for 2 h, a new compound, $Mg(C_{10}H_{17})(C_9H_7)(THF)$ (**12**),[7] was isolated as a pale yellow, extremely air-sensitive solid upon high-vacuum concentration of the yellow reaction mixture. Supports for this formulation are: (1) acid hydrolysis affords 1 mol each of hydrocarbon $C_{10}H_{18}$ (mainly **3**), indene, and THF, (2) the reaction with acetone gives quantitative yield of two tertiary alcohols, **10** and **13**, in exactly 1:1 mole ratio, and (3) the NMR (60 MHz) spectrum in C_6D_6 shows signals[8] assignable in terms of the substituted allyl magnesium compound.[9]

Compound **12** reacts readily (at 25 °C for 2 h in THF) with an equivalent amount of anhydrous $MgCl_2$ to give 3,7-dimethyl-2,6-octadienylmagnesium chloride and indenylmagnesium chloride (Scheme II). As the latter is much less soluble in THF, these two compounds can be separated by filtration.

The present preparation of the endiyl compounds can be applied to isoprene and 2,3-dimethylbutadiene and their analogues. Terminally substituted conjugate dienes like piperylene or cyclic dienes such as 1,3-cyclooctadiene do not undergo the reaction. The halide-free endiylmagnesium compounds promise to have a great potential for organic and inorganic synthesis.

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(8) Chemical shifts (δ ppm), coupling constants (Hz), and intensities for important signals: 0.92 (d), $-CH_2Mg-$, 2 H; 1.90 (d), $-MgCH{=}$(Indenyl), 1 H; 3.45 (t), $\llcorner(CH_2CH_2)_2\text{-}O\lrcorner$, 4 H; 6.01 (t), $=CHCH_2Mg-$, 1 H; 6.18 (d), H^3 (indenyl), 1 H; 6.66 (d), H^2 (indenyl), 1 H; 7.15 (m), H^{4-7} (indenyl), 4 H.

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Susumu Akutagawa
Central Research Laboratory, Takasago Perfumery Co. Ltd.
31-36 5-Chome, Kamata, Ohta-ku, Tokyo, 114

Sei Otsuka*
Department of Chemistry, Faculty of Engineering Science
Osaka University
Toyonaka, Osaka, Japan 560

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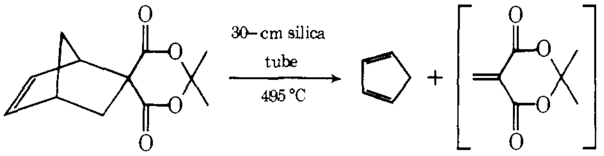
Evidence for the Pyrolytic Generation of Methylene Ketene (Propadienone)

Sir:

Flash vacuum pyrolysis of 5-arylidene- and 5-alkylidene-1,3 dioxan-4,6-diones is a general method for the generation of substituted methylene ketenes. The formation of these highly reactive species has been established[1] by low-temperature infrared spectrometry, by their conversion into substituted acrylic acid derivatives, and by isolation of their dimerization products, 2,4-bis(arylidene or alkylidene)cyclobutane-1,3-diones. Substituted methylene ketenes are also involved in gas-phase rearrangements leading to the synthesis of new aromatic rings,[2] in various thermal or base-catalyzed reactions[3] in solution, and in photochemically induced reactions.[4] Evidence is now presented to show that flash vacuum pyrolysis of the cyclopentadiene adduct (**1**) of 2,2-dimethyl-5-methylene-1,3-dioxan-4,6-dione leads to formation of this 5-methylene compound (**2**) in the gas phase and to its decomposition into acetone, carbon dioxide, and methylene ketene (**3**).



1 **2**

$$\longrightarrow CH_3COCH_3 + CH_2{=}C{=}C{=}O + CO_2$$

3

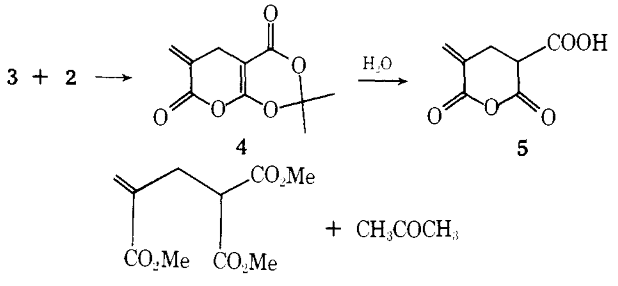
The cyclopentadiene adduct **1** could not be prepared directly[5] from the readily available bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic acid,[6] but was made indirectly by peracid oxidation of 5-phenylseleno-2,2,5-trimethyl-1,3-dioxan-4,6-dione and trapping of the unstable intermediate 2,2-dimethyl-5-methylene-1,3-dioxan-4,6-dione (**2**) with cyclopentadiene. Treatment of the sodium salt of 2,2,5-trimethyl-1,3-dioxan-4,6-dione suspended in methylene chloride with phenylselenenyl bromide (1.0 equiv) at room temperature afforded the 5-phenylseleno compound (67%) as pale yellow needles from ether/hexane, mp 66.6–68.5 °C. Oxidation of the 5-phenylseleno compound with *m*-chloroperbenzoic acid (2.1 equiv) in methylene chloride at −10 °C for 5 min followed by addition of excess cyclopentadiene at −10 °C gave the cyclopentadiene adduct **1** (53%) as colorless needles from ether/hexane, mp 86.5–88 °C.[7] Hydrolysis of adduct **1** with 2 M sodium hydroxide followed by acidification gave bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic acid (93%).

Direct examination of the pyrolysate of adduct **1**, formed in the temperature range 460–570 °C, by passing it into a quadrupole mass spectrometer showed that four of the principal ions which occurred at *m/e* 66, 58, 54, and 44 corresponded to the four products shown. Optimum formation of methylene ketene as indicated by the abundance of the ion at *m/e* 54 occurred between 490 and 520 °C. The abundance of the ion at *m/e* 26 increased markedly from 520 to 570 °C. This we attribute to the decomposition of methylene ketene into acetylene (*m/e* 26) and carbon monoxide, a general mode of fragmentation for methylene ketenes.[8]

The infrared spectrum of a pyrolysate formed at 495 °C (0.005 mm) and condensed directly onto a sodium chloride disk cooled conductively by liquid nitrogen showed a strong, sharp nonsymmetrical absorption band at 2100 cm^{-1}, in good agreement with the frequency range (2080–2113 cm^{-1}) found[1] for aryl- and alkyl-substituted methylene ketenes. The spectrum also showed bands attributed to cyclopentadiene and acetone, and separate examination of the volatile products confirmed the presence of carbon dioxide.

Efficient trapping of methylene ketene with aniline or methanol could only be achieved when the vaporized reagent was introduced ca. 8 cm before the outlet from the heated zone. Acrylanilide and methyl acrylate were obtained in yields of 24 and 25%, respectively.[9]

Pyrolysis of large samples (150–500 mg) of the cyclopentadiene adduct **1** at 495 °C (0.1 mm) and passage of the pyrolysate through a Pyrex tube at room temperature caused deposition of a glassy solid over a narrow zone in the tube; a liquid containing mainly cyclopentadiene and acetone collected in the cold trap. The glassy solid on occasion appeared partly crystalline, but was clearly a mixture. It was unstable to moisture and dissolved in water to give an acidic solution. The infrared spectrum (Nujol mull) showed complex carbonyl absorption including peaks at 1785, 1740, and 1685 cm^{-1}. On the basis of the methanolysis described below we consider the glassy solid to be a mixture containing principally the bicyclic compound **4**, formed by the addition of methylene ketene **3** to the 5-methylene compound **2**, and the anhydrido-acid **5** formed by partial hydrolysis of **4**.



6

The ^1H NMR spectrum of the glassy solid in $CDCl_3$ showed the presence of free acetone, and signals assigned to the bicyclic compound **4** (δ 1.80, s, CMe_2; 3.47, t, $J_{allylic}$ ca. 2.2 Hz, ring CH_2; 6.0, m, and 6.7, m, $=CH_2$) and to the anhydrido-acid **5** (δ 3.06, br m, CH_2CH; 3.88, t, J ca. 6.5 Hz, CH_2CH; signals due to $=CH_2$ assumed to be coincident with those of **4**).

Methanolysis of the glassy solid and treatment with a limited amount of diazomethane gave an oily product which we have shown to contain at least 90% of the unsaturated triester **6** (approximately 20% yield from adduct). In some runs this triester (mol wt 230) could be shown by mass spectrometry to contain a minor congener of m/e 316, which we suspect to be a tetraester formed by further addition of methylene ketene to the bicyclic compound **4**, with subsequent methanolysis and esterification. The identity of the triester **6** was confirmed by synthesis from trimethyl hydrogen propane-1,1,3,3-tetracarboxylate with formaldehyde and diethylamine.[10]

The range of reactions which has been demonstrated for substituted methylene ketenes is extremely limited;[1-4] despite repeated attempts we have so far failed to achieve an intermolecular cycloaddition to an alkene or diene, and our current work on systems which would permit intramolecular trapping has as yet yielded no result. An apparent exception to this experience, the addition of a ketene formed from dimethylacryloyl chloride and triethylamine to cyclopentadiene, is considered[11] to involve initial attack by a vinyl ketene rather than a methylene ketene. Thus, the ready cycloaddition of methylene ketene to its precursor **2**, shown by the present results, is the first unambiguous example of a cycloaddition other than dimerization.

Methylene ketene does react with nucleophiles in these experiments, but we have so far failed to isolate or detect any product of recombination with cyclopentadiene or any dimer, although the substituted methylene ketenes[1] which we have studied dimerize so readily as to frustrate all attempts to obtain them in solution.

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Roger F. C. Brown,* Frank W. Eastwood
Gabrielle L. McMullen
Department of Chemistry, Monash University
Clayton, Victoria 3168, Australia
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Photochemical Reactions in Organized Monolayer Assemblies. 5. Photochemical and Thermal Reactions of Reactive Intermediates Formed by Ligand Photoejection in Ruthenium Porphyrins

Sir:

During recent years, much effort has been directed toward the synthesis of metalloporphyrin complexes to serve as models for the biologically important oxygen transport and redox systems.[1-9] In recent studies of other surfactant molecules containing reactive chromophores, we have found that reactivity in the semirigid environment of organized monolayer assemblies is often quite different from behavior of the same compounds in solution.[10-17] Spectroscopic study of such assemblies has allowed the investigation of a variety of photochemical and photophysical processes. Results of such studies demonstrate that the monolayer environment may exert a striking influence on reactivity which can be explained in terms of the structure of the organized monolayer assembly.[18] In the present paper we report an extension of our investigations to the study of surfactant ruthenium(II) carbonyl porphyrins. This study was initiated on the premise that the monolayer assembly technique could be utilized to isolate and study reactive intermediates which are not isolable in solution.

The synthesis of porphyrins capable of forming monolayer assemblies was accomplished by converting mesoporphyrin IX to the corresponding dioctadecyl ester, from which the ruthenium(II) carbonyl derivative [Ru^{II}(CO)(py)Meso IX, DOE] (**1**) was readily obtained.[19] The compound was found to form stable films both from the pure compound (via spreading of chloroform solutions) or from mixtures with arachidic acid. Pressure-area studies indicate that films containing (**1**) and arachidic acid in various proportions were stable over a pressure range of 5–30 dyn/cm. Monolayers containing **1** were readily transferred to glass support slides, and several layers of **1** could be deposited in the usual manner.

Spectra of condensed assemblies of **1** were similar to those of dilute solutions of **1** and/or other ruthenium(II) carbonyl porphyrins and indicate that the porphyrin in the assemblies absorbs as a monomeric species. This behavior is in contrast to the ground-state dimer formed with accompanying spectral alteration when monolayer assemblies of the corresponding free base porphyrin were constructed.[15] For **1** a surface pressure-area isotherm similar to that for the free base[15] is obtained even though significant spectral interaction does not occur; thus stacking of two rings occurs but probably with a larger interporphyrin distance. Studies of the spectra of assemblies of **1** with polarized light reveal that the porphyrin