and then poured into water and extracted with chloroform. The combined extracts were sequentially washed with water, dried (magnesium sulfate), filtered, and evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel using ether. The faster moving red-brown fraction yielded 45 mg (25%) of **13** identical with that obtained in the previous experiment. The next fraction was green and on evaporation yielded 44 mg (23%) of the imino nitroxide nitronyl nitroxide biradical **14**: mp 170° dec; $\nu_{\max}^{\mathrm{KBr}}$ 1140, 1380 cm$^{-1}$; $\lambda_{\max}^{\mathrm{EtOH}}$ 238 m$\mu$ ($\epsilon$ 11,500), 298 (15,950), 350 (8500), 380 (8300); *m/e* 322 (M$^+$).

*Anal.* Calcd for $C_{16}H_{26}N_4O_3$: C, 59.60; H, 8.13; N, 17.38. Found: C, 59.39; H, 8.10; H, 17.30.

In addition to the above products 35 mg (17%) of the starting biradical was recovered from a slow-moving fraction.

**1,2-Bis(4′,4′,5′,5′-tetramethylimidazoline-2′-yl)-1,2-dichloroethane Bis-3′,3′′-oxide 1′,1′′-Oxyl (12, X = Cl).** To a solution of the ethylene bisnitronyl nitroxide **11** (500 mg, 1.48 mmol) in 50 ml of chloroform was added all at once 1.5 ml of chloroform saturated with chlorine gas and the mixture left to stand for 30 min. The chloroform was removed *in vacuo* and the residue extracted with methanol followed by petroleum ether and dried to yield 450 mg (74.5%) of the title compound: decomposes at 202–203° (rapid heating); $\nu_{\max}^{\mathrm{KBr}}$ 1135, 1380 cm$^{-1}$; *m/e* 408, 410, 412 (M$^+$). The absence of strong oxidizing properties and the presence of a strong esr signal in this product require that the chlorines be covalently bound.

**1,2-Bis(4′,4′,5′,5′-tetramethylimidazoline-2′-yl)-1,2-dibromoethane Bis-3′,3′′-oxide Bis-1′,1′′-oxyl (12, X = Br).** The preceding procedure was repeated using 200 mg of the biradical **11** and 470 mg of bromine. The highly insoluble product precipitated from the reaction mixture and was purified by extracting with methanol to yield 228 mg (77%) of the title compound: *m/e* 496, 498, 500 (M$^+$), 418, 416 (M − HBr); decomposes ~202°. On treatment with sodium methoxide in tetrahydrofuran this product is converted in poor yield to the starting biradical **11**.

**1,4-Bis(4′,4′,5′,5-tetramethylimidazoline-2′-yl)benzene Bis-1′,1′′-oxyl (26).** A few milligrams of the *p*-bisnitronyl nitroxide **25** in 1 ml of chloroform was shaken with 1 ml of water containing several crystals of sodium nitrite and 1 drop of acetic acid. The color changed rapidly to dark brown and the chloroform layer was dried and evaporated. Separation by tlc on silica gel using ether gave an orange brown solid: mp 230–233° dec; *m/e* 356 (M$^+$).

**Calculations.** Zero-field splitting parameters $X$, $Y$, and $Z$ expressed in gauss along the major molecular axes of the biradicals were evaluated from the expression $\mu_0 r^{-3}(3\cos^2\theta - 1)$ where $\mu_0$ is $0.927 \times 10^{-26}$ erg/G, $r$ is the distance between the two unpaired electrons in centimeters, and $\theta$ is the angle between the electron–electron axis and the molecular axis.[20] $D$ and $E$ values were derived from the relationships[21] $D = 3Z/2$ and $E = (X - Y)/2$. Each unpaired electron was assumed to be distributed over two points as described in the text. Distances and angles were estimated using Dreiding models. The principal molecular axes of the benzene biradicals **23–27** were taken through the 1 and 3 positions of the benzene ring in the meta derivatives and through the 1 and 4 positions in the para derivatives. The principal axes of the ethylene biradicals **11**, **13**, and **14** were defined by a line passing through a point midway along a nitrogen–oxygen bond of one ring and through a like point having a syn relationship in the second ring. In the two **13** conformations where the oxygens are not syn related, the line passed through a syn related nitogen atom of the second ring.

**Acknowledgment.** The authors with to thank Dr. Ludwig Call and Dr. J. Becher for the preparation of two of the nitronyl nitroxides and for several of the esr spectra. We are also indebted to Dr. Lois Durham for nmr measurements and to Dr. L. Tokas for the mass spectra.

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# Kinetics of the Reaction of Methyllithium with 2,4-Dimethyl-4′-methylmercaptobenzophenone[1a]

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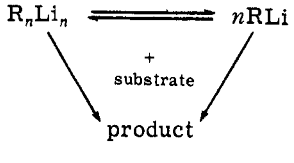
**Abstract:** The rate of the addition of halide-free methyllithium to the carbonyl group of 2,4-dimethyl-4′-methylmercaptobenzophenone has been found to be one-fourth order in alkyllithium and first order with respect to ketone in diethyl ether solvent at 25.0° with a rate constant of 200 ± 7 (l./mol)$^{1/4}$ sec$^{-1}$. Addition of lithium bromide or lithium iodide depresses the rate level but does not change the kinetic order in this system. The data are accommodated by a reaction mechanism involving predominant reaction through monomeric methyllithium which is in equilibrium with tetrameric methyllithium.

The tendency of lithium reagents to form specific aggregates[2] such as the tetrameric methyllithium[3] ($Me_4Li_4$) in diethyl ether necessitates assessing the relative reactivities toward a particular substrate of the aggregate compared to less associated species such as the monomer which might be present in low concentration.



Recently,[4] it has been found that the ethylenation of isopropyl-, *sec*-butyl-, and *tert*-butyllithium at −24.8°

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(1) (a) This research was supported in part by the National Science Foundation through Grants GP 13329 and GP 6396X; (b) National Institutes of Health Predoctoral Fellow, 1969–1971.

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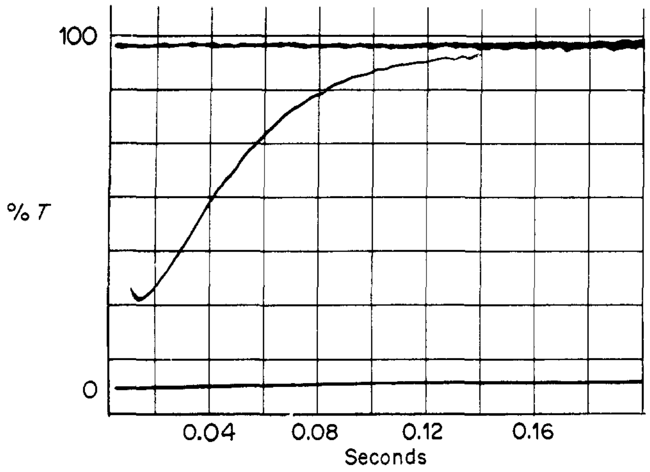


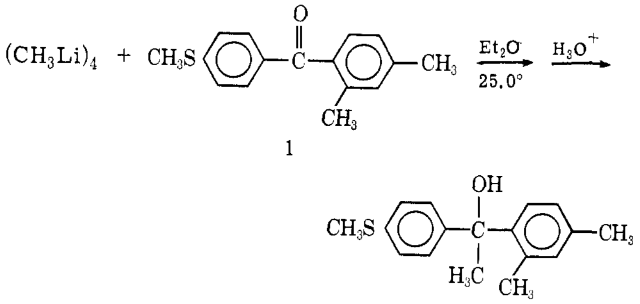
Figure 1. Plot of per cent transmission at 330 nm *vs.* time for the reaction of $2.5 \times 10^{-4}$ *M* ketone **1** with $6 \times 10^{-3}$ *F* methyllithium in diethyl ether at 25.0°.

is first order with respect to the alkyllithium tetramer in *n*-heptane solution. Reaction through tetrameric alkyllithium has also been noted in the polymerization of isoprene, butadiene, and styrene.[5]

However, methyllithium, containing 1 equiv of lithium bromide, has been found to exhibit kinetics which are one-fourth order in stoichiometric methyllithium in addition to 2,4-dimethyl-4′-methylmercaptobenzophenone in diethyl ether.[6] This low kinetic order suggests predominant reaction by way of monomeric methyllithium.[6,7] More recently, Holm[8] has reported that the reaction of halide-free tetrameric *n*-butyllithium with benzonitrile in diethyl ether is 0.33 order in alkyllithium. The deviation between the observed order and the one-fourth order expected for reaction of monomeric alkyllithium was ascribed[8] to medium effects on the monomer–tetramer equilibrium. In an early study, Swain[9] found that the reaction of phenyllithium, $(C_6H_5)_2Li_2$, with Michler's ketone in ether–toluene solvent is nearly first order in phenyllithium.

Since reagents prepared directly from alkyl halides and lithium metal[10] often contain considerable amounts of lithium halide, it is important to further distinguish between the reaction of associated mixed species such as $R_3Li_4X$, $R_2Li_4X_2$, and $RLi_4X_3$, and halide-free alkyllithium. Holm,[8] for example, has reported that 0.1 *M* LiBr accelerates the reaction of 0.01 *M* acetone with *n*-BuLi by a factor of 5. Lithium halides have also been found to affect the reactivity of lithium reagents in anionic polymerization[11] and metalation reactions.[12]

Recently[13] we examined the physical properties of methyllithium–lithium halide complexes in diethyl ether solution. In the present paper the effect of lithium bromide and lithium iodide on the kinetics of the reaction of methyllithium with 2,4-dimethyl-4′-methylmercaptobenzophenone (**1**) in diethyl ether at 25.0° is reported.



## Results and Discussion

The rate[14] of disappearance of the ketone, 2,4-dimethyl-4′-methylmercaptobenzophenone,[15] $\lambda_{max}$ 315 nm, at $(2\text{–}5) \times 10^{-4}$ *M* upon mixing with $3 \times 10^{-3}$ to $5 \times 10^{-1}$ *F* methyllithium in diethyl ether solution at 25.0° was followed by stopped-flow uv spectroscopy.[16] A typical oscilloscope trace of per cent transmission *vs.* time under the pseudo-first-order conditions of excess alkyllithium used in these experiments is illustrated in Figure 1. In all cases good adherence to first-order rate law was observed. In addition to displaying first-order kinetics with a given reaction, the measured first-order rate constant for the disappearance of ketone absorbance was appropriately independent of initial ketone concentration, as illustrated by the results shown in Table I.

**Table I.** Effect of Ketone Concentration on the Pseudo-First-Order Rate Constant for the Reaction of 0.36 *F* Methyllithium (in the Presence of 0.34 *F* Lithium Bromide) with 2,4-Dimethyl-4′-methylmercaptobenzophenone in Diethyl Ether at 25.0°

| $10^3$ *M* [ketone] | $k_{obsd}$,[a] sec$^{-1}$ |
|---|---|
| 0.18 | 49 |
| 0.40 | 50 |
| 0.90 | 49 |
| 2.3 | 47 |
| 5.0 | 48 |
| 13.3 | 47 |

[a] Average of at least three kinetic runs at each concentration. Reproducibility of a kinetic run is *ca.* 5%.

However, the observed first-order rate constant is a function of the concentration of methyllithium, increasing from 31 to 113 sec$^{-1}$ over the concentration range of 0.0035–0.48 *F*. The nonlinear character of the dependence of the reaction on $[Me_4Li_4]$ is illustrated in Figure 2. As summarized in Table II, these data are accurately described by the rate law

$$\text{rate} = k[Me_4Li_4]^{1/4}[\text{ketone}]$$

where $k = k_{obsd}/[Me_4Li_4]^{1/4}$, since dividing the observed first-order rate constant by $[Me_4Li_4]^{1/4}$ gives a constant of $(2.0 \pm 0.1) \times 10^2$ $M^{1/4}$ sec$^{-1}$ (sd 8.8). This result

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**Table II.** Effect of Concentration on the Reaction of Methyllithium with 2,4-Dimethyl-4′-methylmercaptobenzophenone in Diethyl Ether at 25.0°

| [MeLi], $F$ | $10^4$ $M$ [ketone] | $k_{\text{obsd}}$,[a] $\text{sec}^{-1}$ | $10^{-2}k_{\text{obsd}}/[\text{Me}_4\text{Li}_4]^{1/4}$, $M^{-1/4}$, $\text{sec}^{-1}$ |
|---|---|---|---|
| 0.0035[b] | 2.5 | 31 | 1.8 |
| 0.006 | 2.2 | 37 | 1.9 |
| 0.0073[b] | 2.5 | 41 | 2.0 |
| 0.011 | 5.9 | 44 | 1.9 |
| 0.014 | 2.2 | 49 | 2.0 |
| 0.014[b] | 2.5 | 51 | 2.1 |
| 0.021 | 5.9 | 53 | 2.0 |
| 0.025 | 2.2 | 58 | 2.1 |
| 0.029[b] | 2.5 | 62 | 2.1 |
| 0.043 | 5.9 | 67 | 2.1 |
| 0.050 | 3.0 | 67 | 2.0 |
| 0.058[b] | 2.5 | 71 | 2.0 |
| 0.089 | 5.9 | 80 | 2.1 |
| 0.11[b] | 2.5 | 83 | 2.0 |
| 0.12 | 5.9 | 87 | 2.1 |
| 0.13 | 3.0 | 79 | 1.9 |
| 0.20 | 5.9 | 91 | 1.9 |
| 0.22[b] | 3.0 | 95 | 2.0 |
| 0.22 | 2.5 | 104 | 2.1 |
| 0.24 | 5.9 | 101 | 2.0 |
| 0.34[b] | 2.5 | 110 | 2.0 |
| 0.35 | 4.9 | 106 | 1.9 |
| 0.43 | 4.9 | 108 | 1.9 |
| 0.48[b] | 2.5 | 113 | 1.9 |
|  |  | Av | 2.0 ± 1 |

[a] Average of at least three kinetic runs at each calculation; reproducibility of a kinetic run is *ca.* 5%. [b] Foote Mineral methyllithium.

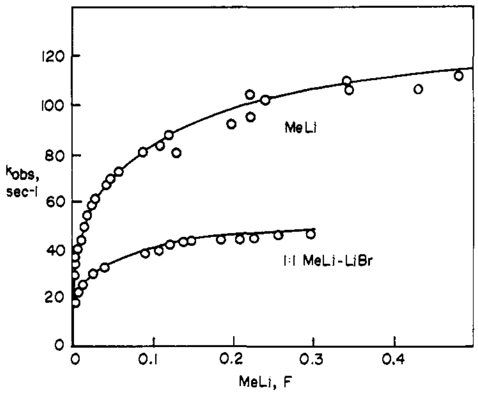

Figure 2. Plot of $k_{\text{obsd}}$ *vs.* concentration of methyllithium in the reaction with 2,4-dimethyl-4′-methylmercaptobenzophenone in diethyl ether at 25.0°. The top line corresponds to a halide-free reagent while the lower line is a 1:1 mixture of lithium bromide and methyllithium.

**Table III.** Summary of First-Order Rate Constants for the Reaction of Ketone **1** with Excess MeLi Solutions Containing LiBr in Diethyl Ether at 25.0°

| [MeLi], $F$ | [LiBr], $F$ | $10^4$ $M$ [ketone] | $k_{\text{obsd}}$, $\text{sec}^{-1}$ [a] | $10^{-2}k_{\text{obsd}}/(\text{MeLi}/4)^{1/4}$, $M^{-1/4}$, $\text{sec}^{-1}$ | [MeLi], $F$ | [LiBr], $F$ | $10^4$ $M$ [ketone] | $k_{\text{obsd}}$, $\text{sec}^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0043 | 0.0045 | 3.9 | 19 | 1.05 | 0.049 |  | 4.7 | 66 |
| 0.0074 | 0.0074 | 3.9 | 22 | 1.06 | 0.048 | 0.0068 | 2.5 | 65 |
| 0.016 | 0.015 | 1.7 | 26 | 1.03 | 0.053 | 0.012 | 4.7 | 59 |
| 0.027 | 0.026 | 1.7 | 29 | 1.01 | 0.050 | 0.015 | 4.7 | 54 |
| 0.045 | 0.046 | 3.9 | 34 | 1.04 | 0.050 | 0.018 | 4.7 | 50 |
| 0.091 | 0.095 | 3.9 | 39 | 1.00 | 0.052 | 0.024 | 4.7 | 47 |
| 0.11 | 0.11 | 1.7 | 40 | 0.98 | 0.051 | 0.030 | 6.8 | 41 |
| 0.13 | 0.13 | 3.9 | 42 | 0.99 | 0.051 | 0.045 | 6.8 | 36 |
| 0.14 | 0.14 | 1.7 | 43 | 0.99 | 0.054 | 0.060 | 2.5 | 34 |
| 0.15 | 0.16 | 3.9 | 43 | 0.98 | 0.053 | 0.070 | 6.8 | 28 |
| 0.18 | 0.18 | 1.7 | 44 | 0.96 | 0.050 | 0.090 | 6.8 | 24 |
| 0.20 | 0.20 | 2.5 | 45 | 0.95 | 0.055 | 0.10 | 2.5 | 22 |
| 0.22 | 0.23 | 3.9 | 47 | 0.97 | 0.051 | 0.12 | 6.8 | 21 |
| 0.23 | 0.26 | 3.9 | 46 | 0.94 | 0.050 | 0.15 | 6.8 | 19 |
|  |  |  |  |  | 0.050 | 0.27 | 6.8 | 12.5 |

[a] Average of at least three kinetic runs at each concentration. Reproducibility of a kinetic run is *ca.* 5%.

is consistent with the addition reaction proceeding predominantly by way of monomeric methyllithium in equilibrium with the tetrameric species.

Qualitatively, curvature of the type illustrated in Figure 2 could also arise from the transformation of a significant fraction of the ketone into a $(\text{R}_n\text{Li}_n)_m$–ketone complex which then, in a slower step, yields product.[7] Such a mechanism[16,17] has been invoked in the reaction of methylmagnesium bromide with this same ketone.[16] However, unlike the Grignard reaction, which exhibits a new band in the uv attributed to a complex between the reactants,[15,16] within the accuracy of our rapid scan measurements of the reaction mixture, no perturbation of the spectrum of ketone **1** in the presence of methyllithium in ether solvent could be detected. Although the reaction may actually go through a complex between reactants, neither the kinetic data nor the spectroscopic studies require accumulation of such an intermediate.

Both the effect of addition of 1 equiv of LiBr on the apparent kinetic order in methyllithium and the effect of added LiBr up to a fivefold formal excess on the reactivity of a constant quantity of methyllithium were examined.

A 1:1 mixture of lithium bromide–methyllithium, the reagent which is directly obtained by reaction of methyl bromide with lithium in diethyl ether, is less reactive than the halide-free material by a factor of about 2 at equivalent formal concentrations of methyllithium, Figure 2. However, a rate law involving a one-fourth-order dependence on the concentration of the organometallic species also describes these data, as illustrated by the relative constancy of the calculated quantity $k_{\text{obsd}}/[\text{MeLi}/4]^{1/4}$ as a function of concentration given in Table III. The absolute value of the constant obtained by dividing the observed first-order rate con-

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stant by $[MeLi/4]^{1/4}$ is, of course, a sensitive function of the ratio of methyllithium to lithium bromide and this ratio may vary slightly in different preparations of the reagent. Furthermore, because of the relatively polar character of the lithium bromide in these solutions, rate laws, such as those employed here, which fail to consider ionic strength effects may not be directly applicable at high concentrations.

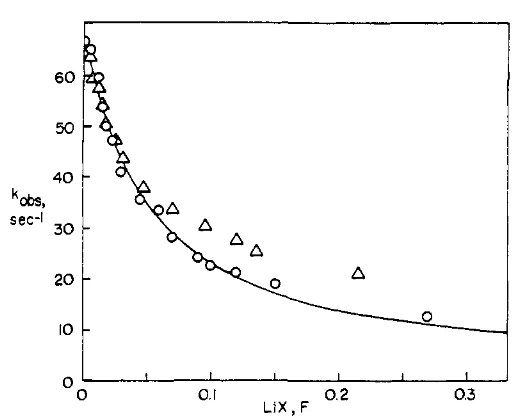

Figure 3. Plot of $k_{obsd}$ *vs.* concentration of lithium halide for the reaction of 0.05 *F* methyllithium with (3–7) × $10^{-4}$ *M* 2,4-dimethyl-4′-methylmercaptobenzophenone in diethyl ether at 25.0°: ○, LiBr; △, LiI. The line is calculated for reaction through monomeric methyllithium in equilibrium with a statistical distribution of mixed complexes of lithium halide and methyllithium.

**Table IV.** Summary of Reaction Rate Constants for the Reaction of Ketone 1 with Methyllithium–Lithium Iodide Solution

| [MeLi], *F* | $[I^-]$, *F* | $10^4$ *M* [ketone] | $k_{obsd}$, $sec^{-1\,a}$ |
|---|---|---|---|
| 0.053 | 0.0047 | 6.5 | 64 |
| 0.052 | 0.0070 | 6.5 | 60 |
| 0.053 | 0.012 | 6.5 | 58 |
| 0.053 | 0.016 | 6.5 | 55 |
| 0.054 | 0.019 | 6.5 | 50 |
| 0.052 | 0.024 | 6.5 | 47 |
| 0.052 | 0.031 | 6.5 | 44 |
| 0.051 | 0.047 | 6.5 | 37 |
| 0.052 | 0.070 | 4.8 | 33 |
| 0.052 | 0.095 | 4.8 | 30 |
| 0.053 | 0.12 | 4.8 | 28 |
| 0.052 | 0.135 | 4.8 | 26 |
| 0.052 | 0.215 | 4.8 | 21 |

[a] Average of at least three kinetic runs at each concentration. Reproducibility of a run is *ca.* 5%.

The functionality of the depressive effect of LiBr on this carbonyl addition reaction is illustrated graphically in Figure 3. If it is assumed that in the halide-containing solutions addition of a methyl group to the carbonyl group still occurs primarily by way of monomeric methyllithium, a nearly quantitative account of the effect of added salt may be obtained by a consideration of the extent of formation of mixed complexes containing LiBr which serve to decrease the fraction of alkyllithium present in monomeric form. The simple assumptions of a statistical distribution[18] of halide between the five possible species,[12,13,19] $Me_4Li_4$, $Me_3Li_4Br$, $Me_2Li_4Br_2$, $MeLiBr_3$, and $Li_4Br_4$, adequately describes the observed kinetics, with 0.05 *F* MeLi and LiBr concentrations ranging up to *ca.* 0.1 *F*, Figure 3.

Nmr studies[13] at −90 to −50° of lithium bromide–methyllithium mixtures suggest that the species $MeLi_4Br_3$ is not present in appreciable amounts at equilibrium. To the extent that these data can be extrapolated to 25°, the temperature at which the kinetic measurements were made, the observed rate constants at high concentration would be expected to be slightly higher than calculated, assuming a simple statistical mixture of tetrameric species.

Failure of a simple statistical distribution model is particularly marked in the case of lithium iodide–methyllithium mixtures, in keeping with nmr indications[13] that at −90 to −50°, in this case, the predominant organometallic species are reported to be $Me_4Li_4$ and $Me_3Li_4I$ and $Li_2I_2$. However, imposing only the equilibrium

$$2Li_2I_2 + 3Me_4Li_4 \rightleftharpoons 4Me_3Li_4I \qquad (1)$$

predicts reaction rates which are higher than observed. For example, if methyllithium is 0.05 *F* and lithium iodide is 0.2 *F* and if equilibrium 1 goes essentially to completion, then a rate constant which is higher than that observed by a factor of 1.4 is calculated. Since the temperature dependence[13] in the interval −90 to −50° of the nmr spectrum of a mixture of $CH_3Li$ and LiI indicates that the relative amount of the mixed species $MeLi_4I$ increases with increasing temperature, it is not unlikely that at 25° additional species such as $Me_2Li_2I_2$ may be present in concentrations which are sufficient to describe the available kinetics. Independent physical evidence for such a species is, however, desirable; further experiments are in progress.

## Experimental Section

**2,4-Dimethyl-4′-methylmercaptobenzophenone.** Preparation of this material has been described elsewhere.[15]

**Methyllithium.** Halide-free methyllithium was prepared in a drybox[20] from dimethylmercury and high purity lithium metal (Foote Mineral nuclear reactor grade). The reaction of methyl bromide with high purity lithium was carried out on a vacuum line under a positive pressure of argon. Diethyl ether was freshly distilled from either methyllithium or *n*-butylmagnesium bromide solutions. For kinetic studies, solutions of MeLi were diluted on a vacuum line or in a drybox with freshly purified ether and sealed in screw-cap vessels containing silicone rubber septans. All reagents were stored at 0 or lower and were used within 20 hr of the start of the preparation. Total base and halide titrations were made on aliquots after kinetic runs had been conducted. Gilman double titration[21] failed to detect nonlithium reagent base. The Foote Mineral methyllithium used in some experiments contained *ca.* 4% LiCl and 2% nonorganolithium base.

**Kinetics and Rapid Scan Spectroscopy.** The stopped-flow apparatus was constructed of stainless steel and Teflon with quartz windows on a 1.0 cm cell. The ³/₄-in. diameter stainless steel syringes have spring loaded Teflon V packings and are equipped with a positive pressure of argon on the back side to exclude oxygen contamination. Two eight-jet Gibson–Chance type[22] stainless steel mixers are connected to the drive syringes by type 7165 G2S Hoke valves. Drive and stop syringes are positioned by solenoid-controlled hydraulic cylinders operated at 400 psi. Estimated time between mixing and observation is 0.8 msec with a flow velocity of 1600 cm/sec. The entire apparatus is submerged in a thermostated ethylene glycol bath. First-order rate constants

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were calculated by reproducing transmittance *vs.* time oscillographs with an analog computer. Rapid scan features have been described previously.[16]

**Product of Kinetic Runs.** The effluent of the stopped flow was quenched on ice and the mixture was titrated to pH 7.0 with dilute $H_2SO_4$. The ether layer and an ether extract of the $H_2O$ layer were combined and washed with dilute $NaHCO_3$ and $H_2O$. The ether was dried ($Na_2SO_4$) and removed from the product on a rotary evaporator. Ir and nmr spectra of the product were consistent with expected properties of the addition and dehydration products.[15]

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# Bishomotropylium Ions under Conditions of Long and Short Life[1]

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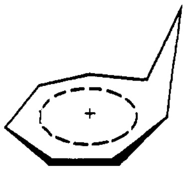
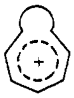
**Abstract:** The existence of three 1,4-bishomotropylium ions and one 1,3-bishomotropylium ion is demonstrated under conditions of long life, *i.e.*, in superacid media. The ions are the 1-methylbicyclo[4.3.0]nonatrienyl cation, the bicyclo[4.3.0]nonatrienyl cation, the bicyclo[4.3.1]deca-2,4,7-trienyl cation, and the 1,3-bishomotropylium ion, protonated *cis*-bicyclo[6.1.0]nona-2,4,6-triene. The electronic structure as inferred from the nmr is extensively discussed and the homoaromatic character of the ions emphasized. Evidence is presented for the existence of 1,4-bishomotropylium ions under conditions of short life, *i.e.*, solvolytic conditions.

In 1962 Pettit and coworkers[3] reported the first generation and direct observation of a homotropylium ion, the monohomotropylium ion **1**. The homoaromatic[4] character of **1** has been inferred from the nmr parameters of **1** and of its $Mo(CO)_3$ and $Fe(CO)_3$ complexes, taking advantage of the different electronic requirements of the metal tricarbonyls, as well as of the uv properties of **1**, etc.[4] Many substituted monohomotropylium ions with more or less pronounced homoaromatic character have been synthesized since that time. The discovery of the existence of the monohomotropylium ion has stimulated the search for polyhomotropylium[4] ions. Here we wish to report in a collective way some of the first discovered bishomotropylium ions.



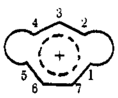
**1**

Because of the presence of only one homointeraction in monohomotropylium ions, there exists only one principle type of them, symbolized with structure **2**.



**2**

Depending on the relative position of the two bridges in bishomotropylium ions, we can distinguish three principally different types of ions, symbolized with structures **3, 4,** and **5**. All three ions are six electron and, potentially, aromatic species and they are named 1,4-, 1,3-, and 1,2-bishomotropylium ions, respectively.



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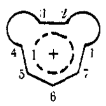

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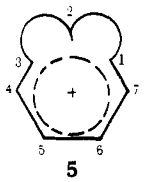
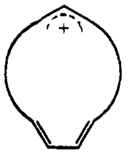
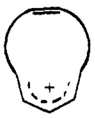


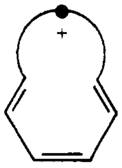
**5**



**6**



**7**



**8**

In **6, 7,** and **8** we assume no interactions between the positively charged ionic part and the unsaturated part of the structures. Furthermore, if the assumption is made that the strain is the same in all three structures, the thermodynamic stability order is going to be **7** > **6** > **8**. If we allow interaction between the two parts in **6, 7,** and **8** (through overlap intermediate between $\sigma$ and $\pi$), we obtain the structures **3, 4,** and **5**. From relative estimates of the interaction between the highest occupied molecular orbital of the saturated part and the lowest unoccupied molecular orbital of the positively charged part of the three structures **6, 7,** and **8**, we would expect **5** to be more stabilized than **3** and **3** more stabilized than **4** due to the intramolecular interactions. Again the strain is assumed to be the same in all three structures.

Thus, the stabilization order, due to intramolecular interaction, is the reverse of the thermodynamic stability

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(3) (a) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962); (b) C. E. Keller and R. Pettit, *ibid.*, **88**, 604 (1966); (c) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

(4) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969)

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