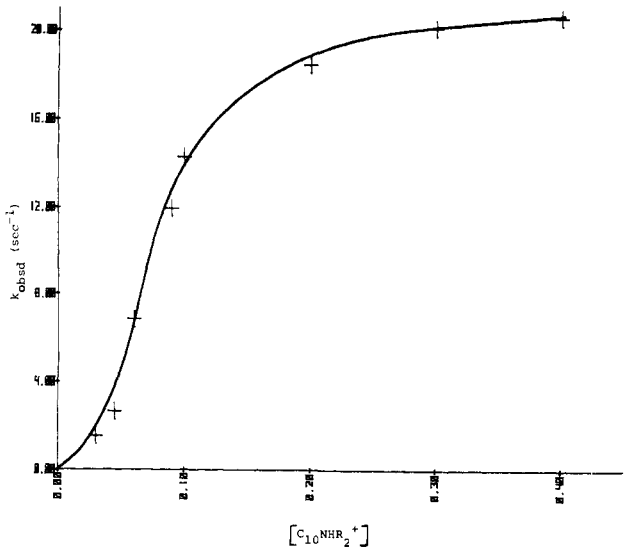

Figure 1. Observed rate constants for proton exchange of *N,N*-dimethyldecylammonium ion at 25° and pH 1.00 as a function of the concentration of the surfactant.

Table I. Rate Constants for NH-Proton Exchange at 25° in Aqueous Solutions[a]

[Amine], *M*	pH	k_{obsd}, sec^{-1}
	N,N-Dimethylhexylamine[b]	
0.15	3.25	4.4
0.30	3.26	6.2
0.45	3.26	7.8
0.15	3.66	7.9
0.30	3.66	11.5
0.45	3.66	16.1
	N,N-Dimethyldodecylamine[c]	
0.20	0.00[d]	6.2
0.20	0.00[d]	6.8
0.20	0.00[d]	6.9
0.20	0.16	8.8
0.20	0.40	12.9
0.20	0.70	20.3

[a] This table lists only a portion of the collected rate data. A detailed report of all the results is planned. [b] 0.01 *M* tartrate buffer. [c] Aqueous HCl solutions. [d] Repeat runs performed on three different days.

ion (k_b), and buffer.[11] Values of the parameters are k_a = 1.3 sec^{-1}, k_{-a} = 1.7 × 10^{10} M^{-1} sec^{-1}, k_2 = 7.3 × 10^7 M^{-1} sec^{-1}, and k_b = 3.4 × 10^{10} M^{-1} sec^{-1}. It was not possible to extract k_H from the raw data, but a value of 3 × 10^9 sec^{-1} is reasonable on the basis of previous work with aliphatic amines.[12]

Micellar $C_{12}NHR_2^+$ was examined at a high acidity (Table I) where catalysis by hydroxide ion and buffer does not contribute to the exchange rate. In contrast to its nonaggregating analog, $C_{12}NHR_2^+$ has a k_{obsd} which is independent of the amine concentration (0.1–0.3 *M*). We found that k_a = 40 sec^{-1} and k_HK_a = 6.4 *M* sec^{-1}, both of which are 30-fold larger than the corresponding values for $C_6NHR_2^+$. If one assumes that the rate of diffusion-controlled k_{-a} reaction in eq 1 is identical for micellar and nonmicellar systems, then the large k_HK_a for $C_{12}NHR_2^+$ can be ascribed solely to a modified K_a. This follows from the fact that k_a and k_HK_a increase by the same factor and that $K_a = k_a/k_{-a}$. Therefore, the enhanced $C_{12}NHR_2^+$ exchange at the micelle surface stems primarily from an abnormally fast Grotthus proton transfer (k_a) rather than an abnormally fast amine desolvation (k_H).

An apparent pK_a for $C_{12}NHR_2^+$ was calculated from its log k_a and the linear log k_a vs. pK_a plot for four amines studied by Grunwald.[5] The pK_a so obtained equals 8.7 (1.4 units less than the pK_a of $C_6NHR_2^+$). Likewise, inserting a "normal" k_H of 3 × 10^9 sec^{-1} into k_HK_a = 6.4 *M* sec^{-1} provides an apparent micellar pK_a of 8.7.

Close proximity of the ammonium groups at the micelle surface could conceivably lead to efficient proton transfer from one surfactant "head" to another (similar to the bimolecular exchange observed with $C_6NHR_2^+$ at pH 3–4). Transfer of this type is *not* necessarily excluded by the independence of k_{obsd} on the $C_{12}NHR_2^+$ concentration above its CMC. Nevertheless, the reaction mode appears unlikely because mixed micelles composed of *N,N,N*-trimethyldodecylammonium bromide and $C_{12}NHR_2^+$ in a 2:1 molar ratio have a k_{obsd} only 29% less than micelles of pure $C_{12}NHR_2^+$. Diluting the $C_{12}NHR_2^+$ by a large quantity of bulky nonreactive surfactant would have diminished k_{obsd} to a much larger extent if bimolecular exchange were important. We conclude that the fast proton transfer takes place primarily between the micellar ammonium groups and the interfacial water.[13]

Acknowledgment. This work was supported by a grant from the National Science Foundation (GP-42919X) and from the National Institutes of Health (GM-20336 and GM-21457).

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(8) The reliability of our methods was demonstrated by duplicating to within 15% rates derived by "total" line-shape analysis.
(9) The CMC values of dodecylammonium and *N,N,N*-trimethyldodecylammonium ions are 0.013 and 0.022 *M*, respectively. I. J. Lin and A. Metzer, *J. Phys. Chem.*, **75**, 3000 (1971); R. A. Parker and S. P. Wasik, *ibid.*, **63**, 1921 (1959).
(10) The CMC of decylammonium ion is 0.054 *M*. H. W. Hoyer and A. Greenfield, *J. Phys. Chem.*, **61**, 818 (1957.
(11) The overall rate expression is

$$k_{obsd} = \frac{k_a k_H}{k_H + k_{-a}[H^+]} + \frac{k_2 K_a[R_2NH^+]}{[H^+]} + \frac{k_b K_w}{[H^+]}$$

where k_{obsd} is the observed rate constant corrected for the buffer reaction, K_w is the autoprotolysis constant for water, and K_a is the acidity constant for the ammonium ion. See D. E. Leyden and W. R. Morgan, *J. Phys. Chem.*, **73**, 2924 (1969).
(12) See Figure 2 in ref 5.
(13) Surprisingly, neither inorganic salts nor solubilized benzene appreciably affect the fast rate of micellar proton transfer. The effects of these and other additives will be discussed in the full report.
(14) Recipient of a Camille and Henry Dreyfus Teacher–Scholar Grant and a National Institutes of Health Research Career Development Award.

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Stereoselective Alkylation of 1-Lithiocyclopropyl Bromides

Sir:

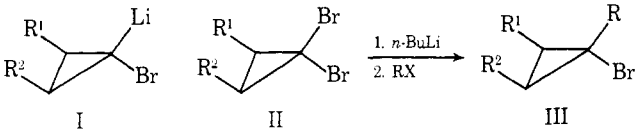
The synthetic application of the title carbenoids (I) has been limited to intramolecular reactions leading to allenes and/or bicyclobutanes.[1] As this is mainly due to the thermal lability, the carbenoids generated at sufficiently low temperatures do react with aldehydes, ketones, and diethyl carbonate to provide otherwise difficultly accessible com-

Table I. Monoalkylation of *gem*-Dibromocyclopropane (II)

Run	R^1	R^2	RX	Condition[a]	Yield (%)[b] of III	Cis:trans[c] (endo:exo)
1	Ph	H	MeI	A	90	38:62[d,e]
2	Ph	H	MeI	B	92	75:25
3	Ph	H	MeI	C	70	100:0
4	$-(CH_2)_4-$		MeI	A	86	80:20[f]
5	$-(CH_2)_4-$		MeI	B	67	81:19
6	$-(CH_2)_4-$		MeI	C	60	100:0
7	$PhCH_2OCH_2$	H	MeI	A	71	97:3[f]
8	n-C_6H_{13}	H	MeI	A	65	(33:67)[g]
9	Ph	H	EtI	D	54	94:6[h]
10	Ph	H	$CH_2{=}CHCH_2Br$	E	59	89:11[h]
11	$-(CH_2)_4-$		$CH_2{=}CHCH_2Br$	F	72	100:0[f]

[a] Reaction conditions. (A) Dibromocyclopropane (1.0 mmol) was mixed with methyl iodide (2.0 mmol), THF (5 ml), and HMPA (1 ml). To this mixture *n*-butyllithium (1 *M* in hexane) (1.0 ml) was added at −95° (toluene–liquid nitrogen bath) under nitrogen atmosphere. (B) Reaction was performed similarly without adding HMPA. (C) Dibromocyclopropane (1.0 mmol) in THF (5 ml) was treated with *n*-butyllithium (1.0 mmol) at −95°. Ten minutes thereafter methyl iodide (2.0 mmol) was added. (D) Cuprous phenylacetylide (1 molar equiv) was added in advance. Five minutes after the lithiation ethyl iodide (1.0 equiv) was added, and 15 min later HMPA (20 volume %) was added. (E) Thirty minutes after the lithiation cuprous iodide (0.5 equiv) was added. Allyl bromide (1.0 equiv) was treated with the carbenoid (30 min thereafter) and the mixture was diluted with HMPA (20%) (20 min after the addition of allyl bromide). (F) Cuprous iodide (0.5 molar equiv) was added 30 min after the lithiation and 30 min thereafter was added allyl bromide (1.0 equiv). [b] Isolated yield. All the new compounds were identified spectrometrically and analytically. [c] Determined by gas chromatography and NMR integration. [d] The stereochemistry of the product was ascertained by NMR. The methyl signal of the cis isomer appeared at δ 1.43, whereas that of the trans isomer at δ 1.93. Cf. C. H. Depuy, F. W. Breitbeil, and K. R. Debruin, *J. Am. Chem. Soc.*, **88**, 3347 (1966). [e] The ratio was not affected by the temperature variations (temperature, alkylation yield, cis/trans ratio being −78°, 81%, 35/65; −60°, 65%, 33/67). [f] The stereochemical assignment is based upon the low-field shift of the cyclopropane proton which is cis to the bromine atom. There exists a popular assumption that a 7-endo halide of bicyclo[4.1.0]heptane preferentially undergoes cyclopropane ring opening to give the cycloheptene compound upon treatment with silver nitrate (P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, 80, 2024 (1958)). Notably, this is not the case with 7-alkyl-7-bromonorcaranes. Under the similar solvolytic reaction condition ($AgBF_4$–AgOAc–AcOH, room temperature) the cyclopropyl bromide (III) (R^1, R^2 = $-(CH_2)_4-$, R = endo Me) was found to be susceptible to the acetolysis without any skeletal rearrangement. The analogous observation with 7-chloro-7-phenylnorcarane was recorded by D. B. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1175 (1969). [g] The stereochemical assignment could not be attained. [h] The stereochemistry was determined by NMR in a similar manner described in the legend *d*.

pounds.[2,3] This communication deals with the unprecedented alkylation of I affording 1-alkylcyclopropyl bromides stereoselectively.

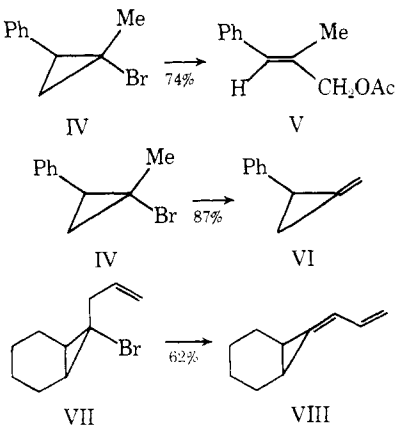


Monomethylation was conducted first, as the methyl-substituted cyclopropane moiety is often found among natural products. The dibromocyclopropane II (R^1 = Ph, R^2 = H) was subjected to lithium–bromine exchange at −95° with equimolar *n*-butyllithium in tetrahydrofuran (THF). The resulting carbenoid was treated with methyl iodide under the specified conditions (Table I). Evidently, the selectivity in the alkylation is dependent upon the solvent as well as the aging period of the carbenoid. As the addition of hexamethylphosphoric triamide (HMPA) prompts the coupling of the carbenoid with alkyl halides,[4] the selectivity under condition A supposedly reflects the susceptibility of each geminal bromine atom to the lithium–bromine exchange reaction; that is, the kinetic control is operative under this condition (run 1). In contrast the methylation performed after 10 min aging of the metal exchange product gives mainly the cis alkylated product (run 3) and this is ascribed to the thermodynamically preferred configuration of the carbenoids.[5] In the norcarane system the best selectivity was realized by the thermodynamic control (run 6) and this is compatible with the reported stereochemical behavior of the intervening carbenoid (I).[3c] The predominant cis alkylation of the cyclopropane II (R^1 = $PhCH_2OCH_2$, R^2 = H) is attributed to the interaction of the lithium ion with the ethereal oxygen of the R^1 group (run 7).

The alkylation with less reactive alkyl halides requires the presence of HMPA cosolvent, since the carbenoids gradually decompose even at −95°. Furthermore the addition of copper(I) salts or an acetylide proved to be highly effective[6] in suppressing the formation of the accompanying reduction product III (R = H).[7]

The present selective monoalkylation coupled with the stereocontrolled transformation (retention of configuration) reported by Walborsky et al.[8] provides a facile route to geminally disubstituted cyclopropanes with different groups in contrast to the previous, uncontrollable *gem*-dimethylation.[9]

The synthetic utility of the monoalkylated cyclopropanes is demonstrated by the transformation to a trisubstituted ethylene and to alkylidenecyclopropanes. The cyclopropane IV was successively treated with silver acetate–silver tetrafluoroborate in acetic acid to give an (*E*) β-methylcinnamyl acetate (V) in a stereospecific manner.[10] This reaction sequence constitutes an additional, stereoselective olefin synthesis.[11] The exposure of the monoalkylated cyclopropane, IV and VII, to the action of potassium *tert*-butoxide (1.2 equiv.) in dimethyl sulfoxide at room temperature for 2 hr afforded the corresponding alkylidenecyclopropanes VI and VIII, respectively, in good yields.[12] The rather mild reac-



tion condition prevents the subsequent thermal isomerization of the products.

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(4) For example, lithiation of II (R^1 = Ph, R^2 = H) with *n*-butyllithium in the presence of PhC≡CCu and in the absence of alkyl halides, followed by the addition of HMPA, afforded *n*-butylbromocyclopropane (III) (R^1 = Ph, R^2 = H, R = *n*-C_4H_7) in a 35% yield (>97% cis). This fact suggests that the *n*-butyl bromide generated by the lithium–bromine exchange reacts with the resulting carbenoid by virtue of HMPA.

(5) The lithium carbenoid generated from 1,1-dichlorocyclopropane is recorded to be relatively conflgurationally stable. See G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967).

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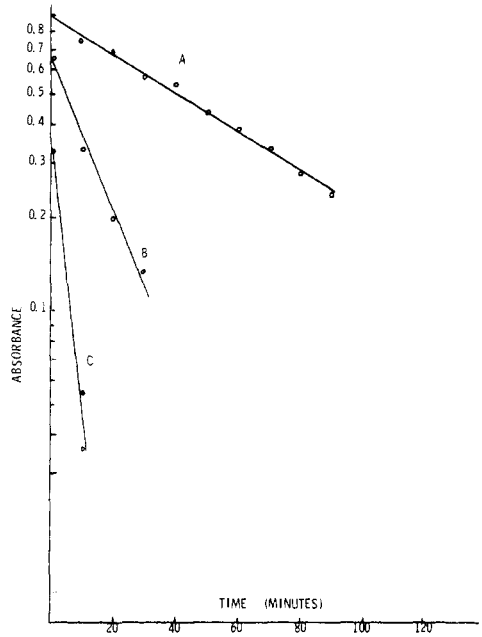

Figure 1. The effect of halide ion on the rate of reaction of [Rh(Ph_3As)$_2$(CO)I] (0.03 M) with CH_3I (3.25 M) in CH_2Cl_2: A, with no added halide ion; B, Bu_4NI (0.0003 *M*) added; C, Bu_4NI (0.003 *M*) added.

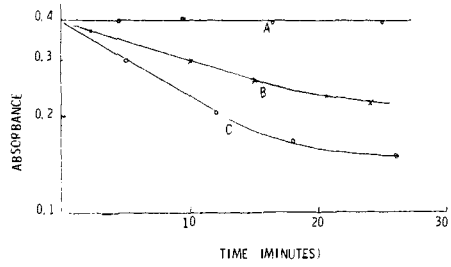

Figure 2. The effect of halide ion on the rate of reaction of [Rh(Ph_3Sb)$_2$(CO)I] (0.03 *M*) with CH_3I (3.25 *M*) in CH_2Cl_2: A, with no added halide ion; B, with Bu_4NI (0.003 *M*) added; C, with Bu_4NI (0.006 *M*) added.

Halide Catalysis of the Oxidative Addition of Alkyl Halides to Rhodium(I) Complexes

Sir:

The oxidative addition reaction has become widely recognized as one of the most characteristic reactions of d^8 and d^{10} complexes. Despite the importance of the oxidative addition reaction of methyl iodide to rhodium complexes, detailed studies of such reactions with rhodium(I) phosphine complexes have encountered several difficulties of interpretation.[1] The generally accepted first step in these reactions is nucleophilic attack of the metal complex on the carbon of the methyl iodide.[2] Since halide ions might act to displace neutral ligands to produce highly nucleophilic rhodium(I) anions and halide ions might well be present in systems involving complexes with labile phosphine and arsine ligands in methyl iodide, we felt it worthwhile to explore the effect of halide ions on methyl iodide addition reactions. Accordingly we studied the effect of Bu_4NI on the rate of methyl iodide addition to [Rh(Ph_3As)$_2$(CO)I], [Rh(Ph_3Sb)$_2$(CO)I],[3] and [Rh(Ph_3P)$_2$(CO)I]. The reaction involving the triarylstibine complex is a particularly interesting test because triarylstibines are not quaternized by alkyl iodides, and hence this system should be free of halide ions.

The results of these studies are presented in Figures 1 and 2.[4] It can be seen that added halide ions exert a powerful catalytic effect on the rate of oxidative addition of methyl iodide to the arsine and stibine complexes. However, by contrast there is a negligible effect on the rate of reaction with the phosphine complex.

In so far as increased nucleophilicity should increase the rate of reaction with methyl iodide, a logical mode of rate enhancement by halide ion is generation of anionic rhodium species. Accordingly we have studied the following equilibria spectrophotometrically.[5]

$$[Rh(L)_2(CO)I] + I^- \rightleftharpoons [Rh(L)(CO)I_2]^- + L$$

We find that the equilibrium constants in CH_2Cl_2 at 22° are as follows: for L = Ph_3P, $K < 3 \times 10^{-5}$; for L = Ph_3As, $K \approx 0.05$; and for L = Ph_3Sb, $K \approx 2 \times 10^{-3}$. It is apparent that the neutral species are strongly favored in systems containing small amounts of excess halide, but of course a mechanism involving anionic species as intermediates might still be possible if the rate of reaction of the anionic species with methyl iodide greatly exceeds that of the neutral species. We therefore studied the relative rate of reaction of the anionic and neutral species with methyl iodide. While we find that the anionic rhodium species react so rapidly at room temperature, even at very low concentrations of meth-