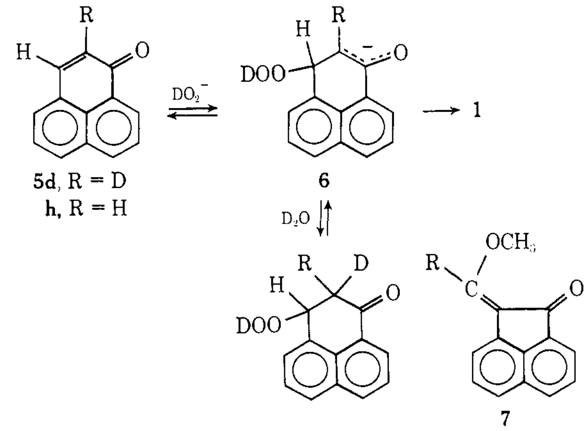
Scheme II



an intermediate, presumably the enolate adduct, which undergoes C_α–C_β rotational equilibration during its lifetime. The present results indicate that cyclization to epoxide is considerably faster than ketonization of the enolate which, we consider, constitutes a remarkably high, lower limit for nucleophilic attack on the peroxide linkage. The facility of this process, which appears to be unprecedented in peroxide reactivity toward nucleophiles,[9] probably reflects a favorable disposition of the enolate carbon orbital. The results further demonstrate that reversal of hydroperoxide addition, for which evidence has been presented,[7] occurs faster than ketonization.

Irradiation of **1d** yielded a product mixture from which the desired aldehyde was conveniently and cleanly separated by adsorption on basic alumina and elution with basic methanol. Unfortunately, neither nmr nor mass spectrometry was useful for determining the extent of deuterium retention: the former because of its complexity, the latter because of a major M-1 fragmentation. However, complete retention of deuterium was demonstrated by conversion into the corresponding methyl ether, **7d**,[10] as evidenced by mass spectrometry.

Thus, aldehyde **3** and, presumably, α-diketone **2**, which represent 90% of the isolated products, are generated by C_β–O scission. This mode of fragmentation is considered diagnostic of the low-lying π,π^* triplet of naphthyl ketones, in which excitation is "localized" in the aromatic chromophore: a model based on phosphorescence data[11,12] and supported by low photoreactivity of these systems in typical, n,π^* reactions.[13] The formation of β-diketone **4** may occur *via* C_α–O cleavage of the low-lying singlet, which has been postulated as the reactive state[14] in this mode of photoisomerization of epoxyketones.[15] These excited-state designations are also in accord with findings on intramolecular photocyclization of α- and β-naphthyl ketones which implicate competing T_1 and S_1 reactivity.[16]

Acknowledgment. We wish to express our appreciation to Dr. James J. Worman and Mr. Marvin J. Miller (National Science Foundation Undergraduate Research Participant) for their assistance on this project.

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(10) E. Ghigi, A. M. Drusiani, and L. Plessi, *Ann. Chim. (Rome)*, **53**, 266 (1963).

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Received July 27, 1973

Simplified Preparation of π-Vinyl Alcohol Platinum(II) Complexes[1]

Sir:

The recent literature has evidenced a growing interest in π-vinyl alcohol complexes, stimulated in part by the postulated π-vinyl alcohol intermediate[2] in the Wacker process,[3] the palladium-catalyzed oxidation of ethylene to acetaldehyde. At present three π-vinyl alcohol transition metal complexes have been isolated,[4–6] and nmr evidence for the formation of a fourth has been reported.[7] In a study of oxoalkyl iron complexes, Ariyaratne and Green[4] found that cyclopentadienyldicarbonyl(β-oxoethyl)iron could be protonated to give a complex which they tentatively described as the π-vinyl alcohol. Wakatsuki, Noyakura, and Murahashi[5] synthesized 1,3-bis(π-ethenol)-2,4-dichloro-μ-dichloro-platinum(II); however, Thyret[7] recently reported that the synthesis was not reproducible and reported nmr evidence for the formation of tetracarbonyl(π-ethenol)iron at −80°.

Due to the stability and high solubility of the chloro(acetylacetonato)(π-ethenol)platinum(II) complex, prepared in this laboratory, it has been possible to well characterize this vinyl alcohol complex by nmr,[6] X-ray diffraction,[8] and exchange studies.[9] The reported preparation[6] involved the formation and hydrolysis of the intermediate vinyl trimethylsilyl ether complex, the same general procedure employed by Wakatsuki and Thyret. Since the preparation of the readily hydrolyzed vinyl trimethylsilyl ether[10] and the subsequent formation and hydrolysis of the metal–vinyl ether complex require carefully controlled reaction conditions[6,10] and considerable time, we report a novel, simplified preparation of this complex and the analogous π-propen-2-ol complex by the direct reaction of chloro(acetylacetonato)(π-ethylene)platinum(II) with acetaldehyde and acetone. This facile method of

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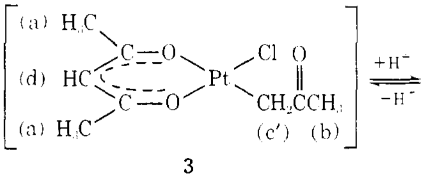
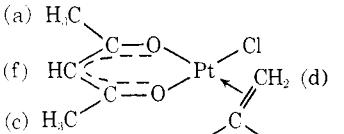
preparation of π-vinyl alcohol metal complexes may stimulate further interest in these complexes and the chemistry of vinyl alcohols.

Addition of aqueous KOH (0.2 ml of 0.663 *N*) to a THF solution of chloro(acetylacetonato)(ethylene)platinum(II) and excess acetaldehyde (31.03 mg and 2 ml, respectively, in 10 ml of solvent) at 0° results in effervescence and a deepening of the yellow color. After 30 min the solvent and excess acetaldehyde can be removed *in vacuo* at 0° and the residue recrystallized from warm absolute methanol with the addition of ether–hexane (1:1 by volume) to give a 55% yield (19.03 mg) of potassium chloro(acetylacetonato)(β-oxoethyl)platinate(II) (**1**) as greenish yellow crystals. As previously reported **1** can be readily converted to the π-ethenol, **2**, by protonation in aqueous solution; the two complexes existing in equilibrium in aqueous acetone as an acid and conjugate base.[6] The above products were identified by comparison of their ir spectra with those of authentic samples of **1** and **2**; within instrumental error, the spectra were identical.

The reaction conditions and the effervescence noted on the addition of aqueous KOH suggest that the reaction proceeds *via* carbanionic displacement of ethylene, rather than a possible oxidative mechanism, and is verified by the fact that under similar conditions acetone reacts with the ethylene complex to give the potassium chloro(acetylacetonato)(β-oxopropyl)platinate(II) complex, **3**, in 80–90% yields. One-half milliliter of 0.680 *N* KOH was added to 10 ml of acetone containing 100.6 mg of chloro(acetylacetonato)-(ethylene)platinum(II). After stirring at room temperature for 30 min the solution was evaporated to dryness under reduced pressure and the residue recrystallized from acetone and 1:1 ether–hexane to give 106 mg of **3** as bright yellow crystals, dec pt 158–172°. *Anal.* Calcd for $K[C_8H_{12}O_3PtCl]$: C, 22.6; H, 2.84; Pt, 45.8; Cl, 8.33. Found: C, 22.8; H, 2.68; Pt, 46.6; Cl, 9.46. The structure is confirmed by the intense ir absorption at 1645 cm^{-1} (C=O) and the nmr spectrum:[11] δ 2.42 (6 H_a, s), 2.75 (3 H_b, s), 3.94 (2 H_c, s), and 6.16 ppm (1 H_d, s). The ^{195}Pt–H coupling constants are <5, 18, 116, and 8 Hz, respectively. The value of 116 Hz for the two methylene protons is very near the value of 114 Hz observed for the β-oxoethyl complex.[6]



3



4

As in the case of the acetaldehyde complex, **3** can be converted to a vinyl alcohol complex by protonation. However, the sensitivity of the π-propen-2-ol complex, **4**, to water necessitates the use of anhydrous conditions. This was achieved by adding a slight excess of dry HCl, in the form a freshly prepared ether solution, to a suspension of the β-oxopropyl complex in ether. The resulting ether solution was reduced to small volume, dry hexane added until clouding had just initiated, and then cooled at −10°, yielding bright yellow crystals, dec pt 81–83° (yellow to orange), dec pt 165–185° (orange to black). *Anal.* Calcd for $C_8H_{13}O_3PtCl$: C, 24.8; H, 3.38; Pt, 50.7. Found: C, 24.42; H, 3.54; Pt, 51.5. The ir spectrum reveals a moderately intense band at 3230 cm^{-1} (OH) and the nmr spectrum[12] consists of six singlets at δ 1.88 (3 H_a), 2.02 (3 H_b), 2.03 (3 H_c), 3.96 (2 H_d), 5.03 (1 H_e), and 5.42 ppm (1 H_f). The ^{195}Pt–H coupling constants are ~6, 44, <5, 78, (undetected due to exchange broadening), and 8 Hz, respectively. The value of 78 Hz for the vinyl protons is quite reasonable when compared to the value of 71 and 76 Hz observed for the vinyl protons of **2**.[6]

The applicability of this new approach to vinyl alcohol complexes is currently being investigated for other transition metal systems. Attempts to obtain the ethenol and propen-2-ol complexes (**2** and **4**) *via* an acid catalyzed displacement of ethylene in acetaldehyde and acetone solutions have not been successful.

Acknowledgment. We wish to acknowledge the financial support of the R. A. Welch Foundation, Grant No. A-420.

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[11] Measured in D_2O *vs.* external TMS.

[12] Measured in $CDCl_3$ *vs.* internal TMS.

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Received July 11, 1973

Mechanistic Studies of Oxidative Addition to Low-Valent Metal Complexes. II. Reactions of α-Bromo Esters

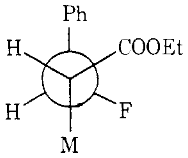
Sir:

We have recently reported evidence for a free-radical chain mechanism in the oxidative addition of several alkyl halides with Ir^I complexes, *e.g.*, *trans*-IrCl(CO)-$(PMe_3)_2$ (Ia).[1] In particular, these reactions show

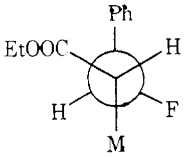
$IrClCOL_2$
I

$IrClBr(CH_3CHCOOEt)COL_2$
III

a, L = PMe_3
b, L = PMe_2Ph
c, L = $PMePh_2$



IVa
Va



IVb
Vb

M = Br
M = $IrClBrCO(PMe_3)_2$

inhibition by radical scavengers, such as duroquinone and galvanoxyl, and are accompanied by loss of stereochemistry at the reacting α-carbon center. In contrast, the reaction of optically active $CH_3CHBrCOOC_2H_5$ (II) with *trans*-$IrCl(CO)(PMePh_2)_2$ (Ic) has been reported to proceed with substantial conservation of stereochemistry[2] suggesting that an alternative nonradical

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[1] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972).