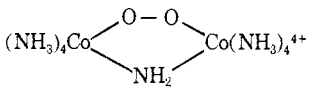
compound is essentially diamagnetic at room temperature. While the cyclopentadienyl ligands probably force the iron atoms into a low-spin configuration, the absence of appreciable paramagnetism is still surprising since allocation of charge in the conventional manner, *i.e.*, Cp^-, $C_2H_5S^-$, and S_2^{2-}, leaves Fe^{3+} ions, with at least one unpaired electron each, there being no metal–metal bond. If, on the other hand, the iron atoms are spin-paired Fe^{2+}, then the two sulfur atoms must be formulated as S_2^0. There are, in fact, three plausible resonance forms

$$\underset{\text{I}}{Fe^{3+}\ {}^{-}S\text{—}S^{-}\ Fe^{3+}} \longleftrightarrow \underset{\text{II}}{Fe^{2+}\ {}^{\cdot}S\text{---}S^{-}\ Fe^{3+}} \longleftrightarrow \underset{\text{III}}{Fe^{2+}\ S{=}S\ Fe^{2+}}$$

and the structure suggests that form II predominates. The dihedral angle about the S–S bond is 0°, as it is for the superoxide bridge in

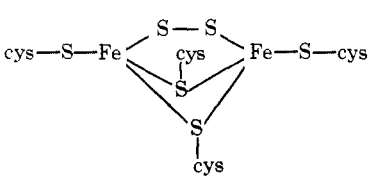


whereas a dihedral angle close to 90° is normal for disulfides.[8] Moreover, the S–S distance, 2.02 Å, is shorter than the expected single bond distance, 2.10 Å, for a planar cis disulfide and suggests a π bond order of about one-third.[8] The distance in double bonded $S_2^0(^3\Sigma_g^-)$ is 1.889 Å.[9]

The apparent diamagnetism can also be ascribed to strong magnetic coupling between Fe^{3+} centers *via* the bridging ligands. Since a superexchange mechanism involves a degree of electron transfer from the bridging ligand to the coupled metal atoms,[10] this formulation is equivalent to electron delocalization through the above resonance forms. A modest contribution from resonance forms II and III would be sufficient to eliminate any observable paramagnetism at room temperature. Alternatively, superexchange might operate through the ethyl sulfide bridges.

The electronic structure of $[CpFe(SC_2H_5)S]_2$ should be capable of better definition through spectroscopic studies, which are currently underway. The redox chemistry is also of interest. A polarogram in acetonitrile (0.1 *M* $LiNO_3$) supporting electrolyte gave an anodic wave at 0.17 V *vs.* sce but no cathodic wave above the breakdown potential of the solvent. The dark green compound was obtained in low yield by alumina chromatography of the products of the reaction of $[Cp_1Fe(CO)_2]_2$ with ethyl polysulfide (a mixture of tri- and tetrasulfide) in refluxing methylcyclohexane.

The present work suggests an addition to the catalog of candidate structures[2] for those ferredoxins which contain two iron atoms and two labile sulfur atoms, *viz.*



A

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(cys = cysteine) structure A. Although it is now well established[11] that the reduced form of these proteins contains high-spin Fe(II) in a tetrahedral sulfur environment, strongly exchanged coupled to a high-spin Fe(III) partner, the oxidation state of the labile sulfur is still uncertain, both sulfide[12] and disulfide[13] being candidates. The possibility that cysteine sulfur is involved in bridging the iron atoms, as in structure A, is of interest in connection with the suggestion of Dunham, *et al.*,[11] that an apparent inconsistency between magnetic susceptibility and nmr data on reduced spinach ferredoxin can be resolved by assuming that a cysteine residue is under the influence of both Fe(II) and Fe(III) centers.

Structure Determination. The structure was solved by direct methods, on intensity data collected to $2\theta = 105°$, using the θ–2θ scan technique on a Picker four-circle diffractometer, with Ni-filtered Cu Kα radiation. The intensities of 1711 reflections were above 2σ. The data were corrected for Lorentz and polarization effects and for absorption. The transmission coefficient ranged from 0.157 to 0.257, based on a value of $\mu = 177.7$ cm^{-1}. Least-squares refinement, with anisotropic thermal parameters for all nonhydrogen atoms, gave a final R factor of 0.039. The crystal was monoclinic, space group $P2_1/c$, with four molecules of $[CpFe(SC_2H_5)S]_2$ per unit cell, of dimensions $a = 17.374$, $b = 8.125$, and $c = 12.782$ Å and $\beta = 108.37°$; $d_x = 1.661$, $d_m = 1.639$ g/cm^3 (flotation).

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Gregory T. Kubas, Thomas G. Spiro*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Aristides Terzis
Department of Chemistry, University of Montreal
Montreal, Quebec, Canada

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Isopropylidenecyclobutenone

Sir:

The methylenecyclobutenone system represents one of the few remaining unknowns among the cyclobutadienes and related compounds.[1] Although several highly substituted derivatives are claimed,[2,3] they do not yield any information on the characteristics of the methylenecyclobutenone moiety. We now report the synthesis of isopropylidenecyclobutenone (**5**), the first simple derivative in which the salient features of the ring system can be discerned.

Our synthesis route involved preparation of a suitable compound **2** which could yield **5** by Diels–Alder retrogression.[4] While this would not be expected to be successful for the synthesis of the unsubstituted cyclo-

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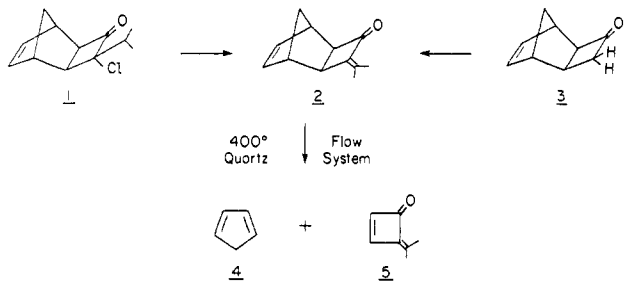
butenone,[5] *i.e.*, by pyrolysis of **3**,[6] the delocalization stability of approximately 1.2β estimated[7] for **5** should allow this system to survive the temperatures required for the retro-Diels–Alder reaction.

Scheme I

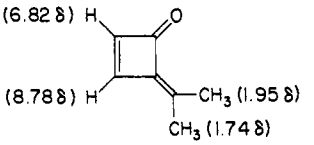


The recently described cycloadditions of haloketenes to norbornadiene[8,9] provided such a route. Thus **1** was prepared in 6% yield from chloroisopropylketene and norbornadiene.[9] Treatment of **1** with 1,5-diazabicyclo[4.3.0]non-5-ene in hexane yielded **2** quantitatively. Alternatively, **3**,[8] obtained by dehalogenation of the dichloroketene cycloadduct of norbornadiene, was converted to **2** in 66% yield by treatment with acetone and 1 *N* aqueous NaOH.[10]

The structural assignment of **2** was based on the two independent methods of synthesis plus the following data: pmr (CCl_4) absorptions at δ 6.24 (m, two olefinic protons), 3.07 (m, two bridgehead protons), 2.75 (m, two bridgehead protons), 2.06 (s, CH_3), 1.84 (s, CH_3), and 1.43 (ab, CH_2); major mass spectral fragments at *m/e* 174 (40% rel abundance, parent (M^+)), 159 (65, M − CH_3, metastable for 174–159), 131 (80, M − CH_3 and CO), 91 (80, tropylium), 108 (28, M − cyclopentadiene, rel abundance varies with conditions—possible thermal cleavage), 80 (87, 108 − CO, metastable for 108–80), 79 (87, 108 − HCO), and 66 (100, M − **5**, rel abundance varies with conditions—possible thermal cleavage); uv $\lambda_{max}^{C_6H_{12}}$ 256 nm (log ϵ 3.70), 357 (1.78), and 375 (1.78); ir ν_{max}^{neat} 1550 cm^{-1} (C=C), 1650 (C=C), and 1730 (CO); bp 59° (0.07 mm). *Anal.* Calcd for $C_{12}H_{14}O$: C, 80.0; H, 9.3. Found: C, 79.9; H, 8.9.

Slow passage of **2** in a stream of nitrogen through a quartz tube 2.5 cm in diameter packed with 20 cm of quartz chips heated at 400° and into a liquid nitrogen cooled trap caused about 25% conversion to **4** and **5** as estimated by pmr examination of the crude reaction product. The crude product could be recycled for higher conversions. The **4** was removed readily at room temperature and 20 mm and **5** distilled at room temperature when the pressure was reduced to 0.1 mm and was collected as a colorless crystalline solid in a trap cooled by Dry Ice–isopropyl alcohol. Compound **5** is a colorless lachrymatory liquid at room temperature which polymerizes to a colorless glass with a half-life of about 5 min. The solution stability was greater and allowed spectroscopic studies.

The 60-MHz pmr spectrum of **5** (CCl_4) had absorptions at δ 6.82 (m, $J_{\alpha\beta}$ = 3.0 Hz, $J_{\alpha\text{-}CH_3} < 1$ Hz, 1 H α to carbonyl), 8.78 (d, $J_{\beta\alpha}$ = 3.0 ± 0.1 Hz, 1 H β to carbonyl), 1.74 (m, $J_{CH_3\text{-}\alpha}$ and $J_{CH_3\text{-}CH_3} < 1$ Hz, CH_3), and 1.95 (m, $J_{CH_3\text{-}\alpha}$ and $J_{CH_3\text{-}CH_3} < 1$ Hz, CH_3). The absorptions for the olefinic protons α and β to the carbonyl are remarkably similar to those reported for cyclobutenone (α, δ 6.17; β, δ 8.35; $J_{\alpha\beta}$ = 2.5 Hz)[5] but shifted to slightly lower fields owing to additional unsaturation in **5**. The chemical shift of the ring proton



of phenylcyclobutenedione[11] measured for this study is slightly lower yet at δ 9.56 in $CDCl_3$ and 10.13 in DMSO-d_6. As suggested by Sieja[5] for cyclobutenone, this chemical shift is probably due to the unique geometric position of these protons with respect to the magnetic anisotropy of the unsaturated system and is not necessarily a reflection of some abnormal polarization of the system, which should also be evident in the ultraviolet spectrum.

Both ^{13}C satellites of the lowest field proton (β to the carbonyl) were observable and yielded $J_{^{13}CH}$ = 177.0 ± 0.4 Hz (CCl_4) and confirmed the $J_{\alpha\beta}$ = 3.0 Hz. This indicates a somewhat larger s character than a "normal" sp^2-hybridized carbon as in benzene ($J_{^{13}CH}$ = 159.0 Hz) and ethylene ($J_{^{13}CH}$ = 157.0 Hz).[12] Similarly, the ring proton of phenylcyclobutenedione[11] showed $J_{^{13}CH}$ = 181.7 Hz in $CDCl_3$ and 185.4 Hz in DMSO-d_6 measured for this study by the ^{13}C satellite method and confirmed by ^{13}C magnetic resonance spectroscopy. These coupling constants may be of some diagnostic value in examining related systems.

The mass spectral fragmentation of **5** was not unusual, with major peaks at *m/e* 108 (86% rel abundance, parent (M^+)), 93 (31, M − CH_3), 80 (54, M − CO, with metastable for 108–80), 79 (100, M − HCO), 65 (71, 93 − CO, with metastable for 93–65), 39 (79, 65 − C_2H_2 with metastable for 65–39). The ir absorptions at ν_{max}^{neat} 1640 cm^{-1} (C=C), 1680 (C=C), and 1740 (CO) are correlatable with such a strained system.[1] The uv absorptions at $\lambda_{max}^{C_6H_{12}}$ 223 nm (log ϵ 4.42) and 305 (log ϵ 2.73) bear some similarity to those reported for 3,4-dimethylcyclobutenedione [λ_{max}^{EtOH} 216 nm (log ϵ 4.27) and 340 (log ϵ 1.41)],[13] both of which are similar to α,β-unsaturated ketones and indicate that the chromophore is behaving as a cross-conjugated system.

We are now studying the extension of this method to the syntheses of related systems and to the chemical reactions of all of these.

Acknowledgment. The authors wish to thank Dr. T. H. Regan for 90-MHz pmr and ^{13}C magnetic reso-

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nance studies and Mr. D. P. Maier for mass spectral studies.

(14) IAESTE Student, Summer 1971. Department of Organic Chemistry, University of Geneva, 1211 Geneva 4, Switzerland.

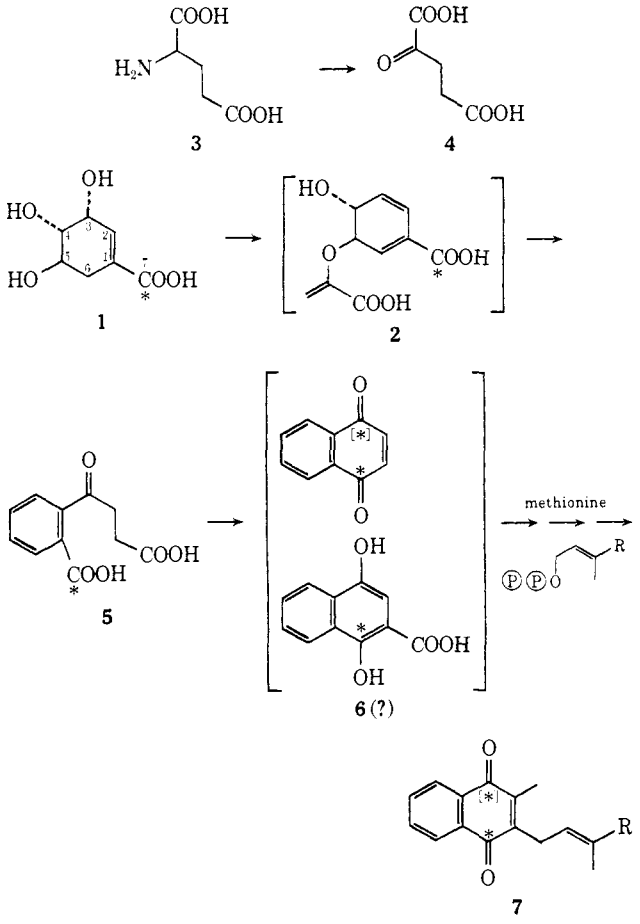
Roy C. De Selms,* François Delay[14]
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650
Received August 4, 1972

Biosynthesis of Menaquinones. Dissymmetry in the Naphthalenic Intermediate

Sir:

The biogenesis of bacterial menaquinones has been studied for many years and, in spite of experimental difficulties, intermediates and their sequence of involvement can now be identified with some degree of confidence (Scheme I). Experiments with numerous

Scheme I

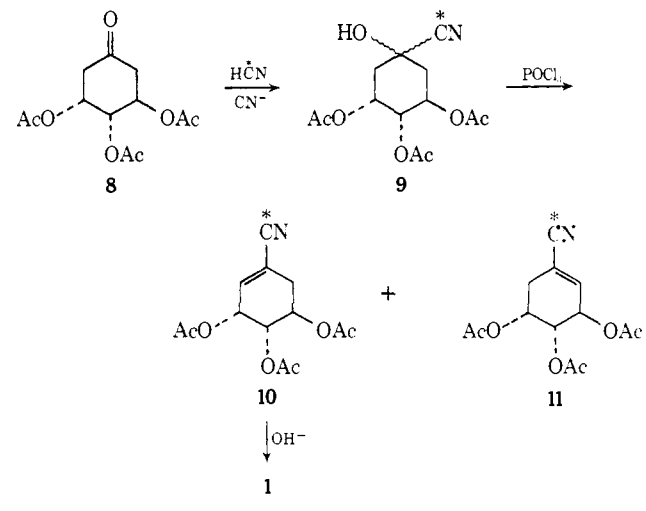


organisms allow definite assignment of the seven carbons of shikimic acid (**1**) to the benzenoid portion of the naphthoquinone nucleus,[1] with the carboxyl carbon forming one of the quinone carbonyls.[1b,c,f,h] The remaining three carbons of the naphthalene system are provided by C-2, -3, and -4 of glutamate (**3**)[1h,2] or its transamination product, 2-oxoglutarate (**4**),[3] C-2 becoming the other quinone carbonyl. Furthermore, the carbons (C-1 and -2) forming the ethylenic bridge of shikimic acid become the corresponding 9,10-bridge in the naphthoquinone.[1e,g] Efficient incorporation of *o*-succinylbenzoic acid (**5**)[1h,4] seems to provide strong evidence that the primary addition product of 2-oxoglutarate (or glutamate) and shikimate [or chorismate (**2**)[1a,g,4]] is immediately aromatized. The final sequence of cyclization and alkylation, however, remains in doubt. Several preformed naphthalenoid compounds, *i.e.*, 1,4-naphthoquinone,[1h] 2-methyl-1,4-naphthoquinone,[1h] α-naphthol,[1c-g,5] and 2-hydroxy-naphthoquinone,[1h] have been tested as precursors. In general, the results have been negative, although *S. aureus*,[1e] *A. aerogenes*,[1f] and *F. nigrescens*[6] will apparently incorporate 2-methyl-1,4-naphthoquinone and/or 1,4-naphthoquinone. A final restriction placed upon naphthoquinone biosynthesis is that the quinone oxygens must be derived from water.[7]

In view of the above state of knowledge we have directed our attention to the symmetry or dissymmetry of the as yet unidentified naphthalenic intermediate **6**. For example, if 1,4-naphthoquinone or 1,4-naphthohydroquinone were an intermediate, then a label introduced unsymmetrically would result in symmetrically labeled menaquinone. On the other hand, if no symmetrical intermediate were involved, the location of label in the menaquinone would allow one to define the orientation of the alkylations with respect to the carbonyl derived from shikimic acid. In order to ascertain the symmetry of the unknown intermediate, we have chosen the MK-9(II-H_2)–*Mycobacterium phlei* system, using [7-^{14}C]shikimic acid as the label source.

Specifically labeled shikimic acid was prepared (Scheme II) by addition of H^{14}CN to ketone **8**,[8] yielding

Scheme II



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