the residue was chromatographed from 60 g of alumina (F-20). The material was eluted with hexane, a mixture of hexane and benzene, and finally benzene. The hexane fraction gave *p*-chlorophenyl disulfide and the benzene fraction produced **6** (yield 0.52 g) (58%), which was characterized by its yeliow color, its biting lachrymatory odor, and 2,3-dibromoindanone: mp 62–63 °C (lit.[13] mp 64–65 °C); NMR ($CDCl_3$) δ 6.4–6.9 (m, 2), 7.4–7.8 (m, 4). **6** readily dimerizes to truxone in the presence of a trace of acid catalyst.

Typical Procedure for Diels–Alder Reactions. A solution of 0.5 g (1.7×10^{-3} mol) of **3** and a small excess of diene (3×10^{-3} mol) in 30 mL of toluene was heated to reflux for 8–10 h. The solvent was removed under vacuum and the crude residue was transferred onto a column of 100 g of alumina (F-20) in hexane containing 0.3 to 0.5 mL of toluene. The material was eluted with hexane, 75:25 and 50:50 mixtures of hexane and toluene, and finally toluene. The hexane fraction yielded *p*-chlorophenyl disulfide, the hexane–toluene fraction gave the Diels–Alder adduct in the case of the cyclopentadiene, and the toluene fraction gave the Diels–Alder adduct in the case of hexachlorocyclopentadiene and anthracene.

Cyclopentadiene adduct (10): yield 180 mg (53%); colorless liquid; NMR ($CDCl_3$) δ 1.9 (br s, 2), 2.9–4 (m, 4), 5.3 (q, 1), 5.9 (q, 1), 7.2–7.4 (m, 4). Anal. Calcd for $C_{14}H_{12}O$: C, 85.69; H, 6.26. Found: C, 85.34, H, 6.61.

Hexachlorocyclopentadiene adduct (11): yield 210 mg (30%); mp 158–60 °C; NMR ($CDCl_3$) δ 2.7 (d, 1), 3.2 (d, 1), 7.2–7.5 (m, 4). Anal. Calcd for $C_{14}H_6Cl_6O$: C, 41.78; H, 1.49; Cl, 52.79. Found: C, 42.00; H, 1.59; Cl, 53.09.

Anthracene adduct (12): yield 360 mg (68%); mp 198–200 °C; NMR ($CDCl_3$) δ 3.1 (q, 1), 3.9 (q, 1), 4.6 (d, 1), 4.8 (d, 1), 6.9–7.5 (m, 12). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.22. Found: C, 89.39; H, 5.36.

Acknowledgment. We wish to thank the MHW Laboratories, Phoenix, Arizona 85018, for the microanalysis.

Registry No.—**2,** 62967-56-0; **3,** 62937-76-2; **4,** 61463-21-6; **5,** 35116-20-2; **6,** 480-90-0; 1-acetoxy-2-(*p*-chlorophenylsulfinyl)indine, 65495-98-9; 2,3-dibromoindanone, 50870-59-2.

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Radical Anions of Substituted Cyclobutene-1,2-diones[1]

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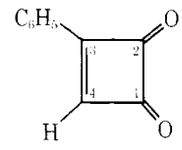
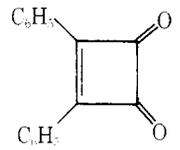
Received December 1, 1977

A recent report[2] on the observation of a paramagnetic reduction product of phenylcyclobutene-1,2-dione (**1**) prompts us to describe some observations we have made in this and other systems.

We have observed that the reduction of **1** in a static system at 25 °C yields the spectrum reported by Concepcion and Vincow (a^H = 11.25, a^C = 8.5, 4.5 G) in hexamethylphosphoramide (HMPA)–lithium, in dimethyl sulfoxide (Me_2SO)–potassium *tert*-butoxide, or in dimethylformamide (DMF)–electrolysis. We have hesitated upon assigning this species to



1



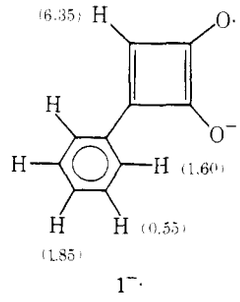
2

$1^{-}\cdot$ for several reasons. The half-life of the species in Me_2SO was several hours which is inconsistent with structure $1^{-}\cdot$, particularly in view of the high spin density of ~11.25/27 on C-4.[3] If the spin densities at C-3 and C-4 were to be equated, it would appear that the semidione function is nearly devoid of spin density. We have been unable to prepare alkyl derivatives in this system, for example, by the treatment of 1,2-dimethylcyclobutene-1,2-dione with basic Me_2SO,[3] but still the reported spectrum indicates little spin delocalization by the aromatic ring. Finally, under flow conditions with basic Me_2SO, **1** was observed to yield an ESR spectrum (Chart I) more consistent with the hyperfine splitting constants (hfsc) expected for $1^{-}\cdot$ and also consistent with the spectrum observed for $2^{-}\cdot$ when **2** is continuously electrolyzed in DMF. Under stopped-flow conditions the species we assign as $1^{-}\cdot$ disappeared in seconds as did $2^{-}\cdot$ when electrolysis was halted. The observed hfs constants for $1^{-}\cdot$ are quite consistent with the Hückel spin density calculations reported by Concepcion and Vincow[2] with all β_{cc} values equal (the predicted values of a^H being[2] $a_4^H = -7.5$, $a_o^H = -2.05$, $a_m^H = -0.11$, and $a_p^H = -2.45$ G).[14]

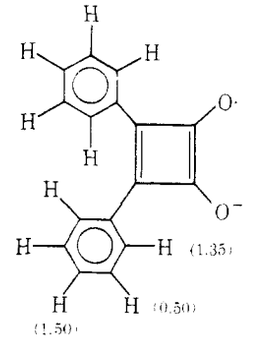
Reduction of **2** with HMPA–lithium or HMPA–(trimethylsilyl)sodium[5] presented some complications which may be related to the observation of the species with a^H = 11–12 G from **1.** With alkali metal reducing systems at 25 °C the radical attributed to $2^{-}\cdot$ was the major species detected, but a second radical anion with a^H = 3.00 (2), 2.4 (4), and 0.8 (4) G was observed. Upon irradiation with a low-pressure UV lamp $2^{-}\cdot$ disappeared and only the spectrum of the second radical anion remained. The second radical anion appears to be benzophenone ketyl but without the usually observed metal hfsc.[6] Reduction of benzophenone (0.25 M) by HMPA–(trimethylsilyl)sodium yielded a spectrum with a^H = 3.5 (2), 2.5 (4), and 0.75 (4) G and a^{Na} = 0.75 G, consistent with literature values of benzophenone ketyl in dimethoxyethane[5] or HMPA.[7]

We presume that the 11.25-G doublet arising from the reduction of **1** and benzophenone ketyl from **2** arise from 1,2 migrations in the cyclobutene-1,2-dione system. Attack by traces of hydroxide ion could initiate a benzilic acid type of rearrangement (Scheme I). Reduction of **1a** to the radical trianion **3** is feasible but now H-4 would be in the nodal plane of the allylic system and a small hfsc would be expected. On the other hand, loss of an electron from **1a** to yield **4** would give a semitrione for which a^H might reasonably be 11 G, and the

Chart I. Observed Hyperfine Splitting Constants



$1^{-}\cdot$



$2^{-}\cdot$, DMF, 25 °C, Bu_4N^+, line width 0.1 G

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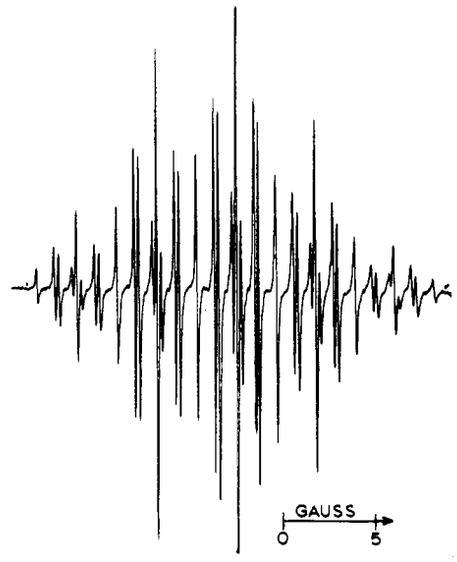
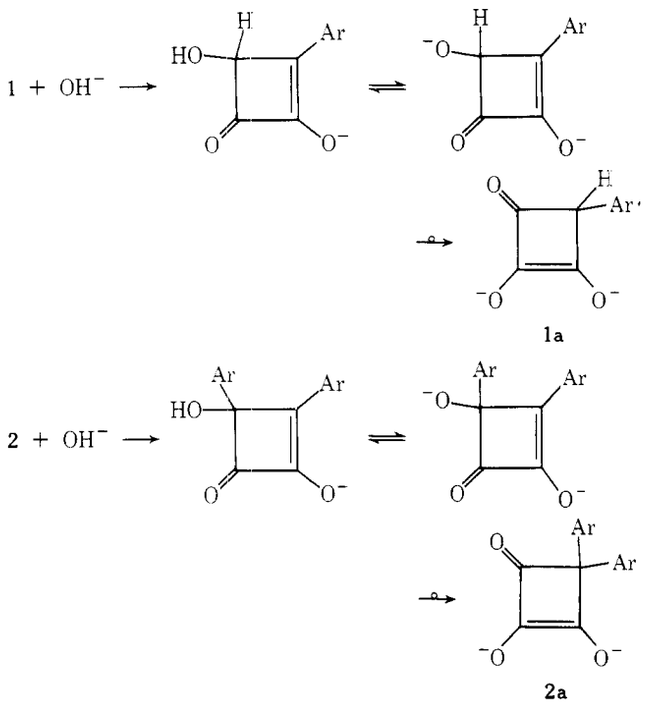
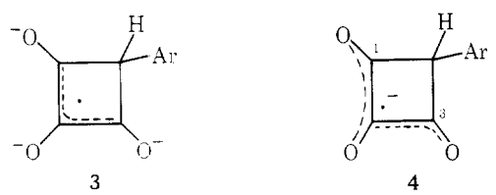


Figure 1. ESR spectrum of **8** at 25 °C observed in HMPA–(trimethylsilyl)sodium at a 0.5 mL/min flow rate through a cell with 0.05-mL dead volume. The initial concentration of **7** was 1×10^{-3} M.

Scheme I



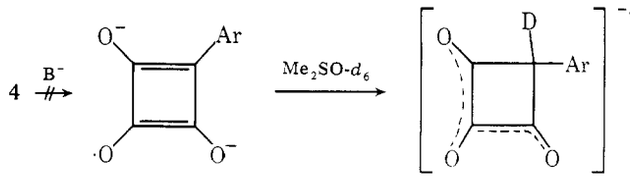
hfsc by the aromatic ring would be absent. In a system such as **4** the magnitude of the hfsc for H-4 will be a function of $(c_1 + c_3)^2$ where c_1 and c_3 are the coefficients in the singly occupied MO. The absence of hydrogen–deuterium exchange in Me_2SO-d_6 as reported by Concepcion and Vincow[2] can be rationalized with structure **4** in terms of the cyclobutadienoid structure required for this process (Scheme II).



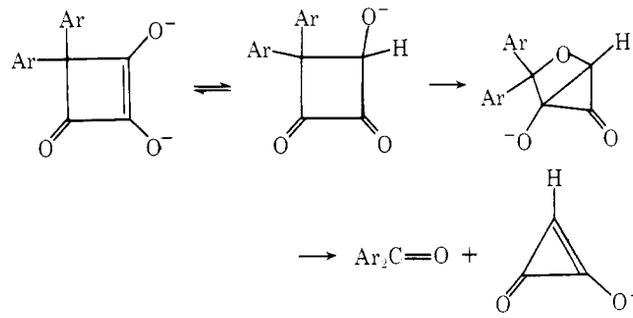
3 **4**

The observation of benzophenone ketyl from **2** is a perplexing observation to rationalize even after **2a** is considered as an intermediate. The possibility exists that it may occur partially or wholly from a photochemical transformation. A Haller–Bauer type cleavage of the carbocyclic ring in **2a** by an oxy anion seems to be the required reaction course. A possible intramolecular formulation is presented in Scheme III.

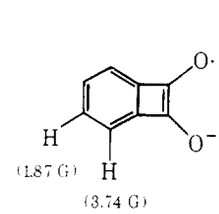
Scheme II



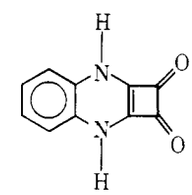
Scheme III



In the search for other cyclobutene semidiones in addition to the known **6**,[8] we have investigated the reduction of **7**. A

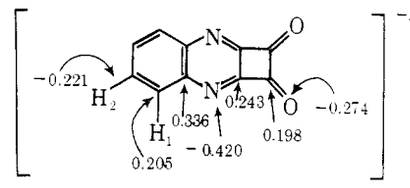


6



7

radical anion was easily detected by treatment with HMPA–lithium in a static system or HMPA–(trimethylsilyl)sodium in a flow system. The hfsc consistent with Figure 1 were a^N = 4.75 (2) G and a^H = 1.25 (2), 0.95 (2) G with a line width of 0.25 G. The persistency of this species as well as the number and magnitude of hfsc suggests that disproportionation or oxidation occurred to give the quinoxaline derivative **8**. Coefficients in the HOMO calculated by the Hückel technique with $\alpha_N = \alpha_O = \alpha_C + 1.2\,\beta_{CC}$, $\beta_{CC} = \beta_{CN}$, and $\beta_{CO} = 1.56\,\beta_{CC}$ as listed in structure **8**, led to predicted hfsc using $Q_{CH}{}^H = -27$ and $Q_N{}^N = +25$ of $a^N = -4.5$, $a_1{}^H = -1.1$, and $a_2{}^H = +1.3$ G.



8

In the quinoxaline radical anion itself the corresponding hfsc are a^N = 5.6 G and a^H = 2.3, 1.0 G, whereas in the phenazine radical anion the assignments are a^N = 5.1, $a_1{}^H$ = 1.9, $a_2{}^H$ = 1.6 G.[9]

Experimental Section

3-Phenylcyclobutene-1,2-dione,[10] 3,4-diphenylcyclobutene-1,2-dione,[11] and 1,2,3,8-tetrahydro-1,2-dioxocyclobuta[*b*]quinoxaline[12] were prepared by literature procedures.

ESR spectra were recorded with a Varian E-3 spectrometer using a flat aqueous sample or flow cells. Spectra were simulated with a

Japan Electron Optics Laboratory Co. JNM-RA-1 spectrum accumulator presuming Lorentzian line shapes.

Static experiments were performed by use of an inverted H-type mixing cell under nitrogen or argon.[13] HMPA was distilled immediately before use from calcium hydride under reduced pressure. Me_2SO was thoroughly dried with molecular sieves before use. For HMPA–lithium reductions a volume of HMPA sufficient to form a 10^{-3} M solution of the ketone was placed in the two arms of the cell and deoxygenated by a stream of nitrogen for 0.5 h. The ketone was added to one arm of the cell and a pellet of freshly cut and cleaned lithium added to the other arm. The nitrogen purge was continued for a few minutes after the lithium solution had turned deep blue. At this point the solutions were mixed and drained into the fused silica cell for measurement. HMPA–(trimethylsilyl)sodium reductions were performed in a similar manner except that sodium methoxide was dissolved in a HMPA solution of hexamethyldisilane (Pierce Chemical Co.) in one arm of the cell. Flow experiments were performed as previously described for the Me_2SO–potassium *tert*-butoxide system using upflow through a Varian V-4549A cell with a dead space of ~0.05 mL. Flow rates could be adjusted by motor driven syringes so that ESR measurements could be made from 0.1 s to a few minutes after mixing.

Registry No.—**1**, 3947-97-5; $1^{-}\cdot$, 65405-28-9; **2**, 24234-76-2; $2^{-}\cdot$, 65405-27-8; **7**, 20420-52-4; **8**, 64014-05-7.

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(14) **Note Added in Proof.** Diphenylcyclobutene-1,2-semidione is also formed slowly when diphenylcyclopropenone is treated with potassium *tert*-butoxide in Me_2SO (experimental results with Dr. T. Morita). Under these conditions $2^{-}\cdot$ has a lifetime of hours. The reaction involves an example of carbonyl insertion, $R_2C{=}O + CO + e^- \rightarrow RC(O\cdot){=}C(O^-)R$: see G. A. Russell, D. E. Lawson, and L. A. Ochrymowycz, *Tetrahedron*, **26**, 4697 (1970).

An Ethoxycarbonyl Migration from an Amide Nitrogen to Oxygen[1]

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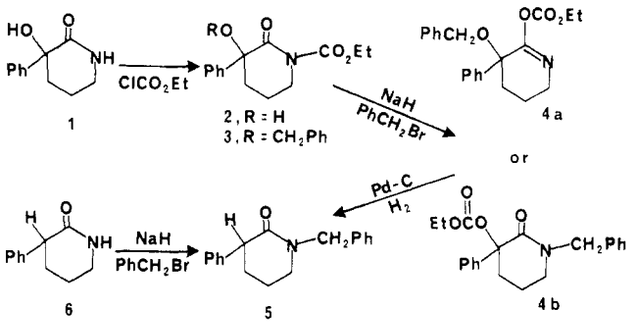
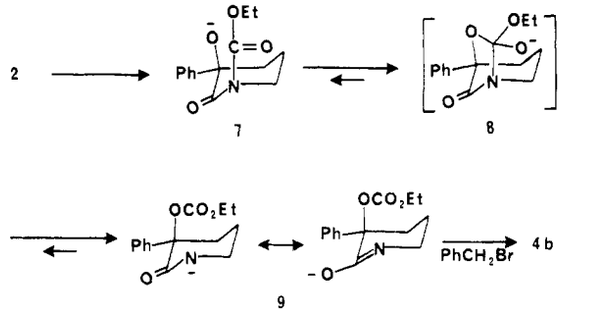
We wish to report what appears to be the first example of an ethoxycarbonyl group migration from an amide nitrogen to oxygen. Previous literature reports have shown that migration of the ethoxycarbonyl group can be a facile process. As early as 1906 it was shown by Blaise and Courtot[2] that an ethoxycarbonyl group could migrate more readily than a methyl group to a positive center. Subsequent reports have been very few in number but have included examples of alkoxycarbonyl shifts to positive, neutral, and negative centers.[3] The only studies that we have seen involving alkoxycarbonyl migration between nitrogen and oxygen are those on the 2-aminophenols,[3,4] *N*-ethoxycarbonylhydrastinine,[5] and substituted isoquinolines,[6] none of which involved an amide nitrogen.

Scheme I



Scheme II



Attempted O-benzylation of **2**, prepared from $ClCO_2Et$ and **1** as shown in Scheme I, did not yield the expected product **3**. The ^{1}H-NMR spectrum of the product was consistent with structure **3**, but the IR spectrum contained carbonyl absorptions at 1750 (carbonate) and 1660 cm^{-1} (lactam or lactim), suggesting a rearranged product such as **4a** or **4b**. The largest fragment in the mass spectrum was *m/e* 263 ($M^+ - 90$). Hydrogenolysis of this product yielded a compound for which the IR spectrum indicated an N-substituted lactam (1640 cm^{-1}),[7] and the ^{1}H-NMR spectrum showed loss of the ethoxycarbonyloxy group and the presence of two types of benzylic protons at δ 4.7 (singlet, 2 H) and 3.7 ppm (multiplet, 1 H). These observations were consistent with structure **5**. Since amides undergo N-alkylation under basic conditions,[8] an unambiguous synthesis of **5** (Scheme I) using 3-phenyl-2-piperidinone (**6**),[9] $PhCH_2Br$, and NaH confirmed the structure assignment. The rearranged product was therefore formulated as structure **4b**. The lack of a parent ion in the mass spectrum of **4b** is consistent with a facile loss of the ethoxycarbonyloxy group via a McLafferty rearrangement, which is not possible in **4a**.

Either an intermolecular or intramolecular mechanism can be envisioned for the conversion of **2** to **4b**. However, it is unlikely that an intermolecular mechanism is operative since none of the O-benzylated product **3** was detected, even though $PhCh_2Br$ was present before NaH addition. A mechanism which is consistent with previous studies on ethoxycarbonyl migrations from nitrogen to oxygen[5,6] is suggested in Scheme II.

As depicted in Scheme II, it is likely that any equilibrium between **7** and **9** favors the delocalized amide anion **9**. Alternatively, it is possible that the equilibrium favors anion **7** and that the $PhCH_2Br$ simply reacts much faster with the amide anion **9**, thus trapping a relatively small fraction of **9** as it is formed to yield **4b**. In order to test this possibility, compound **2** was subjected to the conditions of rearrangement but without $PhCH_2Br$ (Scheme III). In this case the only product formed was **10**, and TLC showed no remaining starting material.

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