

Figure 2. Absorbance difference spectrum for $\text{Ni}(\text{Et}_4\text{dien})\text{Cl}_2$ in ethanol, $10^{-3} \text{ mol dm}^{-3}$. Laser irradiation at 530 nm.

and although the relatively high conductance of the solutions precluded transient conductivity studies, spectrophotometric measurements in the 380–500-nm range showed a rapid absorbance increase and subsequent decay with a first-order time constant of $0.3 \mu\text{s}$ at 20°C when the solution was irradiated at 530 nm. The transient spectrum is shown in Figure 2 and is very similar in shape to the corresponding spectrum in acetonitrile, but with λ_{max} showing a slight blue shift. There can be little doubt that this is the spectrum of a five-coordinate species formed in an association reaction between Cl^- and the photoexcited NiLCl^+ complex, especially since there is no evidence for the five-coordinate complex in ethanol in normal, equilibrium (“dark”) conditions.

The explanation for the ready occurrence of the photoassociation reaction may lie in the distortion of the (vibrationally equilibrated) excited state produced by the laser pulse. Our previous studies^{4b,9} of the laser flash photolysis of planar Ni(II) complexes, as well as earlier spectral and photochemical evidence,¹⁰ strongly suggest that some of the ligand field excited states of d^8 planar complexes may be tetrahedrally distorted. In the present system, repulsion between the filled d_{z^2} orbital in planar NiLCl^+ and an approaching Cl^- ion might be lessened in the event of such a distortion of the complex away from a planar configuration. A parallel factor to be considered is the spin change accompanying the formation of paramagnetic five-coordinate product since in the altered electronic configuration the d_{z^2} orbital becomes singly instead of doubly occupied. The role of the solvent must also be taken into account,¹¹ and the details of the solvent and structural relaxation processes leading from the initially populated Franck–Condon state to the observed five-coordinate species remain a matter for future investigation.

The photoreversibility of the system widens the access to the kinetic parameters which characterize the ground electronic state interconversions and thus provides a check on the internal consistency of the assignments of the relaxation processes which follow photoexcitation. Systems of this type should also be useful models for testing some current proposals¹² concerning the similar nature of transition states for thermal reactions and the thermally equilibrated excited states which are thought to mediate the photochemical reactions of metal complexes.

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References and Notes

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- (5) Similar conductivity decreases were observed for the bromide complex and also in acetone as solvent. No conductivity changes could be detected when $\text{Et}_4\text{NCl}/\text{CH}_3\text{CN}$ solutions of comparable resistance to the test solutions were irradiated at either 530 or 1060 nm.
- (6) As discussed in ref 3, NiLCl^+ and $\text{NiLCl}^+\|\text{Cl}^-$ have identical absorption spectra but the latter species is strongly favored at equilibrium.
- (7) Low-temperature experiments are in progress to study the faster relaxation. The two relaxations are evidently strongly coupled, and the observed τ values will be approximations to the true relaxation times. Following the photoassociation, the relaxation spectrum is dominated by the ion pair \rightleftharpoons ion relaxation ($\sim\tau_1$), while at a later time the major contribution comes from the five-coordinate complex \rightleftharpoons ion-pair relaxation ($\sim\tau_2$).
- (8) See, e.g., C. F. Bernasconi, “Relaxation Kinetics”, Academic Press, London and New York, 1976, Chapter 3.
- (9) J. J. McGarvey and J. Wilson, *J. Am. Chem. Soc.*, **97**, 2531 (1975).
- (10) (a) For a recent discussion see P. C. Ford, R. E. Hintze, and J. D. Petersen in “Concepts of Inorganic Photochemistry”, A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, p. 237; (b) see also papers cited in ref 9.
- (11) Investigations on other four-coordinate Ni(II) complexes in polar media suggest a significant role for the solvent in the excited-state reactivity: C. J. Cairns, L. H. Campbell, and J. J. McGarvey, experiments in progress.
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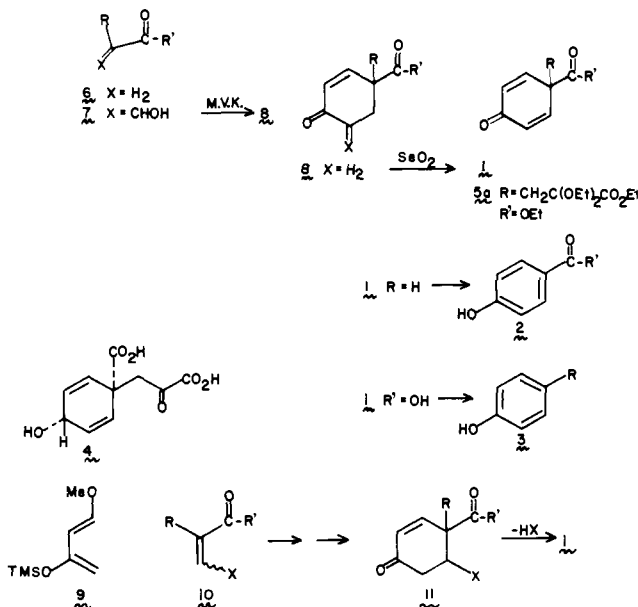
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Diels–Alder Reactions of α -Phenylsulfinylmethylene-carbonyl Compounds. The Synthesis of Disodium Prephenate Dimethyl Acetal

Sir:

Cyclohexadienones such as **1** might well service several synthetic objectives. If $\text{R} = \text{H}$, phenol **2** would be produced, presumably under the conditions of the formation of **1**. Alternatively, if $\text{R} \neq \text{H}$, decacylation (e.g., decarboxylation) of the vinylogous β -dicarbonyl system would lead to phenol **3**. Of course, acid-catalyzed dienone–phenol rearrangements¹ and photochemical transformations² could also be exploited.

In addition to such general possibilities, a suitable version of **1** might serve as a precursor to prephenic acid (**4**), a central

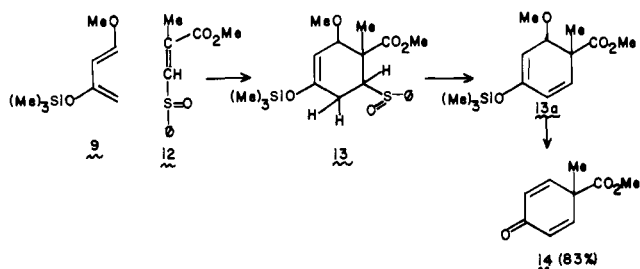


biosynthetic intermediate between shikimic acid and various aromatic natural products.³ Indeed, Plieninger had employed compound **5a** in a route to prephenic acid.⁴ However, no intermediates beyond **5a** were characterized. The actual evidence for the synthesis of prephenic acid rested on presumptive kinetic arguments rather than on the more discriminating regimen of isolation, purification, and comparison with authentic material.⁵

Improved access to such dienones, traditionally obtained⁵ through the route **6** → **7** → **8**, was envisioned by a Diels–Alder logic, via the highly reactive **9**⁶ with a modified dienophile, **10**. The modifying group, X, must fulfill several conditions. First, **10** must be readily available from **6** (or **7**). Second, the function X must neither seriously undermine the dienophilicity of the system nor compete with the acyl group in defining the sense of cycloaddition. Finally, the elimination of HX (**11** → **1**) should be straightforward.⁷

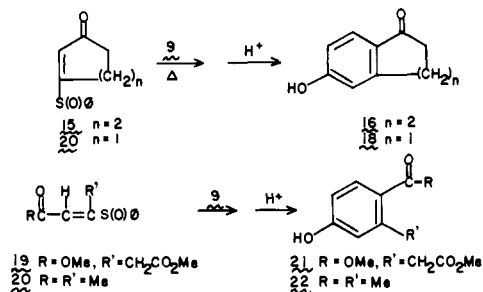
We have found the arrangement X = phenylsulfinyl to nicely harmonize these conditions.^{8,9} Accordingly, we describe below (i) the synthesis of a variety of systems such as **1**; (ii) the use of such systems, R = H, in a new synthesis of phenols (**2**); and (iii) the synthesis of disodium prephenate dimethyl acetal (**32a**). Our experience in this synthesis defines with greater precision than heretofore the difficulties to be anticipated in a synthesis of the free prephenic acid (**4**).

Reaction of diene **9** (8 equiv) with sulfoxide **12**^{10,11} took place in toluene under reflux. After 50 h, the reaction mixture was hydrolyzed with 4:1 THF–1% HCl. Chromatography on silica gel afforded an 83% yield of 4-carbomethoxy-4-methylcyclohexadienone (**14**).¹² Evidently, the homoallylic phenylsulfinyl group of the presumed adduct, **13**, suffers pyrolytic elimination under these conditions of cycloaddition.⁷



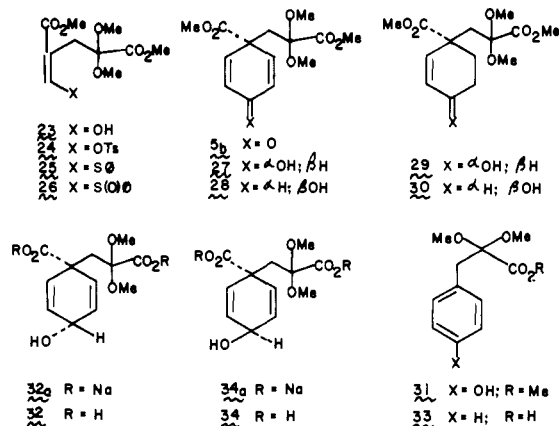
The application of the method to the de novo synthesis of phenols is now described. For this purpose, R in structure **10**, and thus in **1**, is hydrogen. Hence the cycloaddition–elimination sequence culminates in aromatization (**1** → **2**). Reaction of sulfoxide **15**^{10,11} with diene **9** in xylene under reflux for 24 h afforded an 80% yield of tetralone **16** (mp 150–152 °C; lit.¹³ 150–152 °C). Similarly sulfoxide **17**^{10,11} reacts with **9** under similar conditions to provide, after unravelling, a 68% yield of indanone **18** (mp 183–184 °C; lit.¹⁴ 182°).

Oriental dominance is also exerted by the carbonyl group over the phenylsulfinyl function, even when this requires initial bond formation at a disubstituted, rather than monosubstituted, carbon. Thus, sulfoxides **19** and **20**^{10,11} gave respectively phenols **21** and **22** after cycloaddition with diene **9**.



In no case could one discern any products which would have arisen from the alternate mode of cycloaddition.

The application of this new cyclohexadienone synthesis to the prephenate problem is now described. Tosylation of readily available **23**⁵ afforded **24**¹⁵ which, upon reaction with sodium thiophenoxide, gave sulfide **25**¹⁵ in 90% yield. Oxidation of **25** with sodium metaperiodate provided the dienophile **26**,¹⁵ mp 85–87 °C, in 87% yield. Heating **26** with diene **9** (4 equiv) in toluene under reflux for 72 h, followed by mildly acidic workup and chromatography on silica gel, gave a 50% yield of dienone **5b**, mp 73–75 °C.^{15,16}



Treatment of **5** with sodium borohydride gave complex mixtures of the dienols (**27** and **28**), allylic alcohols (**29** and **30**), and cleavage product **31**.¹⁷ Much better results were achieved by reduction of **5** with 9-borabicyclo[3.3.1]nonane (THF, room temperature) according to Brown.¹⁸ This afforded an 80% yield of the dienols **27** and **28**, after chromatography on silica gel. Rechromatography on silica gel and elution with 1% methanol–chloroform gave homogeneous **28**^{15,19} (26% yield; mp 96–98 °C; R_f^{20} (5% MeOH–CHCl₃) 0.65) and homogeneous **27**^{15,19} (35% yield; R_f^{20} (5% MeOH–CHCl₃) 0.50).

Treatment of **27** with 2 equiv of aqueous NaOH–THF for 3 days gave homogeneous disodium prephenate dimethyl acetal (**32a**) (δ^{21} (D₂O, 250 MHz) 2.29 (s, 2), 3.11 (s, 6), 4.51 (t, $J = 3.0$ Hz, 1), 5.80 (dd, $J_1 = 10.2$, $J_2 = 3.0$ Hz, 1), 5.94 (dd, $J_1 = 10.2$, $J_2^{22} = 1.3$ Hz, 1) ppm). When an aqueous methanolic solution was acidified to pH 3.5 at 0 °C and extracted with chloroform, a 64% isolated yield of phenylpyruvic acid dimethyl acetal (**33**) was obtained. No substance corresponding to prephenic acid dimethyl acetal (**32**) could be discerned. However, treatment of an identical solution with Amberlite acid resin at –60 °C, followed immediately by esterification with diazomethane, gave a 70% isolated yield of **27**.

The epi compound **28** undergoes, qualitatively,²³ very similar reactions. Saponification of **28** gives the epi disodium salt **34a** (δ^{21} (D₂O, 250 MHz) 2.33 (s, 2), 3.14 (s, 6), 4.38 (t, $J = 3.44$ Hz, 1), 5.82 (dd, $J_1 = 10.1$ Hz, $J_2 = 3.44$ Hz, 2), 5.96 (dd, $J_1 = 10.1$ Hz, $J_2^{22} = 0.84$) ppm). Under identical acidic conditions, **34a** is converted (72%) to **33** or, by immediate esterification, recycled to **28**. The free diacid **34** was not characterized. Thus, at least in the dimethyl acetal series, the prephenate and *epi*-prephenate systems are quite stable as the carboxylate salts. In both cases, the free acids decarboxylate very rapidly but are viable for short periods of time, as seen by the recycling experiments.

In future research, we hope to study any rate differences which might be present in the dehydrative decarboxylations of **32** vs. **34**.²³ Furthermore, we hope to address the synthesis of **4**. This must involve a highly labile blocking group for the ketone. For the moment, it must be said that the central bio-

synthetic intermediate, **4**, which is the subject of considerable discussion and the object of extensive biochemical experimentation, remains uncharacterized from natural or synthetic sources.

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- (8) H. Hogveen, G. Maccagnani, and F. Montanari, *J. Chem. Soc. C*, 1585 (1967).
- (9) Several other X groups were studied. Systems such as **13** (X = OMe and X = SBU) were insufficiently dienophilic. Systems of the type X = OAc were sufficiently dienophilic, but the elimination of HX could not be smoothly achieved.
- (10) The sulfoxides were prepared from the corresponding sulfides by oxidation with sodium metaperiodate. The sulfides were prepared from the β -dicarbonyl compounds using the methodology of Ireland and Marshall. The stereochemistry of the sulfoxides is not known with certainty.
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- (15) The structure of this compound was established by (a) infrared, NMR, and mass spectra; (b) its combustion analyses within 0.4% of theory.
- (16) The diethyl ester, diethyl acetal was described by Plieninger⁵ as an oil.
- (17) Plieninger⁵ had recognized the formation of the "ketone cleavage" product **34** from the sodium borohydride reduction. However, since no NMR spectra were measured, the formation of the tetrahydro allylic alcohols **32** and **33** was missed. In our work these substances were not separated from one another.
- (18) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **42**, 1197 (1977).
- (19) The structures of the synthetic dienols **30** and **31** were rigorously established by their conversion to their tetrahydro acetates. These are in turn readily differentiated through 250-MHz NMR spectroscopy. The details will be published in the full paper.
- (20) The R_f values were determined on commercial (E. M. Merck) precoated silica gel (60F-254 TLC) plates.
- (21) Chemical shifts are reported in parts per million relative to internal 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt hydrate (Aldrich).
- (22) The allylic couplings of the C-3 vinylic proton with the C-1 methine proton are clearly seen in the signals of the former. In the methine signal itself, this appears as line broadening and is not directly measured owing to additional broadening due to the hydroxyl group.
- (23) Eschenmoser and co-workers have effected decarboxylation-dehydration of 4-carboxycyclohex-2-en-1-ols through the use of amide acetals. This elegant reaction, leading to 1,3-cyclohexadienes, is much slower than the direct process described here leading to an aromatic ring. The effect of stereochemistry on the Eschenmoser process has also not been determined; see A. Ruttiman, A. Wick, and A. Eschenmoser, *Helv. Chim. Acta*, **58**, 1450 (1975).

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Differences in the Intrinsic Barriers between Ground- and Excited-State Electron-Transfer Reactions from Spectroscopic Franck-Condon Parameters¹

Sir:

There has been a great deal of recent interest in the electron-transfer reactions of transition metal excited states.²⁻⁴ Much of this interest derives from the possibilities of utilizing the large energy differences between ground- and excited-state species in photovoltaic cells⁵ or to decompose water.^{6,7} These excited-state reactions are also becoming important in the study of highly exergonic electron-transfer reactions in which renewed interest has been stimulated by quantum corrections to the earlier approaches.⁸⁻¹¹ Both the practical and the theoretical interest in such systems depends on the magnitudes of the intrinsic or reorganizational barriers to electron transfer. An important point which seems to have escaped the notice of investigators in this area is that difference between the intrinsic barriers for ground-state and excited-state electron transfer processes is closely related to simple spectroscopic parameters.

The best example of these differences in excited-state and ground-state properties is provided by the Cr(bpy)₃^{3+,2+} couple. Ground-state electron-transfer reactions of Cr(bpy)₃²⁺ tend to be very rapid; e.g., the Cr(bpy)₃²⁺ reduction of Fe³⁺ and Ru(bpy)₃³⁺ have rate constants of 7.3×10^8 and 2.6×10^9 M⁻¹ s⁻¹, respectively, for reactions which have free energy changes of $\Delta G^\circ = -24$ and -35 kcal mol⁻¹.⁴ These observations have been used to estimate a "self-exchange" rate constant of $k_{11} \approx 4 \times 10^8$ M⁻¹ s⁻¹² for the Cr(bpy)₃^{3+,2+} couple using the Marcus relation⁸

$$k_{12} = (K_{11}k_{22}K_{12}f_{12})^{1/2} \quad (1)$$

$$\log f_{12} = (\log K_{12})^2 / [4 \log (k_{11}k_{22}/Z^2)]$$

$$Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$$

In contrast the electron transfer quenching reactions of the ²E excited state of Cr(bpy)₃³⁺ have been found to be approximately an order of magnitude slower with comparable reagents. Thus, for ²E oxidations of Fe²⁺, Ru(bpy)₃²⁺, and Ru(NH₃)₆²⁺, the rate constants are 2.8×10^7 M⁻¹ s⁻¹ (in 0.05 M H₂SO₄; a value of 4.1×10^7 M⁻¹ s⁻¹ has been found when $\mu = 1^4$), 4×10^8 M⁻¹ s⁻¹ ($\mu = 0.2$),⁴ and 5.9×10^8 M⁻¹ s⁻¹ (in 0.05 M H₂SO₄), respectively; the respective free energy changes are -16 , -4 , and -32 kcal mol⁻¹. The value of $k_{11} \approx 4 \times 10^9$ M⁻¹ s⁻¹ for the Ru(bpy)₃^{3+,2+} couple (estimated by Sutin and co-workers),^{2b,c} and eq 1 implies a "self-exchange" rate constant of about 3×10^5 M⁻¹ s⁻¹ for the (²E)Cr(bpy)₃³⁺/Cr(bpy)₃²⁺ couple; the value of $k_{11} \approx 1.6 \times 10^9$ M⁻¹ s⁻¹ reported recently by Meyer and co-workers^{3d} results in a slightly larger value for this rate constant.¹²

That electron-transfer reactions are slower for excited-state than ground-state species implies that a change in bond lengths, angles, etc., occurs in the excited-state reactions (or that these reactions differ in "adiabaticity").¹² These differences in the ground-state and excited-state internuclear coordinates (Franck-Condon parameters) are also manifested in a Stokes shift of the ²E \rightarrow ⁴A phosphorescence compared to the ⁴A \rightarrow ²E absorption. The ⁴A \rightarrow ²E absorption of Cr(bpy)₃³⁺ is obscured by a relatively intense ⁴A \rightarrow ⁴T band. However, assignment of this transition to a shoulder at ~ 600 nm would correspond to a Stokes shift of $\sim 0.15 \mu\text{m}^{-1}$, a reasonably typical value for chromium(III) complexes.¹³ This suggests an average difference of $\sim 0.08 \mu\text{m}^{-1}$ (~ 2.3 kcal mol⁻¹) between the (²E)Cr(bpy)₃³⁺ excited state and the (⁴A)Cr(bpy)₃³⁺ ground-state Franck-Condon parameters. Since the effective reorganizational barriers for the self-ex-