7	103–104 (59)	1.4210	77.63	77.19	12.31	12.28	10.06	9.94
	 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}NC$	1.0	96–97 (69)	1.4212	77.63	77.71	12.31	12.55	10.06	10.19
	$(CH_3)_2(i\text{-}C_3H_7)CNC$	1.1	73–75 (98)	1.4072	75.61	75.09	11.79	11.94	12.60	12.32
	 $CH_2{=}\overset{CH_3}{C}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}NC$	0.88	95–97 (44)	1.4365	78.77	78.36	11.02	11.01	10.21	9.95
	 $CN\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}NC$	0.17	Mp 125–126		73.12	72.77	9.82	9.93	17.06	16.87

The reaction proceeds up to the formation of tris(isocyanide) complex **1**, the halogen anion being retained in the inner coordination sphere. This may be indicative that for hydrogen cyanide to form a complex acid, such as **7** or **8** which will donate a proton to isobutene, requires the simultaneous coordination of a halide ion and hydrogen cyanide to Cu(I). That cuprous cyanide failed to effect the alkylation reaction appears to support this view. The new alkylation reaction with isoolefins is thus closely related to the classical alkylations of cyano silver(I)[20,21] or cyano iron(II)[7,21-23] complexes with such reagents as alkyl halides, dialkyl sulfates, or a mixture of alcohols and strong acids.

Effects of metal ions and their anions on the course of the reaction will be discussed in a subsequent paper. We have been able to conduct the alkylation reaction catalytically by proper choice of a metal ion and its anion.[24]

Experimental Section

Commercial hydrogen cyanide, isobutene, and other olefins were distilled before use. Anhydrous pure grade metal halides were used without further purification. Preparative reactions were carried out under nitrogen.

Alkylation with Isobutene. A. Without Solvents.—In a 1-l. glass pressure bottle were placed 196 g (3.5 moles) of isobutene, 95 g (3.5 moles) of hydrogen cyanide, and 100 g (0.7 mole) of cuprous bromide. Cuprous salt dissolved gradually at above 40°. The bottle was shaken for 15 hr at 70°. Unchanged isobutene and hydrogen cyanide were purged at room temperature. The tan, viscous residue was poured on water to give 190 g of colorless solid. To an aqueous potassium cyanide solution (130 g in 500 ml of water) was added 90 g of the above solid with stirring. The cuprous complexes were decomposed liberating an organic layer which was separated, dried, and distilled under reduced pressure to give a main fraction (46 g), bp 60–63° (314 mm). The colorless, liquid product was identified as *t*-butyl isocyanide by comparison of the infrared spectrum with that of an authentic sample (2143 s, 1472 m, 1368 m, 1230 m, 1208 m, 855 w cm^{-1}), as well as by the chemical reaction such as acid hydrolysis (see Chart I).

Treatment of the above solid with cold ethanol revealed that it contains two cuprous complexes. From the ethanol extract of the above solid (100 g) 65 g of bromo copper(I) complex **1** was

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[20] E. Meyer, *J. Prakt. Chem.*, **1**, 68, 279 (1856).

[21] For review articles, see L. Malatesta, "Progress in Inorganic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1959, p 283–379.

[22] E. G. Hartley and H. M. Powell, *J. Chem. Soc.*, 101 (1933).

[23] F. Holzel and J. Krakora, *Monatsh.*, **64**, 97 (1933).

[24] S. Otsuka, *et al.*, to be published.

obtained. The ethanol-insoluble part (34 g) was cyano copper (I) complex **2**, containing no halogen. An analytical sample of **1** was obtained by recrystallization several times from benzene or from acetonitrile–diethyl ether mixture. The ethanol-insoluble part **2** was sufficiently pure for analysis. It is slightly soluble in hot acetonitrile. Analytical data and physical properties of **1** and **2** are given in Table I. Total yield of the complexes (**1** plus **2**) was practically quantitative based on Cu(I) ion. The complexes **1** and **2** were identified as bromotris(*t*-butyl isocyanide)copper(I) and cyano(*t*-butyl isocyanide)copper(I), respectively, by the elemental analysis, infrared spectra (Table I), and mixture melting point test with the authentic complexes prepared by known methods[21] (see also Chart I).

A mixture of 5.0 g (50 mmoles) of cuprous chloride, 40 ml (1 mole) of hydrogen cyanide, and 24 ml (250 mmoles) of isobutene was heated at 100° for 5 hr. Similar work-up gave 2.6 g of the insoluble complex **2**, and ethanol-soluble solids. Recrystallization of the latter solids from acetonitrile–diethyl ether gave 2.8 g of a mixture of chloro copper(I) complexes. Because of the instability in solution, pure tris(*t*-butyl isocyanide) complex, $[(CH_3)_3CNC]_3CuCl$, could not be obtained. Analysis suggested that it is contaminated with probably bis(isocyanide) complex. Repeated recrystallization of the impure chloro isocyanide complex from a hot mixture of acetonitrile–ether gave a small amount of cyanobis(*t*-butyl isocyanide)copper(I), $[(CH_3)_3CNC]_2CuCN$, mp 173–175°, which did not show a melting point depression with an authentic sample.

Anal. Calcd for $CuC_{11}H_{19}N_3$: C, 51.64; H, 7.09; Cu, 24.84; N, 16.43. Found: C, 51.59; H, 7.29; Cu, 24.87; N, 16.18.

A mixture of 19.0 g (0.1 mole) of cuprous iodide, 20 ml (0.5 mole) of hydrogen cyanide, and 47 ml (0.5 mole) of isobutene was heated at 100° for 5 hr. The residual product after freeing from unchanged reactants was soluble in cold ethanol. Iodobis(*t*-butyl isocyanide)copper(I) seems to constitute the major component, although the analytical results were unsatisfactory, since repeated crystallization from ethanol or ethanol–ether mixture resulted in steady decrease in isocyanide ligands. Finally a small amount of the complex **2** was obtained.

Similarly a mixture of cuprous cyanide, hydrogen cyanide, and isobutene was heated up to 100° for 5 hr. Cuprous cyanide was remained unchanged.

B. With Solvents.—A mixture of 3.6 g (25 mmoles) of cuprous bromide, 10 ml (250 mmoles) of hydrogen cyanide, 24 ml (250 mmoles) of isobutene, and 20 ml of water was heated at 50° for 24 hr in a glass ampoule. The reaction mixture after being freed from the unchanged reactants was filtered to isolate 2.8 g of an isoluble complex which was identified as **2**. About 10 g of *t*-butyl alcohol was obtained from an ether extract of the filtrate and 0.15 g of *t*-butylamine hydrogen bromide from the aqueous filtrate. Gas chromatographic analysis of the above *t*-butyl alcohol fraction indicated presence of *t*-butyl bromide in 4–5% of the butyl alcohol.

Similarly the reaction was carried out in various solvents. The results are summarized in Table II.

Formation of Cyano(*t*-butyl isocyanide)copper(I) (2).—Suspension of 1.0 g of bromotris(*t*-butyl isocyanide)copper(I) (**1**) in 30 ml of water was boiled for 2 hr to give 0.37 g (84% yield) of colorless crystals, mp 196–198° (from acetonitrile). The benzene solution of **1** was refluxed overnight to give a small amount of the same product. The infrared spectrum and mixture melting point test revealed it to be cyano(*t*-butyl isocyanide)copper(I) (**2**). The authentic sample was prepared from cyanobis(*t*-butyl isocyanide)copper(I) by repeated recrystallization from a chloroform–ether mixture.

Alkylation with Olefins Other Than Isobutene.—In general, a mixture of an olefin, hydrogen cyanide, and cuprous bromide in a mole ratio of 4:4:1 was heated at 100° for 5 hr. Cuprous complexes were not isolated; instead they were decomposed similarly by aqueous potassium cyanide to release the isocyanide ligands. Table III summarized physical properties, yield, and analytical data of the *t*-alkyl isocyanide thus obtained.

Modified Passerini Reaction of Complex 1.—Complex **1** (4 g, 10.2 mmoles) was dissolved in a mixture of 40 ml of acetone and 10 ml of 6 *N* hydrobromic acid. The solution was stirred at room temperature for 30 min and then heated at 40° for 2 hr. Usual work-up with diethyl ether gave 3.62 g of colorless crystals which were recrystallized from *n*-hexane and sublimed to give analytical sample **6** as platelets, mp 96–97°.

Anal. Calcd for $C_8H_{17}NO_2$: C, 60.34; H, 10.76; N, 8.80. Found: C, 60.40; H, 10.69; N, 8.95.

Compound **6** was identified as N-*t*-butyl-2-methyl-2-hydroxypropionamide by synthesis; *viz*, α-bromoisobutyronitrile prepared according to a known method[25] was subjected to Ritter reaction to give N-*t*-butyl-2-methyl-2-bromopropionamide,[26] mp 87–88°. This was hydrolyzed to **6**. Alternatively **6** can be made by aminolysis of the corresponding hydroxy ester (Chart I).

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Aralkyl Hydrodisulfides.[1] VII. The Reaction with Trisubstituted Phosphites

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Benzyl hydrodisulfide, $C_6H_5CH_2SSH$, is attacked competitively both on sulfenyl and sulfhydryl sulfur atoms by triethyl phosphite, $(EtO)_3P$, and gives triethyl phosphorothionate, $(EtO)_3PS$, α-toluenethiol, dibenzyl disulfide, hydrogen sulfide, and toluene. The reactions of triethyl phosphite with benzhydryl or triphenylmethyl hydrodisulfide and of triphenyl phosphite with benzyl or benzhydryl hydrodisulfide occur only on sulfhydryl sulfur atom yielding the corresponding trisubstituted phosphorothionate and thiol. As for the reaction with tertiary phosphine, steric hindrance is concluded here to predominate over other factors. By using benzyl and benzhydryl hydrodisulfides-^{35}S sulfenyl sulfur of which is specifically labeled, activity measurement of the products with triphenyl phosphite confirms the mechanism of sulfhydryl sulfur attack.

Previous work[3] has shown that aralkyl hydrodisulfide, when attacked by tertiary phosphine on the sulfenyl sulfur atom, gives phosphine sulfide, hydrogen sulfide, the corresponding disulfide, and hydrocarbon, and that, when attacked on the sulfhydryl sulfur atom, it yields phosphine sulfide and thiol. These mechanisms were further confirmed in our previous paper[4] by using aralkyl hydrodisulfides labeled with ^{35}S.

In the present work aralkyl hydrodisulfide (benzyl, benzhydryl, or triphenylmethyl hydrodisulfide) was allowed to react with trisubstituted (triethyl or triphenyl) phosphite. It seems interesting to compare the variety and amounts of the present reaction products to those with the phosphine, to determine whether the phosphites behave similarly.

For further confirmation of the mechanism, benzyl and benzhydryl hydrodisulfides, the sulfenyl sulfur atoms of which were labeled with ^{35}S, were allowed to

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