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Aliphatic Semidiones. 40. Ion Pairing in Cyclic 1,2-Semidiones[1]

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Cyclic 1,2-semidiones in Me_2SO exist as the free ions (observable in the presence of cryptands) or the 1:1 ion pairs with alkali metal counterions. The ion pairs have ESR spectra with lower g values and higher values of a^H than the free ions. Under most conditions the free ions and ion pairs are averaged on the ESR time scale. Values of K for ion-pair formation can be calculated from the g_{av} values, but corrections have to be made for a decrease in activity of the cation at higher concentrations. Values of K_{ip} for the cycloalkane-1,2-semidiones with K^+ increase from C_4 to C_5 to $C_6 \approx C_7 \approx C_9$ semidiones. For the larger rings the value of K_{ip} is approximately equal to that found for *cis*-biacetyl semidione. For the C_5 or C_6 semidiones values of K_{ip} increase from Cs^+ to K^+ to Na^+ or Li^+. Values of K_{ip} and a^H for the ion pair appear to be correlated with the oxygen-oxygen separation in the semidiones which decreases from C_4 to C_5 to C_6 and which determines the tightness of the ion pairing. The rate of dissociation of the cyclopentane-1,2-semidione ion pair with K^+ in Me_2SO is $\leq 4.5 \times 10^5$ s^{-1} at 25 °C.

1,2-Semidiones exhibit ion pairing even in polar solvents such as Me_2SO.[3] Since the cyclic semidiones in the C_4–C_9 rings exist in the Z configuration,[4] only the equilibria between free ions and ion pairs need to be considered as illustrated in Scheme I for cyclopentane-1,2-semidione.

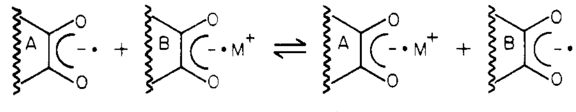
The ESR spectra of the free ions can be obtained by complexing the cations with cryptands.[3] The g values of the free ions are higher than those for the ion pairs, and at the same time a_α^H for the free ions is lower than that for ion pairs.[2] Values of a^H and g are linearly correlated.[3] Table I gives the g and hfsc values observed for a series of semidione free ions observed with K^+ and excess [2.2.2]cryptand at 25 °C in Me_2SO.

For the study of ion pairing, solutions of **1** were prepared by treatment of the appropriate bis(trimethylsiloxy)alkene or α-hydroxy ketone (0.05–0.10 M) with 1 equiv of potassium dimsylate followed by slightly more than 2 equiv of the cryptand. In addition to **1** the solutions contained other oxyanions including

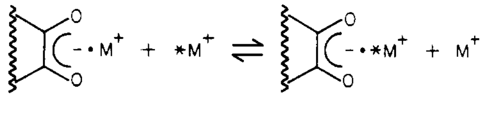
$$RC(O^-){=}C(O^-)R \overset{H^+}{\rightleftharpoons} RCH(O^-)COR \overset{H^-}{\rightleftharpoons} RCH(O^-)CH(O^-)R$$

These species are most likely present in concentrations greater than **1** and must be taken into consideration if values of K_{ip} are to be calculated.

When alkali metal cations are added to solutions of the free semidione radical anion, changes in the ESR spectra indicate the formation of ion pairs (Table II). The 1:1 ion pairs (**2a** and **2b**) display hyperfine splitting by a single Li^+ or Na^+ under appropriate conditions (Figure 1a,b). Because of the exchange reactions 1 and 2, there is a fairly narrow window in the concentration range where this hyperfine splitting can be observed.



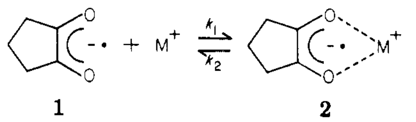
(1)



(2)

$$2RC(O\cdot){=}C(O^-)R \rightleftharpoons RCOCOR + RC(O^-){=}C(O^-)R \quad (3)$$

Scheme I[a]



1 **2**

[a] a, M = Li; b, M = Na; c, M = K; d, M = Rb; e, M = Cs; $k_1/k_2 = K_{ip}$

Table I. g and a^H Values for 1,2-Semidiones (e.g., **1**)[a]

1,2-semidione	g	a_α^H, G
cyclobutane	2.005 10	13.85 (4 H)
cyclopentane	2.005 10	12.93 (4 H)
cyclohexane	2.005 10	9.50 (4 H)
cycloheptane	2.004 98	6.19 (2 H)[b]
cyclononane	2.005 09	5.10 (2 H), 2.14 (2 H)
cis-biacetyl	2.005 11	6.76 (6 H)
trans-biacetyl	2.005 08	5.67 (6 H)

[a] With K^+ and excess [2.2.2]cryptand in Me_2SO at 25 °C. [b] a_β^H = 2.16 (2 H). For assignment, see: Russell, G. A.; Keske, R. G.; Holland, G.; Mattox, S.; Givens, R. S.; Stanley, K. *J. Am. Chem. Soc.* **1975**, *97*, 1892.

Addition of LiI to **1** generated by the use of 0.1 M potassium dimsylate–[2.2.2]cryptand results in a decrease in the ESR signal intensity. The semidione is in equilibrium with the dianion (reaction 3), which apparently complexes with alkali metal cations more efficiently than does **1**. As the signal intensity decreases, the value of g also decreases, suggestive of exchange between **1** and **2a** (reaction 1). At a concentration of 0.07 M LiI where the ratio of **1**/**2a** is ~4, the rates of exchange reactions 1 and 2 are sufficiently low that the spectra of **1** (g = 2.005 10) and **2a** (g = 2.004 72) are clearly resolved; the ion pair **2a** shows lithium hyperfine splitting by a single lithium cation, a^{Li} = 0.50 G (Figure 1a). A 0.15 M LiI only **2a** (with resolved Li^+ hyperfine splitting) can be detected, but at a very low signal intensity. Further addition of LiI results in a broadening of the lines from the lithium hyperfine interaction (exchange reaction 2), but without a decrease in the g value. At [LiI] = 0.5 M the ESR signal is still that of **2a** ($g \simeq$ 2.0048) with partially resolved lithium hyperfine splitting.

With NaI the situation is similar except that the sodium hyperfine splitting (Figure 1b) can be observed only over a narrower concentration range (~0.05–0.07 M NaI). The g value of **2b** (2.004 88) does not change from 0.05 M (Na^+ hyperfine splitting) to 0.10 M (Na^+ hyperfine splitting not observed). However, at higher NaI concentrations the g value of the radical ion decreases (2.004 87 at 0.2 M and

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[1] This work was supported by Grant No. CHE-7823866 from the National Science Foundation.

[2] National Science Foundation Predoctoral Fellow, 1976–1979.

[3] Russell, G. A.; Osuch, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 5979.

[4] Russell, G. A.; Osuch, C. E.; Chau, W. *Heterocycles* **1978**, *11*, 165.

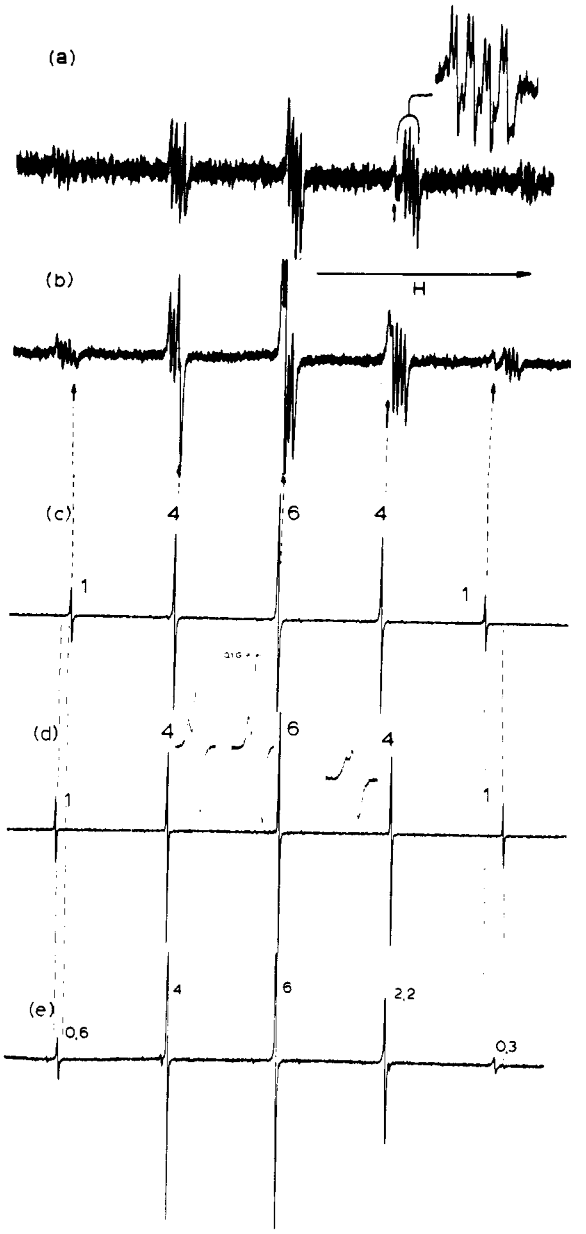

Figure 1. ESR spectra of cyclopentane-1,2-semidiones in dimethyl sulfoxide at 25 °C. (a) Lithium salt **2a** (a^{Li} = 0.50 G). Insert shows hyperfing splitting of the β-methylene group ($a_{CH_2}{}^{H}$ = 0.14 G). A trace of **1** is indicated by the arrow. (b) Mixture of **1** (indicated by arrows) and **2b** (a^{Na} = 0.52 G). (c) **1** in the presence of K$^+$ and [2.2.2]cryptand. (d) **2c** observed in the presence of excess KI. Insert shows second-order splitting observed for three center peaks. (e) Time-averaged mixture of **1** and **2c** observed with 0.075 M potassium dimsylate.

Table II. Values of g, $a_\alpha{}^H$, and K_{ip} for Cycloalkane-1,2-semidiones[a]

cation	g(ion pair)	$a_\alpha{}^H$(ion pair), G	K_{ip}, M^{-1}
	Cyclobutane		
Cs$^+$	2.005 04	14.07 (4 H)	58
Rb$^+$	2.004 57	14.16 (4 H)	14
K$^+$	2.004 98	14.20 (4 H)	14
	Cyclopentane		
K$^+$(18-crown-6)	2.004 99	13.26 (4 H)	69
Cs$^+$	2.004 72	13.36 (4 H)	70
Rb$^+$	2.004 84	13.56 (4 H)	100
K$^+$	2.004 89	13.85 (4 H)	87
Na$^+$	2.004 88	13.84 (4 H)	>500
Li$^+$	2.004 72	14.48 (4 H)	>1000
	Cyclohexane		
K$^+$(18-crown-6)	2.004 99	9.75 (4 H)	240
Cs$^+$	2.004 54	9.84 (4 H)	46
Rb$^+$	2.004 79	9.90 (4 H)	200
K$^+$	2.004 90	10.04 (4 H)	220
	Cycloheptane		
K$^+$	2.004 80	6.69 (2 H) 2.01 (2 H)[b,c]	190
	Cyclononane		
K$^+$	2.004 91	5.28 (2 H) 2.17 (2 H)[b]	260
	cis-Biacetyl		
K$^+$(18-crown-6)	2.004 98		130
K$^+$	2.004 91		254
	trans-Biacetyl		
K$^+$	2.004 88		4

[a] In Me$_2$SO at 25 °C. [b] 0.10 M KI. [c] The 2.01-G hyperfine splitting is for β-hydrogen atoms. The other two α-hydrogen atoms have $a^H \approx$ 0.3 G.

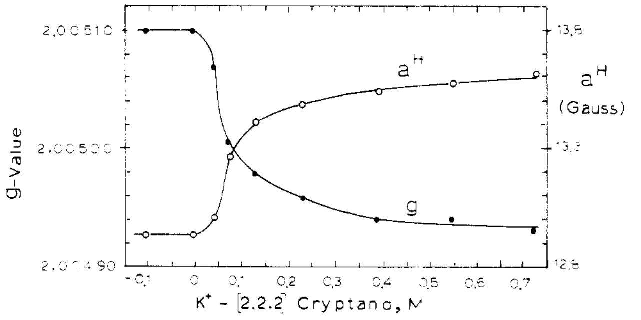

Figure 2. Values of g_{av} and $a_\alpha{}^H{}_{av}$ for mixtures of **1** and **2c** for cyclopentane-1,2-semidione in Me$_2$SO at 25 °C. The value of $a_\alpha{}^H$ was measured between the first downfield peak and the first upfield peak. The initial solution was 0.075 M in potassium dimsylate to which KI or [2.2.2]cryptand was added to give the total free K$^+$ concentrations shown.

2.004 85 at 0.4 M NaI), perhaps indicating the formation of a species with a g value lower than that of **2b**. The ESR lines for **2b** are broad at 0.1 M NaI, but at 0.4 M NaI they are sharp, and if another species is present (e.g., a triple ion), it must be rapidly time averaged with **2b**.

When KI is added to **1** (~10^{-5} M) in Me$_2$SO, there is a sharp drop in g and a corresponding rise in a^H until the concentration of the cation is approximately 0.1 M (Figure 2). The ESR signal intensity is not significantly affected by the addition of KI. We attribute the change in the magnetic resonance parameters to ion pairing to form **2c**. Continued addition of KI causes g to decrease and a^H to increase slowly, but we cannot be certain that limiting values have been reached even at 1.5 M KI. When an excess of the cation is present (10^{-5} M semidione, [K$^+$] > 0.2 M), the spectrum of cyclopentane-1,2-semidione (Figure 1d) is a symmetrical pentet. However, when total [K$^+$] (free and complexed) is in the range of 0.05–0.10 M, an incompletely time-averaged mixture of **1** and **2** is observed (Figure 1e). The effect of $g(1) > g(2)$ and $a^H(1) < a^H(2)$ often causes the low-field lines of the ESR spectra of **1** and **2** to be close together so that sharp time-averaged lines are observed. On the other hand, the high-field lines are separated to a much greater degree. Thus, on the high-field side, exchange-broadened or even resolved lines for **1** and **2** may be seen. Figure 3a illustrates a rather normal situation for bicyclo[3.2.1]oct-6-ene-2,3-semidione[5] (**3** $\rightleftharpoons$ **4**) with K$^+$ as the counterion. If an excess of [2.2.2]cryptand is added to the mixture of **3** and **4**, the equilib-

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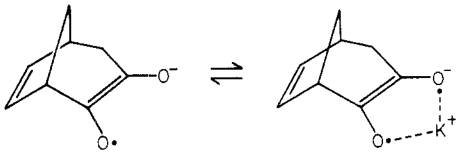
[5] Russell, G. A.; Chang, K.-Y.; Jefford, C. W. *J. Am. Chem. Soc.* **1965**, *87*, 4383.



3
$g = 2.005\,01$
$a^H = 8.47, 7.47, 2.63, 1.20, 0.70, 0.31,$ and 0.15 G

4
$g = 2.004\,84$
$a^H = 8.79, 7.72, 2.67, 1.29, 0.75, 0.33,$ and 0.16 G

rium shifts, and a symmetric ESR spectrum is observed for **3** (Figure 3b) with a high g value. Addition of a large excess of K^+ converts the **3** to **4**, and a second symmetrical ESR spectrum is observed (Figure 3c) with a lower g value but large values of a^H.

With K^+ as the counterion and a deficiency of [2.2.2]-cryptand, we have been unable to resolve the spectra for the mixture of **1** and **2c** at 0 °C in Me_2SO or at −70 °C in DMF. At 25 °C in Me_2SO the lifetimes of **1** and **2c** can be measured from the line broadening shown in Figure 1e. At a total K^+ concentration of 0.075 M, $\tau_1 = 7.2 \times 10^{-7}$ s and $\tau_{2c} = 2.2 \times 10^{-6}$ s (**1**/**2c** = 1:3). If equilibrium between **2c** and the **1** is the only exchange process, the value of k_2 is 4.5×10^5 s^{-1}. Values of K_{ip} cannot be calculated from these numbers because the concentration of uncomplexed K^+ is unknown. Since as shown below the value of K_{ip} is ~90 M^{-1}, it follows that $a(K^+)$ in this experiment was ~0.03 M. This low activity is partially a result of the complexation of K^+ by the other oxyanions present in solution.[6] With cyclohexane-1,2-semidione in Me_2SO at 12 °C the spectra of the free ion and the ion pair can be resolved (Figure 4).

Crown ethers (18-crown-6 with K^+, 15-crown-5 with Na^+) have a significantly different effect on the equilibrium between **1** and **2** than the [2.2.2]- or [2.2.1]cryptands.[7] If an excess of 18-crown-6 ether is added to a solution containing mainly **2c**, there is only a small increase in the g value and a corresponding decrease in a^H. We conclude that in the presence of crown ethers the gegenion in **2** is the crown-complexed cation. No matter how much crown ether is added, the semidione ion pair cannot be dissociated to give the free semidione radical ion according to reaction 4.[8]

$$\text{semidione}^{-}\cdot K^+\text{,18-crown-6} + \text{excess 18-crown-6} \rightleftarrows \mathbf{1} + K^+(\text{18-crown-6})_2 \quad (4)$$

Values of g from which K_{ip} could be calculated were obtained by dilution of the semidione solutions prepared with 0.075 M potassium dimsylate and a large excess (10–20-fold) of KI, RbI, or CsI (in the case of CsI or RbI the K^+ was complexed by the use of a small excess of [2.2.2]cryptand). This technique ensured that at all times the predominant anion present was the iodide ion and that no more than 5–10% of the cation could be complexed by the oxyanions present. Values of K_{ip} were calculated by assuming that only species **1** and **2** were present and that $g_{obsd} = g_{av} = fg(2) + (1 - f)g(1)$, where f is the fraction of semidione present as the ion pair. This leads to eq 5 and 6.

$$[2]/[1] = [g(1) - g_{av}]/[g_{av} - g(2)] = K_{ip}a^{M^+} \quad (5)$$

$$1/\Delta g = 1/[g(1) - g_{av}] = 1/[g(1) - g(2)] + 1/K_{ip}a^{M^+}[g(1) - g(2)] \quad (6)$$

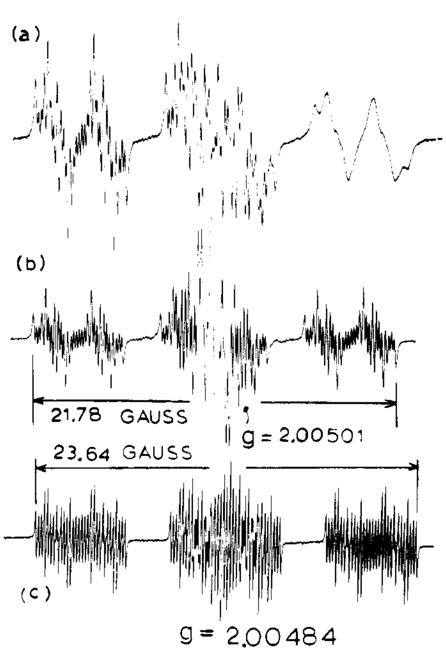


Figure 3. ESR spectra of bicyclo[3.2.1]oct-6-ene-2,3-semidione in Me_2SO: (a) 0.05 M K^+; (b) the free semidione ion in the presence of excess [2.2.2]cryptand; (c) the 1:1 ion pair in the presence of excess KI (0.5 M).

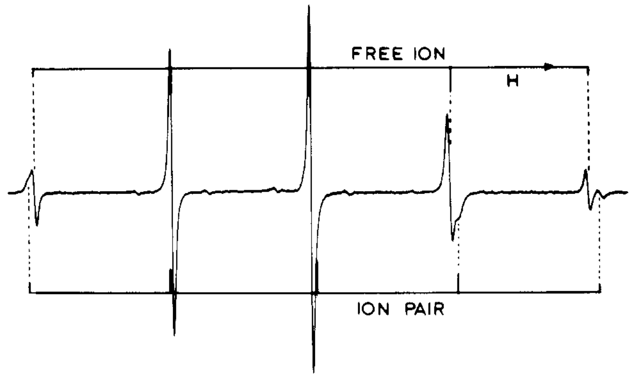


Figure 4. Mixture of free ion and ion pair ($M^+ = K^+$) for cyclohexane-1,2-semidione in Me_2SO at 12 °C.

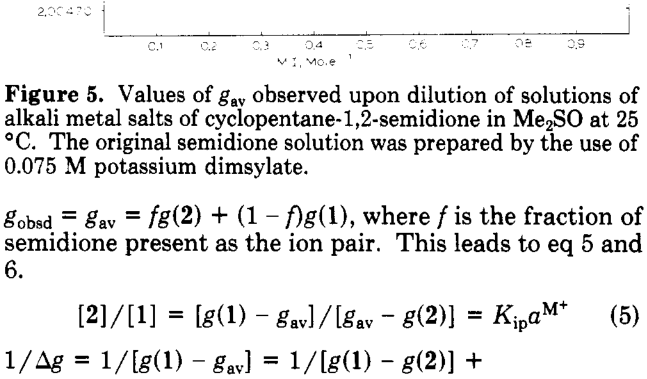


Figure 5. Values of g_{av} observed upon dilution of solutions of alkali metal salts of cyclopentane-1,2-semidione in Me_2SO at 25 °C. The original semidione solution was prepared by the use of 0.075 M potassium dimsylate.

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[6] The K_{ip}'s for dimsylate and *tert*-butoxide ions in Me_2SO are 15 and 270 with K^+ and 127 and 10^6 with Na^+ (Exner, J. H.; Steiner, E. C. *J. Am. Chem. Soc.* **1974**, *96*, 1782).

[7] Russell, G. A.; Wallraff, G.; Gerlock, J. L. *J. Phys. Chem.* **1978**, *82*, 1161.

[8] Crown ethers also have an appreciable effect on the rate of cation exchange. Well-resolved sodium hyperfine splitting can be easily detected in the presence of excess Na^+ when the free sodium ion is complexed with crown ethers (Russell, G. A.; Lawson, D. F.; Malkus, H. L.; Stephens, R. D.; Underwood, G. R.; Takano, T.; Malatesta, V. *J. Am. Chem. Soc.* **1974**, *96*, 5830) or cryptands.[7] However, hyperfine splitting by K^+ is never observed even in the presence of complexing agents.

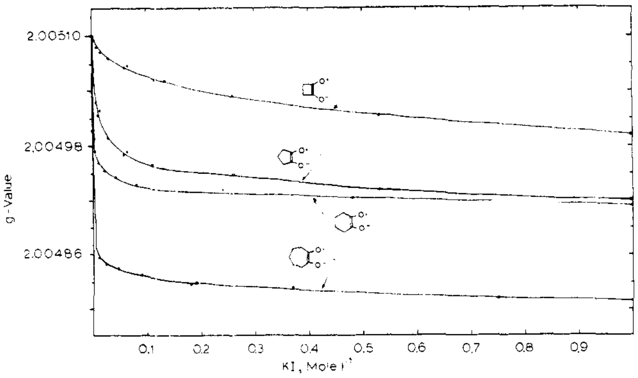

Figure 6. Values of g_{av} observed for cycloalkane-1,2-semidiones obtained by dilution of solutions prepared from the bis(trimethylsiloxy)cycloalkene, 0.075 M potassium dimsylate, and 0–1.5 M KI in Me_2SO at 25 °C.

Table III. Empirical Values of $\gamma(M^+)$ Observed for Solutions of MI[a]

[MI], M	$\gamma(K^+)$	$\gamma(Cs^+)$	[MI], M	$\gamma(K^+)$	$\gamma(Cs^+)$
0.01	0.90	0.93	0.10	0.24	0.42
0.02	0.62	0.86	0.20	0.15	0.33
0.04	0.44	0.57	0.40	0.10	0.28
0.06	0.36	0.50			

[a] In Me_2SO at 25 °C.

Dilution of solutions of the cycloalkanesemidiones in the presence of various alkali metal iodides gave g_{av} plots as shown in Figures 5 and 6. Values of $g(2)$, a^H for 2, and K_{ip} listed in Table II were obtained as follows. Values of $g(2)$ were most conveniently obtained by extrapolation of plots of 1/[MI] vs. $1/\Delta g$ to 1/[MI] = 0, while values of a^H for 2 were obtained by a least-squares fit of the linear relation between g and a^H for each system. Plots of [2]/[1] vs. $[M^+]$ were linear only up to ~0.01 M after which there was a deviation from linearity, suggesting that the activity coefficient of M^+ decreased at higher concentrations (ionic strength effects are discounted because the addition of $PhCH_2NMe_3^+I^-$ to the solutions had no effect upon g). Plots of eq 6 were constructed and a straight line drawn through the intercept $[=1/[g(1) - g(2)]]$ and the $1/\Delta g$ points below 0.01 M. The slope of the lines gave approximate values of K_{ip}, and from the deviation of points for [MI] ≥ 0.01 M apparent values of $a(M^+)$ were defined. The values of $a(M^+)$ thus obtained with different semidiones were essentially the same. Values of $a(M^+)$ were adjusted to give the best fit with all the data for a given cation, and final values of K_{ip} were calculated from eq 6 by using the standard values of $a(M^+)$ given in Table III. A single set of activity coefficients fitted the data for Cs^+, Rb^+, and K^+(18-crown-6) while a slightly different set was required for KI solutions (Table III). The activity coefficients so defined also gave a satisfactory linear plot of eq 6 when applied to *cis*- and *trans*-biacetyl radical anions (Table II). In the case of weakly complexing anions, such as *trans*-biacetyl radical anion or cyclobutane-1,2-semidione with K^+, the values of both $g(2)$ and K_{ip} were obtained from the slope and intercept of the linear plots of $1/\Delta g$ vs. $1/a(M^+)$ by use of eq 6.

From Figure 6 it is apparent that cyclobutane-1,2-semidione has a lower tendency to form ion pairs with K^+ than the C_5–C_9 cyclic semidiones. Cyclobutanesemidione must also be quite ineffective in ion pairing with Na^+ and Li^+, because we have been unable to detect these ion pairs under conditions where the C_5 and C_6 ion pairs are readily seen. Unfortunately, because of the disproportionation equilibrium 3, cyclobutane-1,2-semidione cannot be detected in the presence of an appreciable excess of Na^+ or Li^+ or in the presence of polyvalent cations. The ineffectiveness of cyclobutane-1,2-semidiones in ion pairing is undoubtedly connected with the oxygen–oxygen distance in the semidione moiety. Figure 7 gives scale drawings for cyclobutane- and cyclohexane-1,2-semidiones constructed by using standard Dreiding bond lengths and angles and assuming 25% double bond character for the C–C bond and 75% double bond character for the C–O bonds and with a 1-Å radius for the oxygen atoms (average of covalent and van der Waals radii). The O–O separation decreases from 3.49 Å in the C_4 semidione to 2.98 Å in the C_5 semidione and 2.76 Å in the C_6 semidione. With K^+ the values of K_{ip} increase from 14 for C_4 to 87 for C_5 and 200–300 for C_6, C_7, or C_9, and a similar trend is observed with Rb^+. The value of K_{ip} for the C_6, C_7, and C_9 semidiones is approximately the same as that measured for *cis*-biacetyl radical ion with K^+ (K_{ip} = 254). On the other hand, the data for Cs^+ shows little difference in K_{ip} for the C_4–C_6 semidiones. Thus, the value of $K_{ip}(Cs^+)$ relative to $K_{ip}(K^+)$ decreases from 4 with cyclobutane-1,2-semidione to 0.8 with cyclopentane-1,2-semidione and 0.2 with cyclohexane-1,2-semidione. As the O–O separation decreases from the C_4 to the C_6 semidione, *the larger cesium cation becomes relatively less effective in ion pairing than the smaller potassium cation*.

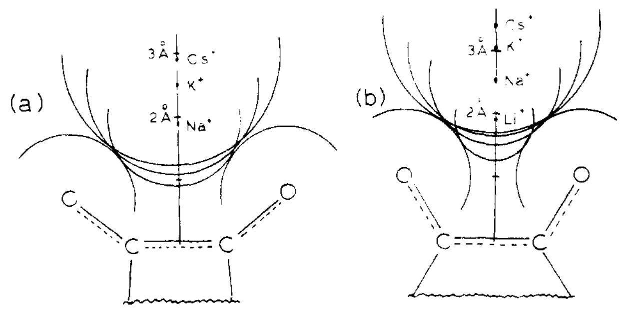

Figure 7. Scale drawing of in-plane ion pairs for (a) cyclobutane-1,2-semidione and (b) cyclohexane-1,2-semidione. Radius of the oxygen atom is taken as 1 Å.

For the C_5 or C_6 semidiones, K_{ip} with Li^+ is considerably greater than with K^+ because **2a** free of **2c** can be seen in the presence of a considerable excess of potassium *tert*-butoxide. Thus, for the C_5 or C_6 semidiones, values of K_{ip} decrease from Li^+ (1.72 Å, ionic diameter) to Na^+ (2.24 Å) to K^+ (2.88 Å) ≈ Rb^+ (3.16 Å) to Cs^+ (3.68 Å). Apparently the reverse sequence holds for cyclobutane-1,2-semidione.

The data of Table II demonstrate that ion pairing with Li^+, Na^+, K^+, Rb^+, or K^+(18-crown-6) causes the g value of the ion pair to decrease and a^H to increase in a regular fashion. For a given semidione the effect increases with the tightness of the ion pair, e.g., for C_5 or C_6 semidiones from K^+(18-crown-6) to K^+ ≈ Rb^+ to Na^+ to Li^+. With Cs^+ the values of a^H for **2e** are lower than for those **2c** but higher than a^H for the K^+(18-crown-6) ion pair. However, the g values for **2e**, and to a lesser extent for **2d**, are out-of-line and are much lower than would be predicted from the g values of **2a–c**. Possibly the large values of the spin–orbit coupling constant for rubidium and cesium give rise to anomalously low g values.[9] Alternately there might be a change in structure of the ion pair between $M^+ = K^+$ and $M^+ = Cs^+$.

The structure of the 1,2-semidione ion pair may be either an in-plane chelate structure or a structure in which the cation rapidly migrates between the two faces of the π

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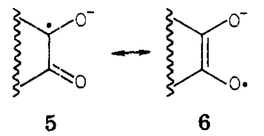
[9] Sharp, J. H.; Symons, M. C. R. "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol. 1, p 177.

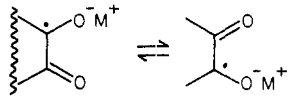
system. The out-of-plane structure would have magnetically nonequivalent α-hydrogen atoms if the cation migration is frozen. In the case of potassium cyclopentane-1,2-semidione we have been unable to detect such magnetic nonequivalence at -100 °C in THF (cooling a mixture of **1** and **2c** causes the percentage of **1** to increase; i.e., ΔH for ion-pair formation is positive).

The fact that ion pairing causes a decrease in g and an increase in a^H must mean that the spin density at the carbonyl carbon in the semidione is increased by ion pairing ($g_{C\cdot} = 2.002$, $g_{O\cdot} = 2.015$). In valence-bond terms we conclude that the importance of structure **5** increases

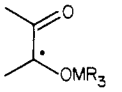


5 6

upon ion pairing. This suggests that the ion pairs may be better represented as fluctional structures, e.g., **7** and **8**,



7 8



9

rather than as rigid chelate structures. In fact α-diones react with trisubstituted silicon, tin, germanium, and lead radicals to form covalent **9** in which the metal atom rapidly migrates between the oxygen atoms.[10]

Experimental Section

The bis(trimethylsiloxy)cycloalkene precursors to the C_4, C_5, C_6, C_7, and C_9 semidiones were prepared by standard procedures.[11]

Potassium dimsylate in Me_2SO was prepared from KH, and standard solutions were stored frozen under nitrogen. The crown ethers (18-crown-6 and 15-crown-5) were obtained from Aldrich Chemical Co., and [2.2.1]- and [2.2.2]cryptands from PCR and E. Merck. The Me_2SO was dried by stirring over CaH_2 followed by fractional distillation at reduced pressure.

The semidiones were prepared by mixing deoxygenated solutions of the bis(trimethylsiloxy)alkene in Me_2SO with a deoxygenated solution of potassium dimsylate in Me_2SO in an inverted H-cell assembly.[12] Dilution experiments were performed by adding the required amount of iodide salt to the base side of the H-cell during degassing. After being mixed, the solutions were diluted by adding measured portions of deoxygenated Me_2SO through a septum.

ESR spectra were measured with a Varian V-4500 spectrometer using flat silica cells in a dual cavity. Splitting constants and g values were measured by using perylene radical cation (H_2SO_4) as a standard with $g = 2.002583 \pm 0.000006$.[13] Field intensities were determined with a modified Alpha Scientific proton NMR gaussmeter and a Hewlett-Packard frequency counter.

Registry No. Cyclobutane-1,2-semidione potassium [2.2.2]cryptand, 72659-21-3; cyclopentane-1,2-semidione potassium [2.2.2]-cryptand, 72659-22-4; cyclohexane-1,2-semidione potassium [2.2.2]-cryptand, 72659-23-5; cycloheptane-1,2-semidione potassium [2.2.2]cryptand, 72659-25-7; cyclononane-1,2-semidione potassium [2.2.2]cryptand, 72659-27-9; biacetyl semidione potassium [2.2.2]-cryptand, 72659-28-0; cesium cyclobutane-1,2-semidione, 72659-29-1; rubidium cyclobutane-1,2-semidione, 72659-30-4; potassium cyclobutane-1,2-semidione, 32587-19-2; cyclopentane-1,2-semidione potassium 18-crown-6, 72658-88-9; cesium cyclopentane-1,2-semidione, 72659-31-5; rubidium cyclopentane-1,2-semidione, 72659-32-6; potassium cyclopentane-1,2-semidione, 32587-21-6; sodium cyclopentane-1,2-semidione, 68058-48-0; lithium cyclopentane-1,2-semidione, 68058-49-1; cyclohexane-1,2-semidione potassium 18-crown-6, 72658-90-3; cesium cyclohexane-1,2-semidione, 72659-33-7; rubidium cyclohexane-1,2-semidione, 72659-34-8; potassium cyclohexane-1,2-semidione, 32587-23-8; potassium cycloheptane-1,2-semidione, 70136-03-7; potassium cyclononane-1,2-semidione, 70136-05-9; biacetyl semidione potassium 18-crown-6, 72658-91-4; potassium biacetyl semidione, 18851-56-4.

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[10] The trialkyltin, -silicon, -germanium, and -lead adducts of biacetyl and benzil have been reported (Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1933. Schroeder, B.; Neumann, W. F.; Hillgaertner, H. *Chem. Ber.* **1974**, *107*, 3494). These are probably covalent adducts similar to **7** ⇌ **8** (Coppin, G. N.; Hudson, A.; Jackson, R. A.; Simmons, N. P. C. *J. Organomet. Chem.* **1977**, *131*, 371), although magnetic nonequivalence of the methyl groups in the biacetyl adduct has not been demonstrated. With silyl or germyl adducts the phenyl groups of benzil are nonequivalent.

[11] Rühlmann, K. *Synthesis* **1971**, 236.

[12] Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807.

[13] Segal, B. G.; Kaplan, M.; Fraenkel, G. K. *J. Chem. Phys.* **1965**, *43*, 4191.

Nickel-Catalyzed Michael Additions of β-Dicarbonyls

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Bis(2,4-pentanedionato)nickel(II) is found to be a mild, efficient, and simple to use catalyst for the Michael additions of β-dicarbonyls. Yields are higher than with traditional strongly basic catalysts, unwanted side reactions are reduced, and workup procedures are greatly simplified. The reactions appear to be quite general as β-diketones, β-keto esters, β-keto amides, and β-diesters are all found to react. A rational mechanism which suggests further research is presented.

The conjugate addition or Michael reaction[1] is one of the most important methods in organic synthesis for effecting carbon-carbon bond formation. Traditionally, these reactions are catalyzed by very strong bases such as alkali metal alkoxides. Several undesirable side reactions can be caused by these strongly basic catalysts,[1] including rearrangements, secondary condensations, isomerizations, polymerizations, bis additions, retrogressions, and transesterifications. Recently, phase-transfer catalysis has been utilized to circumvent some of these problems with α,β-unsaturated aldehydes.[2] Since there is considerable

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[1] For a comprehensive review of the Michael reaction see: Bergman, E. D.; Ginsberg, D.; Rappo, R. *Org. React.* **1959**, *10*, 179.

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