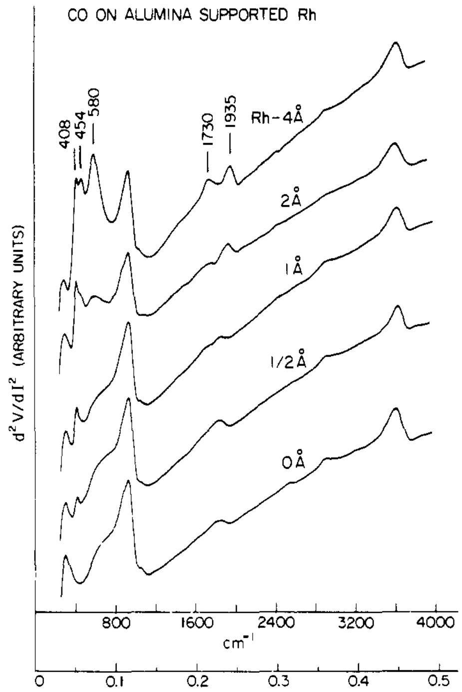

Figure 2. Tunneling spectra of CO adsorbed on various thicknesses of Rh evaporated on alumina. Note that new peaks appear as the thickness of Rh increases implying new types of bonding. For all these spectra the CO exposure was ≈10^3 Langmuir.

these two new peaks implies the existence of new types of bonding. The broad band centered at 580 ± 10 cm^{-1} may contain contributions from carbon-oxygen bending vibrations.[4]

The intensity of the peaks in the carbon-oxygen stretching region is surprisingly small and partially obscured by the second harmonic of the strongest peak in the background spectra. Furthermore, a relatively large peak shift due to the top metal electrode would be expected because of the large dipole derivative of the carbon-oxygen bond (possibly comparable to the 2% downward shift seen in the hydrogen-oxygen stretching frequency).[5] We do not understand why the CO stretching modes are weak relative to the lower energy modes. (It may possibly be due to an orientation effect; the peaks would be expected to be weak if the CO were oriented parallel to the oxide surface.)[3,5] For these reasons we will not discuss these peaks except to note that background subtraction[6] shows that only the higher energy peak, at 1935 ± 10 cm^{-1}, appears only at higher rhodium coverages. This suggests that the adsorbed species that is present only at higher rhodium coverages has a weaker carbon-oxygen bond.

The initial stages of thin film growth based on nucleation theory and electron-microscope observations are first the formation of adsorbed monomers, then the formation of dimers, trimers, etc., leading to the formation of critically sized nuclei that deplete the monomers in the capture zone around them.[7] Thus, an interpretation that is consistent with our data is that at the lowest coverages (much less than a monolayer average coverage) there are adsorbed monomers, i.e., isolated Rh atoms, to which CO can bond in only one way. As coverage increases, small clusters form to which CO can bond in more ways (e.g., possibly in bridged configurations between adjacent rhodium atoms).

Similar experiments on nickel yield only one peak in the nickel-carbon stretching region, at 400 ± 5 cm^{-1}. In contrast to the rhodium experiments, no new peaks form as the coverage of nickel is increased. This suggests that the bonding of CO to small nickel clusters is fundamentally different than to small rhodium clusters.

Though this work is only a start, it illustrates the potential of IETS for the study of chemisorbed species on supported metals. We are especially interested in the investigation of catalytic reactions on supported metals.

Acknowledgments. We gratefully acknowledge support from the Materials Research Division of the National Science Foundation and the Office of Research Development, University of California, Santa Barbara.

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(6) We averaged a number of spectra for each rhodium thickness point by point, and subtracted from these averaged data, averaged background data.

(7) See, for example, L. Maissel and R. Gland, "Handbook of Thin Film Technology", McGraw-Hill, New York, N.Y., 1970, Chapter 8.

(8) Alfred P. Sloan Foundation Fellow.

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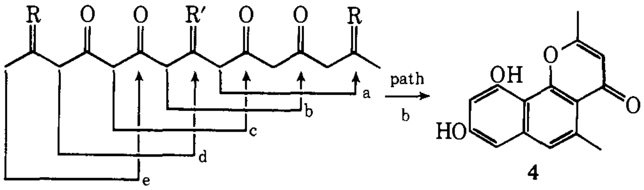
Biogenetic-Type Syntheses of Emodin and Chrysophanol

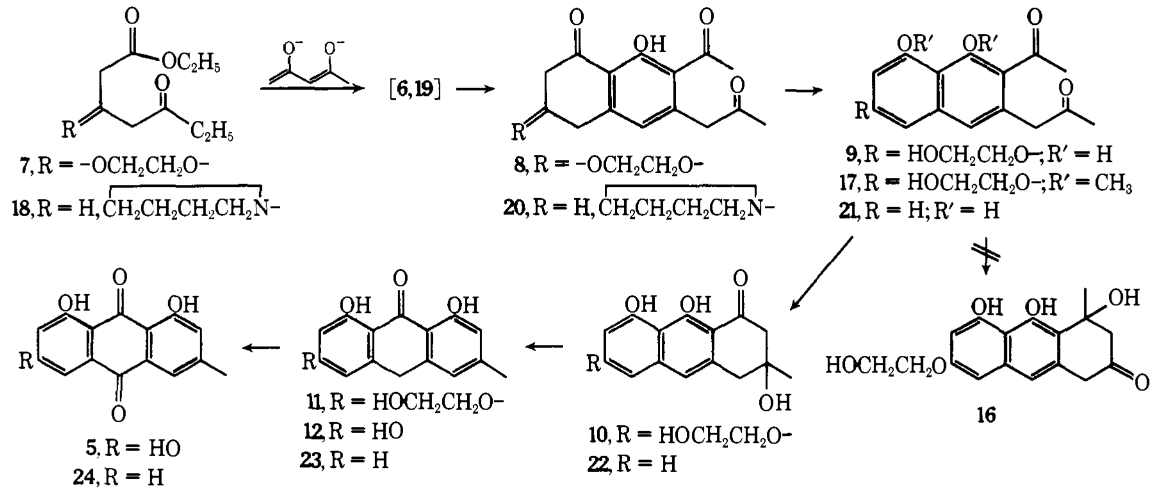
Sir:

For some time we have been studying the biogenetic-type synthesis of phenolic natural products from β-polycarbonyl compounds in a program directed toward the eventual synthesis of pretetramid in this manner.[1] The control of cyclization processes becomes a formidable problem with the higher polycarbonyl compounds.[2] For example, heptaketone **1** might undergo five aldol cyclizations (a-e); all of which with the exception of e look relatively probable.[3] Each of the initial cyclization products can undergo further cyclizations. As one approach to controlling these cyclizations, we have investigated derivatives **2** and **3** in which the terminal keto groups of **1** were protected as ketals.[2b] The ketals blocked cyclizations a and e and retarded d, so that only b and c remained. Cyclizations of **2** and **3** went primarily by path b, leading after two additional



1, $R = O; R' = O$
2, $R = -OCH_2CH_2O-; R' = O$
3, $R = -OCH_2C(CH_3)_2CH_2O-; R' = O$
6, $R = O; R' = -OCH_2CH_2O-$
19, $R = O; R' = H, \overline{CH_2CH_2CH_2CH_2N}-$

Scheme I



7, R = $-OCH_2CH_2O-$

18, R = H, $CH_2CH_2CH_2CH_2N-$

8, R = $-OCH_2CH_2O-$

20, R = H, $CH_2CH_2CH_2CH_2N-$

9, R = $HOCH_2CH_2O-$; R′ = H

17, R = $HOCH_2CH_2O-$; R′ = CH_3

21, R = H; R′ = H

16

10, R = $HOCH_2CH_2O-$

22, R = H

11, R = $HOCH_2CH_2O-$

12, R = HO

23, R = H

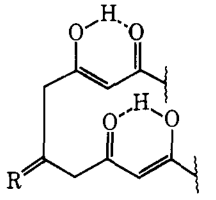
5, R = HO

24, R = H

ring closures to eleutherinol (**4**). Even under the most favorable conditions that could be found, the yield of path c, which could lead to emodin (**5**), was very low.

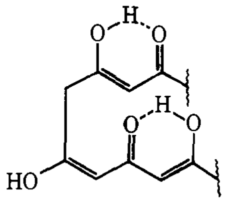
A method has now been developed by which the c cyclization can be effected selectively. Protection of the central keto group of **1** as the ketal (i.e., **6**) blocks the d cyclization and effectively retards the a and b processes. As with **1**, the e cyclization remains unlikely. The twofold condensation of dilithioacetylacetone[4] with ketal-protected diethyl 3-oxoglutarate (**7**)[5] provided a simple, highly convergent synthesis of **6** from readily available starting materials (−78 °C, 2 h followed by −35 °C, 2 h, THF). The condensation product evaded isolation or detection, undergoing two aldol cyclizations and two dehydrations followed by opening of the ketal ring to give naphthalene **9** in 39% yield (based on **7**).[6,7] Even under the mildest conditions that could be devised for workup, the earliest intermediate in the process that could be identified was **8**.[6,8] Aldol cyclization occurred (94%) when **9** was treated with methanolic KOH (0.2 M, 2 h, 23 °C); the product (**10**)[6,9,10] dehydrated to give anthrone **11** on treatment with pyridine (1 h, 23 °C) or HCl in HOAc (5 h, 90 °C). Immediate treatment with HI in HOAc (4 h, 90 °C) gave (78%) anthrone **12**, itself a natural product.[11] Oxidation of **12** with CrO_3 in HOAc gave (70%) emodin (**5**). The structure of **5** was established by comparison with authentic material,[11,12] thus providing proof of the course of the cyclization reactions and the structures of **8–11** (Scheme I).

The ease and specificity of the cyclizations of **6** are noteworthy; no products resulting from other folding operations were observed. Protection of the central keto group on the polycarbonyl chain not only blocks unwanted cyclization reactions but apparently promotes the desired one (path c) as well. β-Polycarbonyl compounds exist as complex mixtures of keto and enol forms but spectra indicate that non-hydrogen bonded keto and enol groups are only rarely present. The most frequent substructures are hydrogen bonded *Z*-monoenols of β-diketones and *Z,Z*-bisenols of β,δ-triketones. This arrangement allows the polyketo chain some freedom of motion but is insufficient for it to turn back on itself far enough for cyclization to take place. The tautomers from which cyclizations can occur are less prevalent and have one carbonyl group isolated from the rest by the adjacent positions being unenolized (**13**) or involved in non-hydrogen bonded *E*-enol structures (**14**). Ketalization of the 8 carbonyl group of **1** effectively blocks enolization of the adjacent methylene groups, thereby allowing free rotation around adjacent C–C bonds. Moreover, the bulky substituent at the 8 position will favor bent conformers (i.e., **15**) in which the two polycarbonyl chains are distant from the substituent and close to each other, a situation conducive to cyclization.



13, R = O

15, R = $-OCH_2CH_2O-$



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The basis of the specificity observed in closure of the second and third rings is not well understood. It might be argued that the final cyclization is controlled by hydrogen bonding, since a hydrogen bond must be broken during formation of **16** but not **10**. However, dimethyl ether **17**[6] of naphthalenediol **9** follows the same cyclization course when treated with $NaOCH_3$.

A synthesis of chrysophanol (**24**) has also been achieved. Diethyl 3-pyrrolidinoglutarate (**18**),[6] prepared by addition of pyrrolidine to diethyl glutaconate (98%), was treated with dilithioacetylacetone (−25 °C, 4 h, THF) to give naphthalenediol **21** (24%);[6,13] **19**, **20**, and other precursors of **21** were not detected.[14] Treatment of **21** with 1 M NaOH (25 °C, 45 min) gave aldol product **22** (88%),[6,15] which was dehydrated by HCl in HOAc (100 °C, 1 h) to give anthrone **23** (96%).[11] Oxidation of **23** with CrO_3 in HOAc (90 °C, 5 min) gave 74% of **24**, the structure of which was established by comparison of the melting point and uv spectrum with values reported for the natural product.[11]

The chrysophanol synthesis is significant because the compound typifies a substantial category of polyketides lacking one or more hydroxyl groups predicted by biogenetic theory.[16] Deletion, as in the present case, of the isolated hydroxyl group is particularly common; examples include musizin, eleutherin, and pretetramid. The general synthetic approach used in the preparation of chrysophanol should be adaptable to the synthesis of other members of this group of natural products. It should be noted that the syntheses of both emodin and chrysophanol compare favorably with more conventional syntheses that have been described previously.[11]

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(3) Several heterocyclic ring closures could also occur.

(4) T. T. Howarth, G. P. Murphy, and T. M. Harris, *J. Am. Chem. Soc.*, **91**, 517 (1969).

(5) Prepared by condensation of ethylene glycol with the keto diester in refluxing benzene (H_2SO_4 catalyst); water was removed azeotropically.

(6) The empirical formula was established by elemental analysis and mass spectrometry.

(7) Compound **9:** mp 162–164 °C dec (vacuo); ir (KBr) 1737, 1702 cm^{-1}; NMR (Me_2SO-d_6) δ 1.96 and 2.5 (2 CH_3's), 3.52 (CH_2), 3.75 and 3.96 (m, CH_2CH_2), 6.3, 6.4, and 6.57 (3 aromatic H's).

(8) Compound **8:** mp 143–144 °C dec (vacuo); ir (KBr) 1710, 1687, 1640 cm^{-1}; NMR ($CDCl_3$) δ 2.25 and 2.6 (2 CH_3's), 2.98 and 3.17 (ring CH_2's), 3.83 (chain CH_2), 4.01 (ketal CH_2CH_2), 6.59 (aromatic H), 13.97 (phenolic OH).

(9) Compound **10:** mp 201–202 °C; ir (KBr) 1630 cm^{-1}; NMR (acetone-d_6) δ 1.44 (CH_3), 2.75 (OH), 2.85 (m, CH_2), 3.1 (s, CH_2), 3.96 and 4.21 (m, ketal CH_2CH_2), 6.5, 6.79, 7.0 (3 aromatic H's), 9.82 (OH).

(10) Closely related natural products are known; they also dehydrate more readily with pyridine than with hydroxide ion: D. L. Dreyer, I. Arai, C. D. Bachman, W. R. Anderson, R. G. Smith, and G. D. Daves, *J. Am. Chem. Soc.*, **97**, 4985 (1975), and references cited therein.

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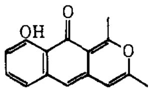
(12) Aldrich Chemical Co.

(13) *Compound* **21:** mp 209–210 °C *dec*; ir ($CHCl_3$) 1720, 1695 sh, 1632 cm^{-1}; NMR (acetone-d_6/Me_2SO-d_6) δ 2.06 and 2.48 (2 CH_3's), 3.76 (CH_2), 6.72–7.34 (4 aromatic H's).

(14) The condensation also gave 12% of pyran i; diketone **21** with heating or acid catalysis gives i. The corresponding cyclization has also been observed with **9**.



i

(15) Compound **22:** mp 203–206 °C; ir (Nujol) 1620 cm^{-1}; NMR ($CDCl_3$/Me_2SO-d_6) δ 1.40 (CH_3), 2.86 and 3.08 (2 CH_2's), 4.68 (OH), 6.72–7.70 (4 aromatic H's), 9.84 and 16.04 (2 OH's).

(16) A. J. Birch, *Proc. Chem. Soc.* (*London*), 3 (1962); A. J. Birch, *Fortschr. Chem. Org. Naturst.*, **14**, 186 (1957).

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Nuclear Magnetic Resonance in Pulse Radiolysis. Chemically Induced Dynamic Nuclear Polarization[1]

Sir:

We wish to report here the first application of nuclear magnetic resonance spectroscopy and chemically induced dynamic nuclear polarization (CIDNP) to the study of pulse radiolysis.

The major part of radiation chemistry involves radicals produced by ionizing radiation.[2] The study of radicals themselves by time—resolved EPR spectroscopy[3] or the study of products of reactions of these radicals by nuclear magnetic resonance spectroscopy can yield useful details of reaction mechanisms. While the study of radical reaction mechanisms in photolysis and thermolysis by CIDNP-NMR methods has been common[4] there has been no successful application of CIDNP or NMR in pulse radiolysis.

Since direct irradiation of NMR samples with the electron beam does not appear feasible at this time we irradiate with the 3-MeV electron beam from the Argonne Van de Graaff accelerator in our EPR magnet (~4000 G) which has axial holes for beam access.[3]

A fast flow system, with transfer speeds of ~1 m/s (pump pressure ~60 psi) transfers the irradiated solution to the rotating 5-mm NMR sample tube in the probe of our Varian A56/60A NMR spectrometer.[5]

We have been able to observe CIDNP in numerous products of radicals in aqueous systems. Large radical concentrations can be produced either by the OH· abstraction reaction or the e_{aq}^- reaction with suitable compounds.

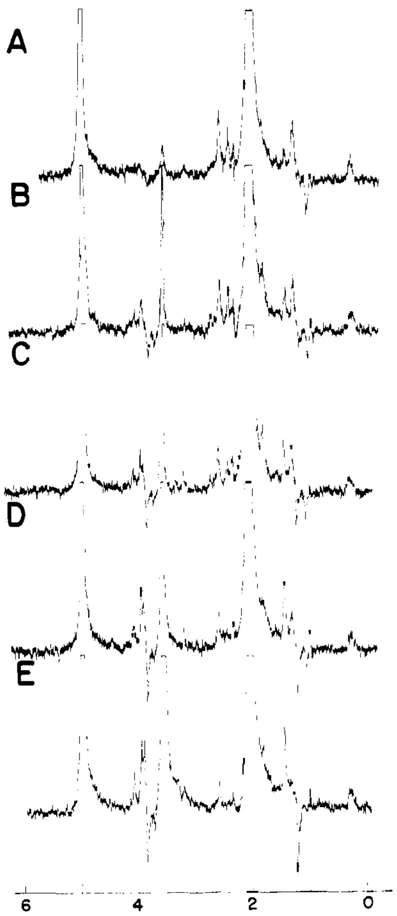

Figure 1. (A) The partial XL-100-15 ^1H NMR spectrum of **6a**, in $CDCl_3$, showing the signals derived from the $C_{11}H_8$ moiety. The inset displays H_g, H_b, and H_d at 270 MHz.[12] (B) The partial XL-100-15 ^1H NMR spectrum of **6b**, in $CDCl_3$, showing the signals derived from the $C_{11}H_4D_4$ moiety.

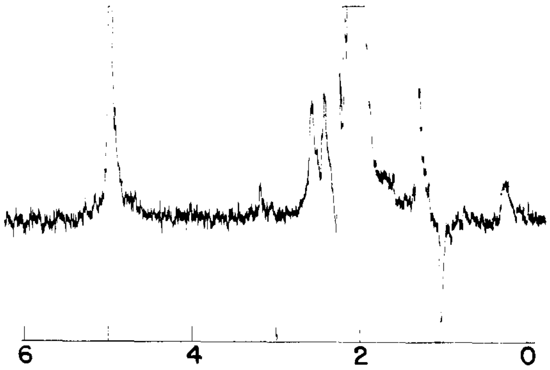

Figure 2. Pulse radiolysis of sodium acetate in D_2O. H_2O in D_2O is at ~5 ppm, and sodium acetate is at 2.1 ppm.

We illustrate some of the features of the CIDNP in pulse radiolysis of mixtures of sodium acetate and methanol. Figure 1 shows the CIDNP in various products in this system. The principal radicals produced are $\cdot CH_2OH$, $\cdot CH_2COO^-$, $\cdot CH_3$ (and ·D). Products corresponding to all possible combinations of these radicals are observed. Assignment is easy since by changing the relative concentrations of methanol vs. acetate different products are brought into prominence.

Irradiation of acetate alone (Figure 2) gives rise to two radicals, $\cdot CH_2COO^-$ and $\cdot CH_3$ (and ·D), and the principal product is propionic acid ($CH_3CH_2COO^-$) with polarized NMR peaks with enhanced absorption-emission (AE) triplet