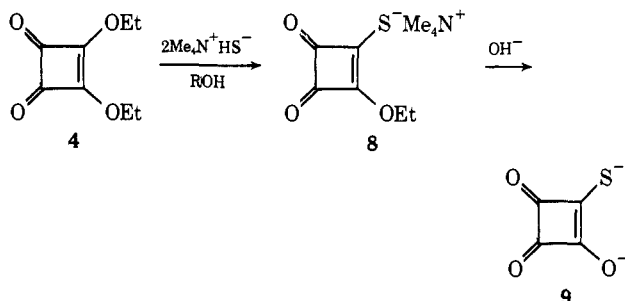


Figure 1. The molecular structure of $K_2Ni(S_2C_4O_2)_2 \cdot 2H_2O$ ($R_1 = 0.018$). The nickel atom sits on a crystallographic center of symmetry. Distances are in ångströms and angles in degrees. The figures in parentheses represent the estimated standard deviation of the least significant digit(s). Water molecules and complete coordination of the potassium have been left out for clarity. The thermal ellipsoids as plotted by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces.

ligands and shows no axial interactions. The ligand itself is very closely planar, and this plane is essentially coplanar with that of the NiS_4 moiety. The exterior angles of the two carbon atoms attached to sulfur are highly distorted from the "ideal" value of 135° to reduce the sulfur-sulfur bite distance to its observed value of 3.26 Å. The quite large oxygen-oxygen bite distance of 3.21 Å, however, is essentially unperturbed. The carbon-carbon, carbon-sulfur, and carbon-oxygen bond lengths are compatible with a description of the anion that gives greatest weight to resonance form **3a** with significant contributions from **3b** and **3c**.⁸ The potassium atoms are irregularly coordinated by oxygens from several ligands and by the water molecules.

Reaction of dipotassium 1,2-dithiosquarate with ethyl iodide in DMF-water yields *S,S'*-diethyl 1,2-dithiosquarate (**6a**). The ir spectrum (CCl_4) shows strong bands at 1770, 1745, 1455, and 1135 cm^{-1} . The mass spectrum shows a strong parent ion peak at 202 m/e , and the nmr spectrum is typical of S-bonded ethyl esters (δ 3.46 and 1.48 ppm with respect to TMS). A similar ester (**6b**) has been prepared by reaction of benzyl mercaptan and 3,4-dichlorocyclobutenedione (**7**).

When diethyl squarate is treated with an alcoholic solution of 2 equiv of tetramethylammonium hydroxide saturated with hydrogen sulfide, displacement of only one ethoxy group occurs, yielding the *O*-ethyl monothiosquarate anion (**8**). The ir spectrum of this anion



shows strong bands at 1760 and 1670 cm^{-1} . The electronic spectrum shows a single peak at 320 nm. The nmr spectrum in acetonitrile shows a quartet at δ 4.80 (2 H), a singlet at δ 3.15 (12 H), and a triplet at 1.38 (3 H). Hydrolysis of the *O*-ethyl monothiosquarate anion appears to give the monothiosquarate dianion (**9**), isolable as the bis(tetramethylammonium),

(8) Full details on the chelation chemistry of the dithiosquarate dianion and the crystal structure of the nickel complex will be given in a subsequent paper. F. Hollander and D. Coucouvanis, manuscript in preparation.

-dipotassium, and -barium salts. Characterization and study of dianion **9** is currently being carried out.

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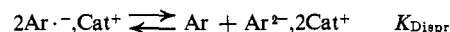
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Disproportionation of the Lithium, Sodium, and Potassium Salts of Anthracenide and Perylenide Radical Anions in DME and THF

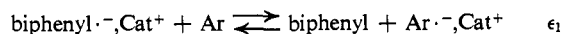
Sir:

Our recent studies of protonation of Li^+ , Na^+ , and K^+ salts of radical anions of anthracene^{1,2} and of perylene³ in THF or DME demonstrated the important role of dianions in the overall process. The evaluation of the results required knowledge of the respective disproportionation constants



and to provide the necessary data we carried out potentiometric titrations of the pertinent hydrocarbons in the above solvents.

The potentiometric titrations, originally developed by Hoijtink, *et al.*,⁴ and subsequently improved in our laboratory,⁵ yield the standard potentials ϵ_1 and ϵ_2 of the following equilibria⁶



(1) A. Rainis, R. Tung, and M. Szwarc, *J. Amer. Chem. Soc.*, **95**, 659 (1973).

(2) A. Rainis, R. Tung, and M. Szwarc, *Proc. Roy. Soc.*, in press.

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(5) J. Jagur-Grodzinski, M. Feld, G. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

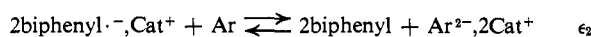
(6) The directly measured potentials ϵ_1 and ϵ_2 refer to the reactions of ion pairs and of the associates such as $Ar^{2-}, 2Cat^+$ because the dissociations, $Ar^{\cdot-}, Cat^+ \rightleftharpoons Ar^{\cdot-} + Cat^+$ and $Ar^{2-}, 2Cat^+ \rightleftharpoons Ar^{2-}, Cat^+ + Cat^+$, are negligible under conditions prevailing in the titrations performed in THF or DME.

Table I. Redox Potential of Anthracene and Perylene as Functions of Solvent and Counterion

Counterion (solvent)	Anthracene, A			Perylene, Pe		
	ϵ_1 , ^a mV	ϵ_2 , ^b mV	K_{Dispr}^c	ϵ_1 , ^a mV	ϵ_2 , ^a mV	K_{Dispr}^c
Li ⁺ (DME)	605 ± 5	140 ± 10	1.8 × 10 ⁻⁸	915 ± 5	350 ± 10	3.8 × 10 ⁻¹⁰
Na ⁺ (DME)	603 ± 5	150 ± 10	2.8 × 10 ⁻⁸	923 ± 5	380 ± 10	8.9 × 10 ⁻¹⁰
K ⁺ (DME)	605 ± 5	190 ± 10	1.2 × 10 ⁻⁷	903 ± 5	480 ± 10	8.9 × 10 ⁻⁸
Li ⁺ (THF)	612 ± 5	220 ± 10	2.9 × 10 ⁻⁷	912 ± 5	390 ± 10	2.0 × 10 ⁻⁹
Na ⁺ (THF)	598 ± 5	310 ± 10	1.6 × 10 ⁻⁸	906 ± 5	560 ± 10	1.7 × 10 ⁻⁶
K ⁺ (THF)	600 ± 5	230 ± 10	6.8 × 10 ⁻⁷	890 ± 5	550 ± 10	2.2 × 10 ⁻⁶

^a ϵ_1 refers to the reaction $\text{Biphenyl}\cdot^-, \text{Cat}^+ + \text{A or Pe} \rightleftharpoons \text{Biphenyl} + \text{A}\cdot^- \text{ or Pe}\cdot^-, \text{Cat}^+$. ^b ϵ_2 refers to the reaction $2\text{Biphenyl}\cdot^-, \text{Cat}^+ + \text{A or Pe} \rightleftharpoons 2\text{Biphenyl} + \text{A}^{2-} \text{ or Pe}^{2-}, 2\text{Cat}^+$. ^c K_{Dispr} refers to the reaction $2\text{A}\cdot^- \text{ or Pe}\cdot^-, \text{Cat}^+ \rightleftharpoons \text{A or Pe} + \text{A}^{2-} \text{ or Pe}^{2-}, 2\text{Cat}^+$.

and



which are related to the pertinent K_{Dispr} by the equation

$$-0.06 \log K_{\text{Dispr}} = \epsilon_1 - \epsilon_2$$

The technique described in ref 5 has been used in our present study, the potential being measured with a Fluke 871A DC differential voltmeter of virtually infinite resistance. The results are collected in Table I. Those obtained for the sodium salts in THF compare favorably with the redox potentials reported previously.⁵ However, our results for the sodium salts in DME are substantially lower than those reported by Hoijtink.⁴

Disproportionation is unfavorable for gaseous radical anions. The reaction is highly endothermic due to a large repulsion energy between the two electrons crowded in a dianion, while the entropy of the system remains virtually unaltered. The endothermicity is reduced for the disproportionation of *free* radical anions in solution because the dianion solvation energy is about twice as large as the solvation energy of two radical anions, the former being approximately $(2e)^2/2r\epsilon$ whereas the latter is about $2e^2/2r\epsilon$. However, the gain in solvation energy is partially compensated by a decrease in the entropy of solvation.

The thermodynamics of disproportionation are more complex for ion pairs of radical anions. Since cations are more strongly bound to dianions than to radical anions, the endothermicity of the reaction is further reduced. This effect is more pronounced for small cations than for large ones; *i.e.*, K_{Dispr} should increase with decreasing ionic radius. Moreover, the orientation of the solvent molecules is partially randomized as the two dipoles associated with the cation-radical anion pairs are replaced by the $\text{Cat}^+, \text{A}^{2-}, \text{Cat}^+$ quadrupole, thereby increasing the entropy of disproportionation.

Disproportionation is even more complex when the degree of cation solvation changes in the reaction. For example, small cations may be strongly solvated when associated with radical anions, while their degree of solvation is greatly reduced on association with dianions. This phenomenon substantially increases the entropy of disproportionation although it decreases its exothermicity. Nevertheless, since the binding of a solvated cation to a radical anion is much weaker than the binding of a desolvated cation with a dianion, the disproportionation is expected to increase in such a process.

The preceding discussion may rationalize the results collected in Table I. Apparently, Li⁺ and Na⁺ cations are strongly solvated in DME whether paired with a

radical anion or dianion, whereas K⁺ is highly solvated when paired with a radical anion but becomes desolvated on its association with a dianion. Therefore, K_{Dispr} of the potassium anthracenide or perylenide in DME is substantially greater than the corresponding disproportionation constants for the lithium or sodium salts. In THF, Li⁺ ions still seem to be substantially solvated even when associated with dianions, while Na⁺ ions, although solvated when paired with radical anions, become largely desolvated on association with dianions. Therefore, K_{Dispr} sharply increases as Na⁺ replaces Li⁺.

The behavior of the potassium salts in THF is more intriguing. The disproportionation constant of potassium perylenide seems to indicate that this salt behaves in THF like the corresponding sodium salt; *i.e.*, the THF solvated K⁺ ions are paired with perylenide anions but much of their solvation shell is lost on association with Pe^{2-} dianions. The extensive delocalization of the charge in the large perylenide anion is probably responsible for the substantial degree of K⁺ solvation in $\text{Pe}\cdot^-, \text{K}^+$. However, the charge is more concentrated in the anthracenide ion, and hence the K⁺ ions appear to be poorly solvated whether associated with $\text{A}\cdot^-$ or A^{2-} . This may account for the exceptionally low value of K_{Dispr} of $\text{A}\cdot^-, \text{K}^+$ in THF. As in the case of $\text{A}\cdot^-, \text{Li}^+$, the disproportionation does not provide any additional reduction of the free energy of the system—the K⁺ ion remains desolvated before and after disproportionation while the solvated Li⁺ ion does not lose its solvation shell in the disproportionation process.

Finally, two additional questions remain to be answered. Why is disproportionation favored for anthracenide as compared with perylenide and more extensive in THF than in DME?

Consideration of the repulsion between the two electrons would suggest a larger degree of disproportionation for perylenide than anthracenide, contrary to our observation. Such a relation may be valid for the free anions; however, in the cation paired system the gain in cation binding energy may be more important than the increase of repulsion energy and the former is greater in the anthracenides.

The comparison of the DME and THF systems suggests that the degree of desolvation, even if small as for Li⁺ salts, is greater in THF than in DME. Moreover, the rupture of Cat^+-O bond leads to entropy increase in the monodentate THF system, whereas such a gain requires the rupture of two Cat^+-O bonds in the bidentate DME system.

It is hoped that this discussion may clarify some intricacies of the disproportionation as affected by the nature of cation, solvent, and anion.

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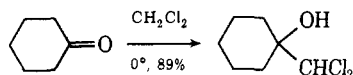
A Practical Synthesis of Polyhalomethylithium Carbonyl Adducts

Sir:

The type of reagent which results from the combination of polyhalomethane with *n*-butyllithium at low temperature, formally a polyhalomethylithium X₂-CHLi or X₃CLi,¹ has proved to be versatile synthetic species.² The significant limitation on the broad utility of these reagents often arises from their extreme thermolability.^{1,3} Thus, the optimum reaction temperature, which is normally between -70 and -120° (internal temperature), is limited at the lower end of the range by the rate of formation and at the upper end by the tendency of carbenoids to decompose.

We now report here the successful use of lithium dicyclohexylamide⁴ as the base in a practical synthesis of polyhalomethylithium carbonyl adducts. The method involves an *in situ* carbenoid formation in the presence of carbonyl compounds, thus avoiding a troublesome procedure with the preformed carbenoid.³

A vigorously stirred solution of cyclohexanone in methylene chloride was treated with lithium dicyclohexylamide at 0° over a period of 5 min. After stirring for an additional 10 min at 0°, the reaction mixture was worked-up as usual to furnish 1-(dichloromethyl)cyclohexanol in 89% isolated yield. The scope of this



new method, illustrated by the reaction between several representative polyhalomethanes with various carbonyl compounds, is summarized in Table I.

It is noteworthy that diiodomethylithium⁵ and tribromomethylithium, both of which are extremely un-

(1) (a) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967); **11**, 473 (1972), and references therein; (b) D. F. Hoeg and D. I. Lusk, *J. Amer. Chem. Soc.*, **86**, 928 (1964); D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965); D. F. Hoeg and D. I. Lusk, *J. Organometal. Chem.*, **5**, 1 (1966).

(2) Polyhalomethylithium carbonyl adducts may be easily converted to a variety of important structural classes (*inter alia*): (a) α -chloro ketone, H. Taguchi, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 4661 (1972); J. Villieras, C. Bacquet, and J. F. Normant, *J. Organometal. Chem.*, **40**, C1 (1972); G. Köbrich and J. Grosser, *Tetrahedron Lett.*, 4117 (1972); I. Kuwajima and Y. Fukuda, *Chem. Lett.*, 327 (1973); G. Köbrich and J. Grosser, *Chem. Ber.*, **106**, 2626 (1973); (b) α,β -unsaturated aldehyde, H. Taguchi, S. Tanaka, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 2465 (1973); (c) α -chloroaldehyde, G. Köbrich and W. Werner, *ibid.*, 2181 (1969); (d) α -hydroxyaldehyde, J. I. Stevens, *J. Org. Chem.*, **37**, 1248 (1972), and references cited therein; (e) dichloroolefin, G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *Chem. Ber.*, **99**, 689 (1966); G. Köbrich, H. Trapp, and I. Hornke, *ibid.*, **100**, 961 (1972).

(3) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(4) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 582 (1973). Villieras also reported the generation of dibromomethylithium solution using lithium diisopropylamide at low temperature: J. Villieras, *J. Organometal. Chem.*, **50**, C7 (1973).

(5) As far as our knowledge, diiodomethylithium was generated for the first time by our new procedure.

Table I. Yields of Polyhalomethylithium Carbonyl Adducts^a

Polyhalomethane (equiv)	Carbonyl	Temp, °C	% yields ^b
Methylene chloride (excess)	Cyclohexanone	-78	100
Methylene chloride (excess)	Cyclohexanone	0 ^d	89
Methylene chloride (2) ^c	Cyclohexanone	-78	86
Methylene chloride (excess)	Cyclopentanone	0 ^d	66
Methylene chloride (excess)	Cyclopentanone	-20 ^d	90
Methylene chloride (excess)	Cycloheptanone	-20 ^d	88
Methylene chloride (excess)	6-Methyl-5-hepten-2-one	0 ^d	84
Methylene chloride (2) ^c	Nonanal	0 ^d	73
Methylene bromide (2) ^c	Cyclohexanone	-78	91
Methylene bromide (2) ^c	Cyclopentanone	-78	82
Methylene bromide (2) ^c	Nonanal	-78	77
Methylene iodide (2) ^c	Nonanal	-78	79 ^e
Chloroform (excess) ^c	Cyclohexanone	-78	94 ^f
Chloroform (2) ^c	Cyclohexanone	-78	92 ^f
Chloroform (excess) ^c	Cyclopentanone	-78	91
Bromoform (10) ^c	Cyclohexanone	-78	89 ^g
Bromoform (2) ^c	Cyclohexanone	-78	91 ^g

^a No attempt has been made to optimize yields. Unless specified, the reactions were carried out on a 1 mmol scale exactly as described for the larger scale preparation of 1-(tribromomethyl)cyclohexanol. All products were completely characterized by spectroscopic methods and elemental analyses. ^b Yields are based on material isolated chromatographically. ^c Tetrahydrofuran was used as co-solvent. ^d Lithium dicyclohexylamide (2 equiv) was added at 0° (or -20°) for 5 min, and the reaction mixture was stirred at 0° for 10 min. ^e Isolated by distillation, bp 140° (bath temp, 0.2 mm). ^f Mp 56° (H. Normant and T. Cuvigny, *Bull. Soc. Chim. Fr.*, 1881 (1965)). ^g Mp 74°.

stable even at -120°, can be generated effectively and the carbonyl adducts could be prepared in good to excellent yields at -78° (external cooling). Even in the presence of cyclopentanone, which is known as a readily enolizable ketone, the generation of polyhalomethylithium is favored over enolate formation; thus the corresponding adducts were produced in good yields. The success of the reaction depends crucially on the nature of lithium dialkylamide which selectively abstracts protons from substrates containing intrinsically more reactive sites toward nucleophilic attack.⁴

The following experimental procedure is illustrative of the method. A well-stirred solution of bromoform (4.35 ml, 50 mmol) and cyclohexanone (2.45 g, 25 mmol) in dry tetrahydrofuran (50 ml) was cooled to -78° (external cooling with Dry Ice-methanol bath) and was treated with lithium dicyclohexylamide (50 mmol; prepared from dicyclohexylamine (9.05 g, 50 mmol) in dry tetrahydrofuran (50 ml) with *n*-butyllithium (50 mmol, 33 ml of a hexane solution) at 0°) dropwise over a period of 15 min. The mixture was then allowed to stand for 1 hr at the same low temperature and an extractive work-up followed. The crude oil thus obtained was subjected to column chromatography (silica gel, 100 g; benzene as eluant) to yield 1-(tribromomethyl)cyclohexanol as a colorless crystalline material (7.96 g, 91% yield): mp 74°; ir (Nujol) 3460 (OH), 1153, 977, 928, 760, 695 cm⁻¹. *Anal.* Calcd for C₇H₁₁OBr: C, 23.96; H, 3.16. Found: C, 23.90; H, 3.18.

The methodology described herein may be applicable to a wide variety of synthetic problems in which the relatively unstable carbenoids or carbanions are involved. Indeed, we have found that a mixture of methyl bromoacetate and cyclohexanone undergoes a facile Darzens-type reaction on treatment with lithium