Decarbonylation and Decarboxylation by Lithium in Hexamethylphosphoramide[1]

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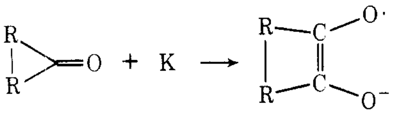
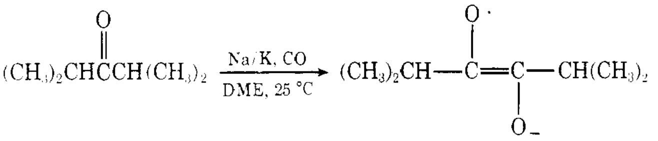
A series of strained-ring ketones and esters were reduced with lithium in hexamethylphosphoramide and the paramagnetic reduction products identified by ESR spectroscopy. Diphenylcylopropenone yielded *trans*-stilbene radical anion, *o*-phenylene carbonate yielded *o*-benzosemiquinone, bicyclo[4.2.1]nona-2,4,7-trien-9-one yielded cyclooctatetraene radical anion, and phthaloyl peroxide yielded the biphenylene radical anion. Tetramethylcyclobutane-1,3-dione can be reduced to yield the same radical anion detected in the acyloin condensation of dimethyl 2,2,4,4-tetramethyl-3-ketoglutarate, which is assigned to 3,3,5,5-tetramethyl-4-oxocyclopentane-1,2-semidione. Diisopropyl ketone is also carbonylated by potassium and carbon monoxide in dimethoxyethane to yield the *trans*-diisopropylsemidione, which is also detected in the reduction of tetramethylcyclobutane-1,2-dione by lithium in hexamethylphosphoramide–tetrahydrofuran mixtures.

It has been previously reported that potassium in THF or DME at 25 °C converts some strained-ring monoketones, such as 2,2,4,4-tetramethylcyclobutanone, 7-norbornenone, or 9-ketobenzonorbornene, into semidiones.[3-5] One interpretation is that the initially formed ketyl undergoes decarbonylation forming $K^+CO^-\cdot$, which reacts with another molecule of the ketone. Some proof for the second step of this process is furnished by the observation that whereas diisopropyl ketone fails to yield a ketyl or semidione detectable by ESR spectroscopy upon reduction by Na/K in DME at 25 °C, a solution of diisopropyl ketone saturated with carbon monoxide yields the known[6] *trans*-diisopropylsemidione detectable by ESR spectroscopy. However, the reaction is not general and numerous other ketones fail to yield the semidione under these conditions.





$$(CH_3)_2CH\overset{\overset{O}{\|}}{C}CH(CH_3)_2 \xrightarrow[\text{DME, 25 °C}]{\text{Na/K, CO}} (CH_3)_2CH\text{—}\overset{\overset{O\cdot}{|}}{C}=\underset{\underset{O^-}{|}}{C}\text{—}CH(CH_3)_2$$

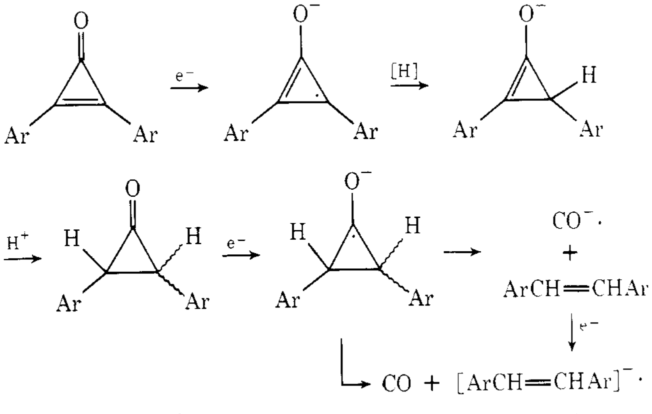
$a^H = 1.9(2), 0.03(12)$ G

$g = 2.00486$

During an investigation of the reducing properties of the system HMPA/Li we have observed some further examples of decarbonylation as well as an example of bisdecarboxylation. Decarbonylation products were detected by ESR spectroscopy when diphenylcyclopropenone, *o*-phenylene carbonate, or bicyclo[4.2.1]nona-2,4,7-trien-9-one were treated with HMPA/Li in a static system (Table I).

Diphenylcyclopropenone, when treated with HMPA/Li in a static or flow system (~0.1 s between mixing and detection), yielded the *trans*-stilbene radical anion which is readily distinguished from the known diphenylacetylene radical anion. The strength of the ESR signal appeared to be increased by the addition of THF to the solution. A plausible explanation is that reduction to diphenylcyclopropanone preceded decarbonation as shown in Scheme I.

Scheme I



Treatment of diphenylcyclopropenone with Na/K in DME at room temperature gave a different result. An ESR signal formed only slowly, but after 18 h of reaction a strong ESR signal for a species with $a^H = 5.30(2)$, 2.65(4), and 0.50(4) G was observed. Under the same conditions diphenylacetylene gave $a^H = 4.8(2)$, 2.65(4), and 0.65(4) G,[15] whereas diphenyl radical anion has $a^H = 5.46(2)$, 2.73(4), and 0.43(4) G. It seems most likely that in DME the reaction of diphenylcyclopropenone with Na/K has involved the cleavage of a phenyl group which is eventually converted to biphenyl radical anion, possibly via the coupling of phenyl radicals with the phenide ion.[16,17]

$$C_6H_5\cdot + K \rightarrow C_6H_5K \xrightarrow{C_6H_5\cdot} [C_6H_5\text{–}C_6H_5]^-\cdot K^+$$

Diphenylcyclopropenone also will give the CO insertion reaction under some conditions. When the ketone in Me_2SO is mixed in a flow cell with potassium *tert*-butoxide, an unstable radical that is not the ketyl can be detected. Upon stopped flow the ESR signal of this species disappears, and slowly the ESR signal of diphenylcyclobutene-1,2-semidione[18] appears; $a^H = 1.30(2)$, 1.20(4), 0.48(4) G (experimental results of Dr. T. Morita).

In the case of *o*-phenylene carbonate and bicyclo[4.2.1]-nona-2,4,7-trien-9-one the reaction appears to involve a simple chelatropic expulsion of carbon monoxide from the ketyl with the formation of the *o*-benzoquinone and cyclooctatetraene radical anions. α-Diones such as diphenylcyclobutenedione,[18] benzocyclobutanedione,[13] or dibenzobicyclo[2.2.2]octane-2,3-dione[14] can be converted to the semidione radical ions under reductive conditions without decarbonylation.

o-Phthaloyl peroxide gave the radical anion of biphenylene upon reaction with HMPA/Li. Solutions of the peroxide in

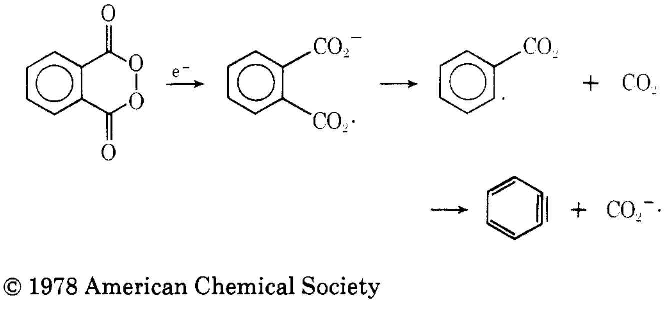


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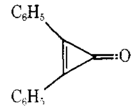
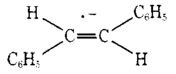
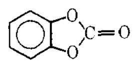
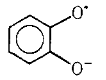
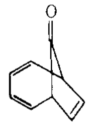
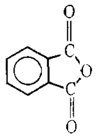
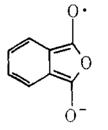
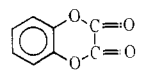
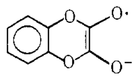
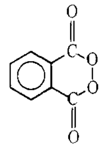
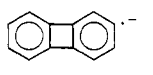
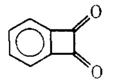
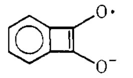
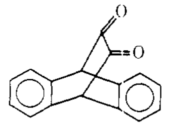
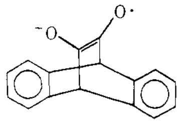
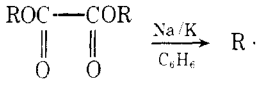
Table I. Radical Anions Observed by ESR Spectroscopy at 25 °C

Carbonyl compound	Registry no.	Hyperfine splitting constants, G (equiv protons)	Obsd radical anions	Registry no.	Lit. ref
	886-38-4	a^H = 4.35(2), 4.00(2), 3.05(2), 1.95(2), 0.82(3), 0.3(2)		34467-73-7	7
	2171-74-6	a^H = 3.4(2), 1.35(2), a^{Li} = 0.42(1)[a]		20526-43-6	8
	34733-74-9	a^H = 3.3(8)		34510-85-5	9
	85-44-9	a^H = 2.22(2), 0.20(2) (slow flow required)		34533-03-4	10
	16536-36-0	a^H = 0.18(4)		65761-22-0	11
	4733-52-2	a^H = 2.7(0.4), 0.2(2)		34478-97-2	12
	6383-11-5	a^H = 3.7(2), 1.9(2) (CH_3CN, $(C_2H_5)_4N^+$)		54165-46-7	13
	22612-93-7	a^H = 0.18(8) (Me_2SO, K^+)		17441-61-1	14

[a] Observed only after UV irradiation.

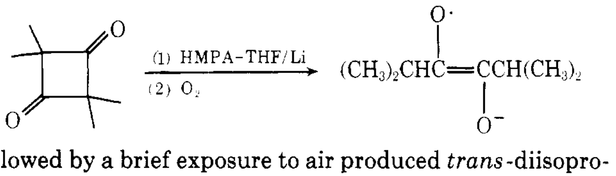
HMPA showed no indication of the formation of biphenylene by UV, and it is concluded that the biphenylene results from benzyne formation by decarboxylation of the first formed unstable radical anion.

The reaction is not surprising because benzoyl peroxide itself is readily cleaved by one-electron transfer agents. 1,2-Benzoxylate yielded the radical anion without decarboxylation as did phthalic anhydride. Berndt has reported the formation of persistent free radicals by the reductive decarboxylation of acyclic oxalic diesters, but this reaction occurs rather slowly.[19]



$$\underset{\displaystyle O}{\overset{}{ROC}}\!\!-\!\!\underset{\displaystyle O}{COR} \xrightarrow[C_6H_6]{Na/K} R\cdot$$

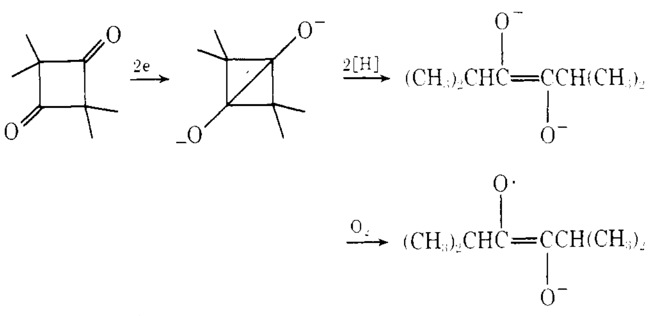
Reduction of 2,2,4,4,-tetramethylcyclobutane-1,3-dione with HMPA/Li at 25 °C failed to yield an ESR signal without added THF. With an HMPA/THF ratio of 35:65, reduction

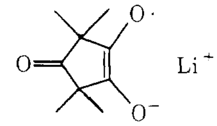


followed by a brief exposure to air produced *trans*-diisopropylsemidione in low yield.[6] In this case decarbonylation may not be involved; for example, see Scheme II.

With HMPA/THF = 67:33 the reaction of the dione with lithium gave a species with a^{Li} = 0.60, a^C = 7.8, 4.9 G. This is not the *cis*-diisopropylsemidione which has a^H = 2.2, $a_{CH_3}{}^H$ = 0.16, a^{Li} = 0.65 G,[6] but it is the same species Ward has ascribed to the tetramethylcyclobutane-1,3-dione ketyl (DME/K, 25 °C, a^C = 7.6, 5.0 G).[20] However, ketyls generally have $a_{CO}{}^C$ in the range of 40–50 G.[4] Moreover, 2,2,4,4-tetramethylcyclobutanone ketyl ($a_{CO}{}^C$ = 50, $a_{CH_3}{}^C$ = 13.4 G) decomposed in THF above −50 °C to yield 2,2,4,4-tetramethylcyclopentane-1,2-semidione ($a_{CH_3}{}^C$ = 6 G).[4] We believe the observed species is most likely the semidione 1 formed by a decarbonylation–carbonylation process. The values of a^C in cyclic 1,2-semidiones are typically in the range of $a_{CO}{}^C$ =

Scheme II





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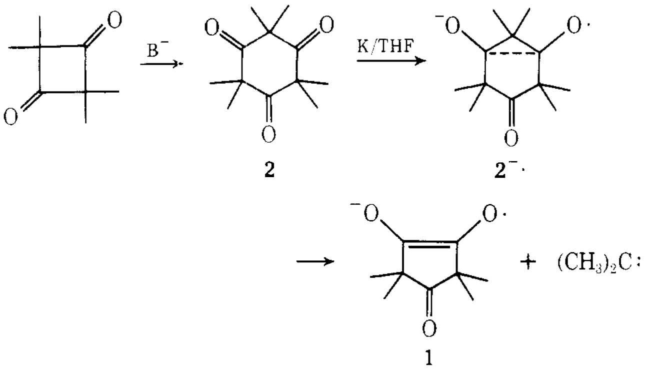
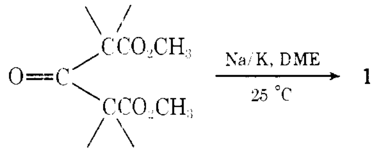
Scheme III

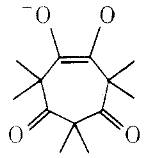


1-1.5, $a_\alpha{}^C$ = 5--6, $a_\beta{}^C \cong$ 6–8 G.[4] HMPA(35%)-THF(65%) containing lithium and excess lithium iodide rapidly produced a strong ESR signal for 1 without the formation of the *trans*-diisopropylsemidione. Apparently high lithium ion concentrations favor the decarbonylation process over the reductive rearrangement process of Scheme II.

Final proof for the correctness of the assignment of structure 1 was furnished by the acyloin condensation of dimethyl 2,2,4,4-tetramethyl-3-ketoglutarate with Na/K alloy in DME at 25 °C wherein the species with a^C = 7.6 and 5.0 G was observed. The acyloin condensation is known to involve semidione radical anions as intermediates.[21]



Tetramethylcyclobutane-1,3-dione is known to yield 2 in the presence of base at elevated temperatures.[22] Furthermore, 2 can be reduced by lithium in ammonia to a *cis*-cyclopropanediol via $2^-\cdot$.[23] This suggested that $2^-\cdot$ might be a precursor to 1, or that 3 might actually be the species observed



3

in the reduction of tetramethylcyclobutane-1,3-dione. However, attempted reductions of 2 by K/THF at 25 or −80 °C have produced no detectable ESR signals and the proposed sequence of Scheme III as well as structure 3 are excluded.

Experimental Section

Diphenylcyclopropenone,[24] *o*-phenylene carbonate,[25] bicyclo[4.2.1]nona-2,4,7-trien-9-one,[26] *o*-phthaloyl peroxide,[27] dimethyl 2,2,4,4-tetramethyl-3-ketoglutarate,[28] and 2,2,4,4,6,6-hexamethylcyclohexane-1,3,5-trione[22] were synthesized by literature procedures.

Reduction with HMPA/Li was conducted by dissolving the substrate in one leg of a H-cell[29] and a pellet of freshly cut lithium in the other leg. The HMPA solutions were thoroughly deoxygenated by prepurified nitrogen or argon, mixed, and allowed to drain into a fused silica flat ESR cell attached to the H-cell. For flow experiments the HMPA solutions were discharged from motor-driven glass syringes through polyethylene tubing and mixed in a fused silica cell (Varian Associates V-4549A) with a dead volume of 0.05 mL. Reductions by Na/K alloy were conducted by stirring an ethereal solution of the substrate with an excess of the alloy under nitrogen or carbon monoxide followed by transfer of a sample of the reduced solution to the ESR cell. Reductions by potassium in THF were performed by adding a degassed THF solution of the substrate to a potassium mirror under vacuum.[3] ESR spectra were determined using a Varian E-3 spectrometer.

Registry No.—HMPA, 680-31-9; lithium, 7439-93-2.

References and Notes

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