the 80-MHz nmr spectrometer. This research was supported in part by the Office of Naval Research.

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Stoichiometry of the Chromic Acid Oxidation of Isopropyl Alcohol as a Function of Time. An Experimental Test of the Role of Chromium(IV)[1]

Sir:

The first step of the chromic acid oxidation by isopropyl and other secondary alcohols almost certainly leads to the formation of chromium(IV).[2] Watanabe and Westheimer[3] suggested several possible sequences for the subsequent reactions which account for two-thirds of the reaction product. Of these, the following two appeared the more reasonable

$$R_2CHOH + HCrO_4 + H^+ \rightleftharpoons R_2CHOCrO_3H + H_2O$$
$$R_2CHOCrO_3H \longrightarrow R_2C{=}O + Cr(IV)$$
$$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V)$$
$$2(Cr(V) + R_2CHOH \longrightarrow Cr(III) + R_2C{=}O) \qquad (I)$$

$$R_2CHOH + HCrO_4^- + H^+ \rightleftharpoons R_2CHOCrO_3H + H_2O$$
$$R_2CHOCrO_3H \longrightarrow R_2C{=}O + Cr(IV)$$
$$R_2CHOH + Cr(IV) \longrightarrow R_2\dot{C}OH + Cr(III)$$
$$R_2\dot{C}OH + Cr(VI) \longrightarrow R_2C{=}O + Cr(V)$$
$$R_2CHOH + Cr(V) \longrightarrow R_2C{=}O + Cr(III) \qquad (II)$$

The reactions, particularly those involving cleavage of the reactant,[4] have frequently been considered in terms of mechanism I. However, Rocek and Radkowsky[5] as well as Nave and Trahanovsky[6] have presented evidence for Cr(IV) as an active oxidant and have favored mechanism II.

Our observation that chromium(V) may be observed spectrometrically during the oxidation of isopropyl alcohol in 97% acetic acid[7] permits a simple experimental differentiation between the two mechanisms. Qualitatively, one can see that in mechanism I the formation of 2 equiv of chromium(V) is accompanied by the formation of 1 equiv of acetone. Conversely, in mechanism II, the formation of 1 equiv of chromium(V) is accompanied by the formation of 2 equiv of acetone. Therefore, an investigation of the stoichiometry of the reaction at several points during its course would permit a differentiation between the two mechanisms.

This may also be stated in a more quantitative fashion. As indicated previously, we can calculate rate constants for the disappearance of both chromium(VI) and chromium(V) from spectrometric data. This may be done for each of the two models. Having the rate constants, the concentration of acetone may be calculated as a function of time giving the two curves in Figure 1. It can be seen that the per cent of acetone formed at any given time is quite different for the two mechanisms.

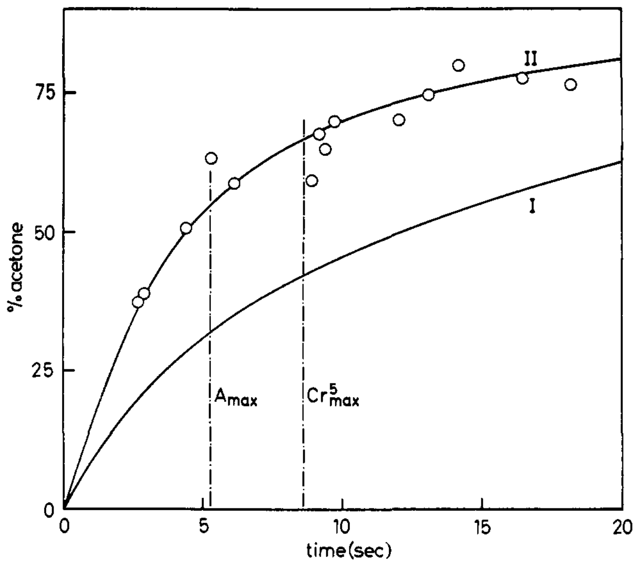

Figure 1. Rate of formation of acetone in the chromic acid oxidation of isopropyl alcohol in 97% acetic acid: [ROH] = 0.1258 *M*, [Cr(VI)] = 0.0050 *M*, $[H^+]$ = 0.0125 *M*, μ = 0.184 ($NaClO_4$), T = 15 ± 0.05°, k_1 (disappearance of Cr(VI), appearance of Cr(V)) = 0.1455 sec^{-1}, k_2 (disappearance of Cr(V)) = 0.0355 sec^{-1}. Curve I is for Scheme I and curve II is for Scheme II.

The stoichiometry experiments were carried out in essentially the same fashion as the kinetic experiments,[7] except that the solutions were quenched with chromium(II) at different times.[8] The concentration of acetone in each solution was determined by gas chromatography using a 25% Carbowax 400 on C-22 Silocel and a flame ionization detector.[9] Methyl ethyl ketone was used as an internal standard. The per cent acetone formed, based on the amount found when the reaction was allowed to proceed to completion, is shown in Figure 1 as the open circles. The yield of acetone at complete reaction was found to be 1.50 ± 0.05 mol of acetone/mol of chromium trioxide used.

The experimental data give a good fit to the calculated curve for mechanism II. Figure 1 also contains lines indicating the time at which the absorbance at 510 mμ reaches a maximum and the time at which the concentration of chromium(V) reaches a maximum. At the absorbance maximum, 55% of the maximum amount of acetone had been formed, and at the chromium(V) maximum, 67% of the maximum amount of acetone had been formed.

The data clearly indicate that mechanism II is operative under the reaction conditions. The agreement with the previous results[5,6] suggests that mechanism II applies to all solutions containing at least a minimal amount of water. However, it does not apply to acetic acid–acetic anhydride mixtures in which chromium(IV) is found to be completely inactive as an oxidant.[10]

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[1] This work was supported by the National Science Foundation.

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The determination of stoichiometry as a function of time should also be of help in resolving some of the problems concerning cleavage reactions which occur during chromic acid oxidation. The oxidation of cyclobutanol[5] under the above conditions is now being studied.

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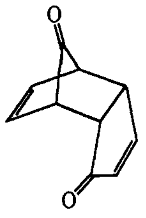
Photochemical Transformations of Substituted Cyclopentadienone Dimers[1]

Sir:

The photochemistry of the norbornen-7-one system has been the subject of sustained interest in recent years.[2] The primary photochemical reaction has been shown to be decarbonylation to the corresponding cyclohexadienes, the subsequent fate of which depended upon its substitution pattern.

Since cyclopentadienone dimers constitute a large class of the norbornen-7-one system, the investigation of their photochemical behavior is of obvious interest, the more so since their structure contains additional features which might open up alternate reaction paths. The two five-membered rings in such dimers occupy nonequivalent positions and in certain derivatives have been shown to be interconvertible[3] in what is, by now, well known as thermally allowed, suprafacial [3,3] sigmatropic rearrangements.[4] Another feature in these compounds is the juxtaposition of two olefinic bonds in an alignment permitting intramolecular cycloaddition which has, indeed, been found to occur in the parent *endo*-dicyclopentadiene and certain derivatives.[5,6] In the initial stage of this work, Schaffner and coworkers reported[7] that the irradiation of tricyclo[4.3.1^{2,5}.0]deca-3,8-diene-7,10-dione (**1**) resulted in the formation of the expected cage compound **2** accompanied by another isomer, **3**. We have therefore confined our investigation to substituted derivatives of **1** and wish to report at this stage some novel results and interpretations.

The Diels–Alder dimer **4** of 1,4-dimethyl-2,3-diphenylcyclopentadienone[8] (mp 183–184°; uv max (dioxane) 235 (ϵ 3 × 10^4), 280 nm (ϵ 4 × 10^4); ir (KBr) 1760, 1680 cm^{-1}; nmr ($CDCl_3$) τ 3.0 (m, 20, C_6H_5), 7.9 (s, 3, CH_3), 8.36 (s, 3, CH_3), 8.75 (s, 3, CH_3), 9.42 (s, 3, CH_3); mass spectrum (70 eV) m/e 520 (M^+)) gave upon irradiation at $\lambda > 300$ nm[9] a product **5** in excellent yield (75%) (mp 272°; uv max (dioxane) 240 nm (ϵ 2 × 10^4); ir (KBr) 1750 cm^{-1}; nmr (C_6H_5Cl) τ 8.8 (s, CH_3); mass spectrum (70 eV) m/e 520 (M^+)[10]) accompanied by minute ammounts ($\leqslant$0.25%) of a second product **6** (mp 318°; uv max (dioxane) 230 nm (ϵ 2 × 10^4); ir (KBr) 1750 cm^{-1}; nmr (C_6H_5Cl) τ 8.2 (s, 6, CH_3), 9.5 (s, 6, CH_3); mass spectrum (70 eV) 520 (M^+)).[10] The structural assignments are based on the above spectral properties as well as on chemical reactivity. The uv spectra indicate the absence of unsaturation in the cage skeletons and the ir spectra indicate the presence of strained five-membered ring ketones. The nmr spectra allow differentiation between **5** and **6** by the signals of the methyl groups and indicate their complete equivalency in **5** (point group C_{2v}) but only pair equivalency in **6** (point group C_2). The fact that the relative disposition of the two five-membered rings in **5** is as shown was proven by $LiAlH_4$ reduction (boiling THF) whereby a cyclic hemiketal **7**, mp 320°, was obtained.[10] The latter gives a monotrimethylsilyl derivative, mp 310°.



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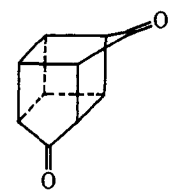

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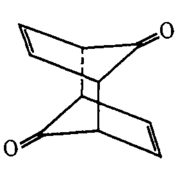

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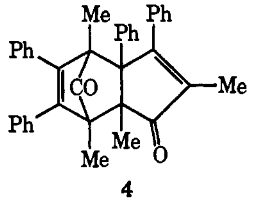

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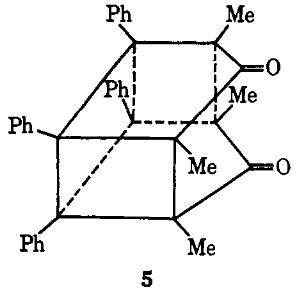

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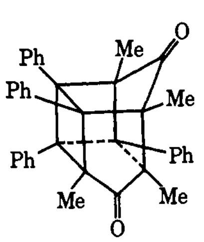

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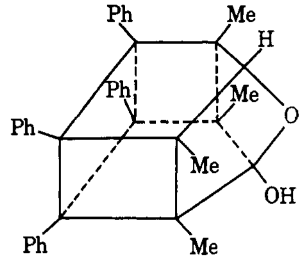

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Structure **5** is novel and its formation can be rationalized only if one assigns an exo configuration to the dimer **4**. The achievement of this apparent thermodynamically more stable configuration may be understood on the basis of the known reversibility of the

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(9) Preparative irradiations were carried out in Rayonet reactors using Sylvania F8T5 Black ray lamps or in immersion reactors using Hanovia 450-W high-pressure mercury lamps. Dioxane solutions in Pyrex vessels were purged with nitrogen prior to and during irradiations. Quantitative, time-dependent, and monitored irradiations were performed on a Jasco-CRM-FA spectro irradiator at 311 nm.

(10) (a) Satisfactory elemental analyses were obtained. (b) The products are unusually resistant to chemical attack and of exceedingly low solubility in all organic solvents.