just to the butadiene moiety. This radical anion is now only a 17-electron system and would be expected to be readily reduced to the 18-electron dianion.[16]

Exhaustive controlled potential electrolysis on a mercury pool electrode of toluenechromium tricarbonyl, **1**, in THF results in a solution which shows an ill-defined oxidative polarographic wave in the region of −0.5 V. Oxidation of this solution regenerates the polarographic wave for **1**, in agreement with the work of Dessy.[1] Furthermore, electrolysis of a propylenecarbonate solution of either of the naphthalene complexes, **5** or **6**, results in a solution with an oxidative polarographic wave in the region of −0.5 V. Oxidation of this solution also regenerates the polarographic wave of the initial complex.

However, in a THF solution (freshly distilled from $LiAlH_4$) exhaustive electrolysis of **5** or **6** results in an oxidative wave only 150 mV anodic to the wave for the initial complex. Oxidation at a potential on top of the oxidative wave regenerates the wave for the initial complex. Ir and uv analysis confirms the regeneration of the complex. Furthermore, cyclic voltammograms of **5** or **6** in THF solution show the cathodic and anodic peaks separated by 150 mV, with much adsorption in the anodic cycle. Also, the polarograms of **5** and **6** in THF have slopes of about 45 mV These data are consistent with the formation of a dianion species by a pseudo-reversible, two-electron process under conditions in which the dianion is stable.[16]

Generation of the dianion solution electrochemically, followed by protonation with either water or benzoic acid (in excess of 2 equiv), generated a solution with an oxidative polarographic wave in the region of −0.5 V. This solution can be reoxidized electrochemically at −0.4 V to generate the wave for the unreduced complex.

The difference between the benzene series, **1** through **3**, and the naphthalene series, **5** through **8**, then is one of degree, and not kind. Both systems undergo a two-electron reduction. The benzene system reduces irreversibly with rapid follow up chemical kinetics. The naphthalene system reduces pseudo-reversibly with relatively slow follow up chemical kinetics, presumably protonation. The products of the follow up chemical kinetics in either case, however, may be oxidized to the original complex.

Compounds **6** through **9** are capable of existing in two different isomers. In fact, NMR on the starting samples indicated that complexes **6**, **8**, and **9** were mixtures of two isomers.[15] Deubzer[14] has shown that in compound **6** the equilibration of the isomers is negligibly slow at ambient temperatures. However, differential pulse polarographic analysis of **6** and **8** showed only one peak. This would suggest that the lowest unoccupied orbital into which the extra electrons are going is predominantly centered on the $-Cr(CO)_3$ group. Two peaks were observed, however, for **9**. Computer simulation of the current–voltage curves indicated that the two peaks resulted from each isomer undergoing a two-electron reduction with a separation of $E_{1/2}$ values of 40 mV. The computer simulation ruled out the possibility that the two peaks simply represented the first and second reduction potential with both isomers having the same first and second reduction potentials.

The possibility existed that the identical reduction potentials of the isomers of **6** and **8** might arise by some fluxional behavior. The two isomers of 2,3-dimethylnaphthalenechromium tricarbonyl were separated by fractional sublimation. The isomeric purity of each isomer was examined by high speed liquid chromatography. Exhaustive controlled potential electrolysis of either of the isomers in THF, followed by reoxidation, resulted in recovery of only the initial isomer. Analysis of products was by liquid chromatographic retention times, and by uv and ir spectroscopy. In the dianion, then, the chromium atom is associated with only one ring of the naphthalene system, as in the unreduced complex.

We are continuing to examine the generality of the reduction of chromium and other metal arenecarbonyl complexes. This along with ac-polarographic and chemical reduction data will be reported in the near future.

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Carbon-13 CIDNP during the Photolytic Decomposition of *tert*-Butyl Hydroperoxide in 2-Propanol. Detection of Transient Intermediates

Sir:

We report the observation of carbon-13 CIDNP signals from keto–enol tautomers and a hemiketal formed during photolysis of *t*-BuOOH in 2-propanol. Direct evidence for these species as well as an insight into the mechanism of their formation was obtained.

Photolysis of 10–50% solutions of *t*-BuOOH in 2-propanol was performed inside the modified probe of a Varian HA-100 pulsed carbon-13 NMR spectrometer. The irradiation from a 600-W mercury–xenon arc source was focused through a water filter and onto the polished end of a quartz rod which terminated 1 mm from the bottom of the Pyrex sample tube. Figure 1A shows a typical carbon-13 proton

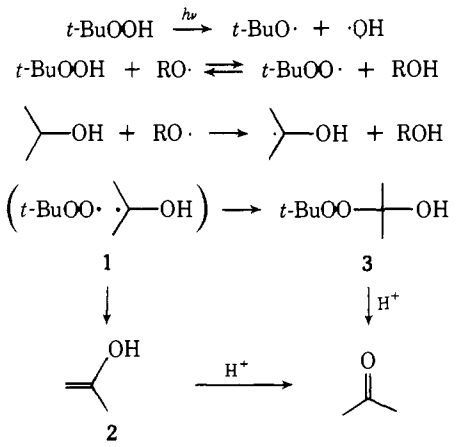
decoupled spectrum obtained during photolysis. Strong emission signals occurred at 207.6, 156.8, and 101.2 ppm from TMS. Performing the experiment under proton coupled conditions demonstrated that these signals were from quaternary carbons. A weak hyperabsorptive signal appeared at 95.3 ppm. The CIDNP signals were assigned to particular carbon atoms on the basis of chemical shift comparison with authentic or closely related compounds. The signal at 207.6 ppm was assigned to the carbonyl carbon of acetone since a 5% solution of acetone in 2-propanol showed the carbonyl carbon resonance at 207.2 ppm. Those CIDNP signals occurring at 95.3 and 156.8 ppm were assigned to C-1 and C-2 of 2-hydroxypropene (**2**) by analogy with the chemical shifts of 2-methoxypropene (C-1, 80.4 ppm; C-2, 160.2 ppm)[1] and 2-acetoxypropene (C-1, 101.2 ppm; C-2, 152.8 ppm).[1] The 101.2 ppm CIDNP signal was assigned to C-2 of 2-*tert*-butylperoxy-2-hydroxypropane (**3**)[2] on the basis that the dioxygenated carbon resonances of the model compounds *tert*-butylperoxyhydroxymethane[3] and 1-*tert*-butylperoxy-1-hydroxyethane[4] appeared at 91.9 and 96.8 ppm, respectively. From these two models a methyl substituent effect of ca. +5 ppm accurately predicts the observed C-2 resonance of hemiketal **3**.

Photolysis of solutions containing a trace of *p*-toluenesulfonic acid showed no enol or hemiketal polarizations but rather a stronger emission signal from acetone (Figure 1B).

The only reaction product observable in the carbon-13 spectrum obtained after photolysis was *tert*-butyl alcohol. Proton NMR analysis of a reaction mixture originally containing 10% *t*-BuOOH revealed complete disappearance of the hydroperoxide after a photolysis time of 2000 sec and that the major products were acetone and *tert*-butyl alcohol.

It has been shown by EPR spectroscopy that photolysis of di *tert*-butyl peroxide or H_2O_2 in alcohols leads to the production of ketyl radicals.[5] In the case of *t*-BuOOH a reasonable first step is oxygen–oxygen bond homolysis (Scheme I).[6]

Scheme I



The *tert*-butoxy and hydroxy radicals thus produced may remove the proton from *t*-BuOOH to form the *tert*-butylperoxy radical.[7] Any of the oxy radicals in solution may remove the methine proton of 2-propanol to form the 2-hydroxy-2-propyl radical. In order to rationalize the observed CIDNP, we propose a diffusive encounter of the *tert*-butylperoxy and 2-hydroxy-2-propyl radicals to form polarizing pair **1**. Collapse of **1** gives the polarized hydroxy carbon of hemiketal **3** whereas disproportionation gives the polarized olefinic carbons of enol **2**. The polarization is remembered during tautomerization and hemiketal destruction to appear in the carbonyl carbon of acetone. In the presence of small amounts of *p*-toluenesulfonic acid the enol→keto rate and the rate of hemiketal destruction are increased, and the polarization is seen only in the carbonyl carbon of acetone.

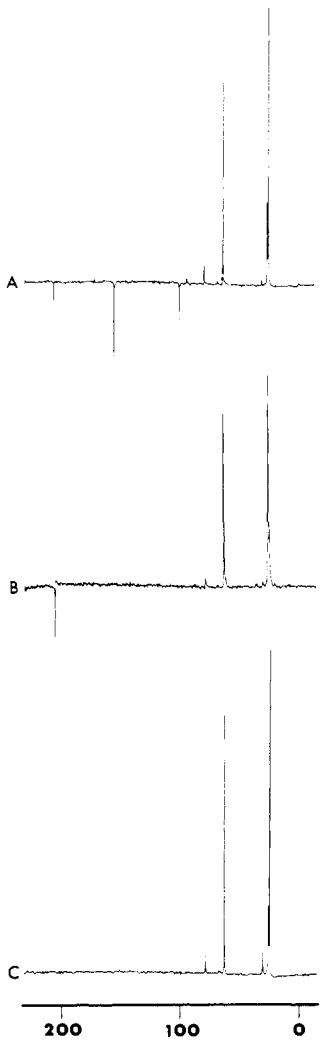


Figure 1. Proton decoupled carbon-13 FT NMR spectra of a 10% *t*-BuOOH solution in 2-propanol. Spectra recorded (A) during irradiation, (B) during irradiation of a sample containing 2×10^{-5} *M* *p*-toluenesulfonic acid, and (C) after irradiation. The spect width is 250 ppm and for each spectrum 100 free induction decays were accumulated at a pulse repetition time of 10 sec.

The validity of the proposed mechanism may be tested by using the simple rules[8] of CIDNP radical pair theory. For this purpose the *g* factors of the radicals are needed: *g* (*t*-BuOO·) = 2.0137;[9] *g* (·>—OH) = 2.00323.[10] In addition, the signs of the electron-carbon hyperfine interaction constants, $a_{C^{13}}$, must be used. The magnitudes of $a_{C^{13}}$ are known for the 2-hydroxy-2-propyl radical.[11] The signs were calculated using the INDO approach.[12] The $a_{C\alpha}$ was calculated to be positive and the $a_{C\beta}$ negative. Thus, for a diffusive encounter of free radicals and products of cage processes the theory predicts emission from C-2 of enol **2** and hemiketal **3**, whereas enhanced absorption is predicted from C-1 of **2**. The carbonyl carbon of acetone is in emission because the polarization in **2** and **3** is remembered during the tautomerization and hemiketal destruction process. These predictions are in agreement with the signs of the experimental polarizations and support the proposed mechanism.

Preliminary studies with other simple alcohols indicate that the mechanism involves enols as the precursors to the carbonyl-containing product. For example, photolysis of *t*-BuOOH in 2-butanol gave rise to CIDNP signals from 2-

butanone and two different enolic species.

In conclusion, the use of carbon-13 CIDNP has revealed an important mechanistic aspect of alcohol oxidation by photolysis of *t*-BuOOH. Direct evidence for enolic species as transient intermediates was found. The possibility now exists to study the carbon-13 chemical shifts of this important class of organic intermediates. Furthermore, acid catalyzed studies may lead to a better kinetic understanding of these unstable species. We are currently exploring these possibilities as well as the synthetic utility of the photooxidation reaction.

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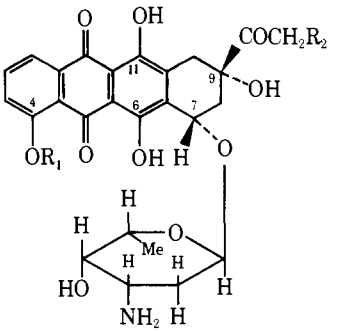
Antitumor Agents. XIII. Isolation and Absolute Configuration of Carminomycin I from *Streptosporangium sp.*[1,2]

Sir:

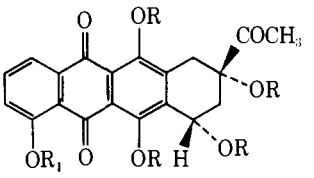
Recent reports on the promising antitumor activity of daunorubicin (**1**)[3,4] and adriamycin (**2**)[5] and carminomycin (**3**)[6,7] in a variety of animal and human cancers has aroused considerable interest in the chemical and biological properties of this group of anthracyclic compounds. Although the gross structure of **3** is known,[6] we now report for the first time the absolute stereochemistry of this important compound[8a] and its isolation from a new source, *Streptosporangium sp.*[9]

Chromatography of the crude extract (10 g) on silicic acid[10] utilizing in vitro and in vivo bioassay procedures to locate active fractions[11] gave 0.3 g of **3**: $C_{26}H_{27}NO_{10}\cdot H_2O\cdot HCl$;[12] mp 183–185° dec; $[\alpha]^{25}D$ +193° (*c* 0.18, MeOH; lit.[6] $[\alpha]^{20}D$ +289°];[13] λ_{max} (MeOH) 234 nm (ϵ 32200), 255 (19600), 292 (12000), 492 (8200), 526 (6000); ir (KBr) 1715 cm^{-1} (CO), 1600 (quinone and aromatic C=C).

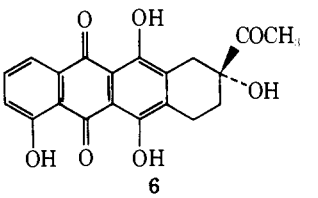
The uv and visible spectra of **3** were similar to those of daunorubicin[3] suggesting the presence of a 1,4,5-trihydroxyanthraquinone chromophore. Mild acid hydrolysis (0.1 *N* HCl, 100°, 0.5 hr) of **3** afforded a red aglycone carminomycinone (**4**) ($C_{20}H_{16}O_8$;[12] mp 233–235° (13% MeOH–$CHCl_3$–EtOAc; lit.[6] mp 224°); $[\alpha]^{28}D$ +171° (*c*, 0.14, dioxane; lit.[6] $[\alpha]^{20}D$ +272° (*c* 0.1, dioxane)];[13] NMR



1, R_1 = Me; R_2 = H
2, R_1 = Me; R_2 = OH
3, R_1 = R_2 = H



4, R = R_1 = H
5, R = R_1 = Ac



6

(CF_3CO_2D) δ 2.64 (s, 3, $COCH_3$), 3.30 (q, 2, C-10), 5.57 (br s, 1, C-7), 7.36–7.83 (m, 3, ArH)) and an amino sugar. The latter was identified as daunosamine[14] by direct comparison of the physical properties (GLC, TLC, mass spectrum) of its triacetate with those of daunosaminetriacetate. Acetylation of **4** gave the pentaacetate **5**: $C_{30}H_{26}O_{13}$;[12] mp 218–220° (CH_2Cl_2–hexane; lit.[6] mp 190°); $[\alpha]^{24}D$ −160° (*c* 0.10, $CHCl_3$; lit.[6] $[\alpha]^{20}D$ +40° (*c*, 0.11, $CHCl_3$));[13] ir ($CHCl_3$) 1740 cm^{-1} (aliphatic acetate), 1775 (phenolic acetate); NMR ($CDCl_3$) δ 2.02 (s, 6, C-7 and C-9 OAc), 2.22 (s, 3, $COCH_3$), 2.36 (s, 3, C-4 OAc), 2.40 (s, 3, C-11 OAc), 2.50 (s, 3, C-6 OAc), 6.36 (br s, 1, C-7), 7.34–8.12 (m, 3, ArH).

The attachment of the sugar moiety to the benzylic C-7 position was established by catalytic hydrogenolysis (5% Pd–$BaSO_4$, MeOH, 1 hr) of **3**. Under these conditions, there was obtained daunosamine and a new aglycone **6**: $C_{20}H_{16}O_7$;[12] mp 261–262° (13% MeOH–$CHCl_3$–EtOAc); $[\alpha]^{26}D$ −54° (*c* 0.13, dioxane).

The absolute configuration of **3** was determined by direct single-crystal X-ray crystallographic analysis. Carminomycin I hydrochloride monohydrate (**3**), $C_{26}H_{28}ClNO_{10}\cdot H_2O$, M = 566.97, crystallizes in the monoclinic system, space group $P2_1$, with a = 19.98 (1) Å, b = 5.50 (1) Å, c = 11.86 (1) Å, β = 93.7 (1) Å, U = 1301 Å^3, d_m (flotation) = 1.43 g cm^{-3}, Z = 2, d_c = 1.447 g cm^{-3}. The crystal structure was solved by a combination of Patterson and direct phase-determining methods involving the "magic integer" approach[15] in conjunction with the MULTAN[16] series of programs. Refinement of the non-hydrogen atom positional and anisotropic thermal parameters by full-matrix least-squares calculations has reduced R to 0.109 over 1324 independent reflections with $I > 2.0\sigma(I)$ from 2649 measurements on an Enraf-nonius CAD 3 automated diffractometer using Ni-filtered Cu Kα (λ 1.542 Å) radiation and operating in the θ–2θ scanning mode. The absolute configuration was established by incorporation of the chlorine anomalous dispersion corrections[17] into the structure-factor calculations. For the configuration depicted by **3**, R was 0.109 in contrast to the significantly higher value[18] of 0.111 for the mirror image, thereby confirming that **3** correctly represents the absolute stereochemistry.[19] Thus the structure of carminomycin I is in complete accord at all asymmetric