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(26) For a general review on structures of metal–nucleoside and metal–nucleotide complexes, see D. J. Hodgson, *Prog. Inorg. Chem.*, **23**, in press.

(27) There is, however, an exception to the N_3-binding rule for cytosine derivatives. In the structure of Mn(5′-CMP)·2½H_2O, cytosine was found to coordinate through O_2 (the carbonyl oxygen in the C_2 position) and not through N_3: K. Aoki, *Chem. Commun.*, 748 (1976).

(28) In over twenty structure determinations of metal complexes of adenine, guanine, and cytosine derivatives, complexation via an exocyclic amino group has never been found.[26]

(29) Alfred P. Sloan Fellow, 1974–1976; NIH Research Career Development Awardee, 1975–1980.

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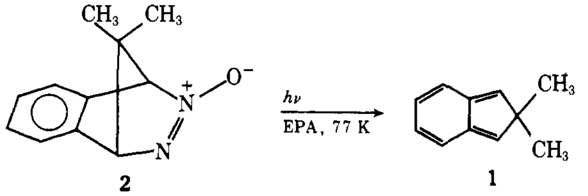
2,2-Dimethylisoindene and 5,5-Dimethylbenzobicyclo[2.1.0]pent-2-ene

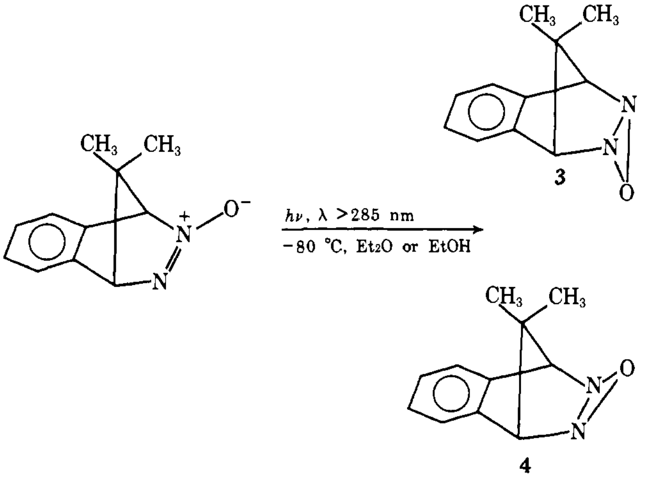
Sir:

While *o*-xylylene[1] and various *o*-xylylene derivatives[2] have been generated, isolated, and characterized spectroscopically, isoindenes have heretofore eluded isolation, although they have been demonstrated to exist as transient intermediates under various reactive conditions.[3]

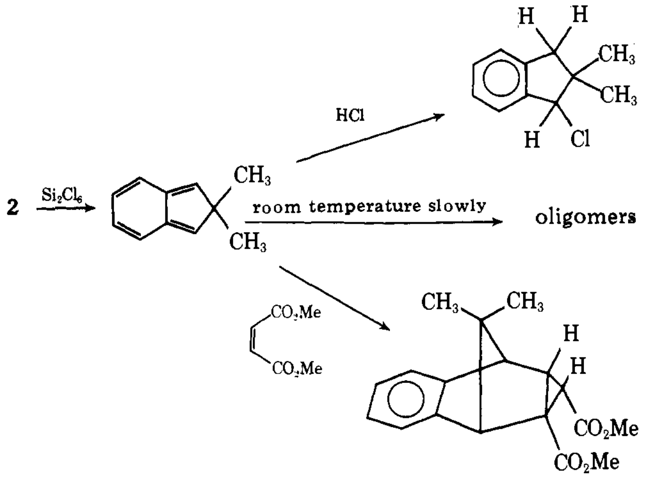
We have found that 2,2-dimethyl-2*H*-indene (2,2-dimethylisoindene), **1**, may be generated and isolated in an EPA glass matrix at 77 K by irradiation of azoxy compound **2**[3b] (high-pressure mercury lamp and λ >285 nm filter, or low-pressure mercury lamp). **1** exhibited a structured absorption band (λ_{max} 405 nm) and a similarly structured light blue fluorescence (λ_{max} 467 nm) in a good mirror-image relationship. Both were quite similar to the spectra reported for alkyl substituted orthoxylylenes[2a] as well as for *o*-xylylene itself,[1] but were red-shifted by about 2000 cm^{-1}, presumably due to cyclic hyperconjugation. The shape of the emission curve of **1** is independent of excitation wavelength and the excitation spectrum follows the shape of the absorption band. The onsets of absorption and emission almost coincide, and the 0–0 bands are clearly discernible as relatively intense peaks (λ_{max} (A) 432 nm and λ_{max} (E) 439 nm). As in the case of other reported spectra of *o*-xylylenes,[1,2] the calculated (PPP) first transition is allowed and occurs near the observed position, and a very weak transition into a predominantly doubly excited state at somewhat higher energies is apparently buried under the first band.



While **1** was found to be stable indefinitely at room temperature in EPA solution, it was produced only in very small quantities upon irradiation (λ >285 nm) of **2** at 25 °C or even at −80 °C. At the latter temperature there was a smooth conversion to species containing the benzene chromophore and isomeric with **2**, stable for days at −80 °C but reconverting to **2** in several hours upon warming to −20 °C. NMR (CD_3OD) showed that two photoisomers were formed in a ratio of about 2.5:1. Both contribute to a narrow multiplet at δ 7.38 (4 H); the major isomer also has singlets at δ 4.64 (2 H), 1.50 (3 H), and 0.57 (3 H), the minor isomer also has singlets at δ 4.81 (2 H), 1.44 (3 H), and 0.60 (3 H). Thus, the probable solution photoproducts are endo and exo oxadiaziridines, **3** and **4**. Greene and Hecht have previously demonstrated the ability of azoxy compounds to cyclize in this manner.[4]

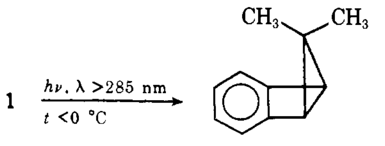


In view of the apparent ability of the *gem*-dimethyl substituents to stabilize the isoindene toward oligomerization, we attempted to generate **1** at room temperature by an alternative method. Thus, it was found that **2** underwent deoxygenation by Si_2Cl_6[5] followed by loss of N_2 from the probable transient azo compound to produce **1**.



The NMR spectrum of the bright yellow solution (100 MHz) showed a singlet at δ 1.16 (6 H) and vinylic multiplets at δ 6.08 (4 H) and 6.55 (2 H). This is the first reported NMR spectrum for an *o*-xylylene derivative, although NMR spectra have been obtained for *p*-xylylene,[6] isoindole,[7] isobenzofuran,[8] and for 1,2-(2,3-naphtho)-*o*-carborane.[9] The reported chemical shift for ring protons of *p*-xylylene (δ 6.49) is indicative of a similar lack of aromaticity in ortho and *p*-xylylene-type molecules. The yellow color of the isoindene was rapidly discharged when the solution was treated with either HCl or dimethyl maleate with products **5** and **6** being formed, isolated, and characterized by comparison with authentic samples.

When a fluid isoindene solution in various solvents was irradiated at 0 °C or below, it rapidly lost its color. When warmed to room temperature, the color soon reappeared. An NMR analysis of this photolytic-thermal interconversion in Si_2Cl_6 showed that 5,5-dimethylbenzobicyclo[2.1.0]pent-2-ene was the photoproduct. **7** gave an NMR with singlets at δ 0.94



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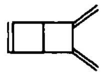
(3 H), 1.06 (3 H), and 2.54 (2 H) and a pair of symmetrical multiplets at δ 6.62 (2 H) and 6.82 (2 H). The singlet bridgehead proton absorption (δ 2.54) was at almost the exact chemical shift which would be predicted for this molecule considering the chemical shifts of the benzylic protons of benzocyclobutene (δ 3.14),[10] the allylic protons of cyclobutene (δ 2.54),[11] and the bridgehead protons of bicyclo[2.1.0]pent-2-ene (δ 2.0).[12] On the other hand, the bridgehead protons of the Dewar-*o*-xylylene species **8** are at δ 3.73.[13] This, plus the



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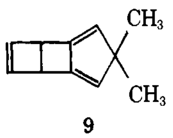

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fact that **8** is relatively stable thermally, makes the alternative photoproduct structure **9** highly unlikely. The ready thermal reconversion of the photoproduct to isoindene **1** taken together with the simplicity of the NMR spectrum makes dimeric structures highly improbable. Hence, the benzobicyclo[2.1.0]-pent-2-ene structure can be invoked with confidence.

Note Added in Proof. Recently, evidence for intermediacy of unsubstituted isoindene in a photobisdecarbonylation reaction has been reported. It is apparently stable to a 1,5-hydrogen shift at −50 °C, but only dimers and trapping products were isolated: R. N. Warrener, R. A. Russell, and T. S. Lee, *Tetrahedron Lett.*, 49 (1977).

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Photochemical Synthesis of Low-Valent Organothorium Complexes. Evidence for Photoinduced β-Hydride Elimination

Sir:

An important chemical property of transition metal organometallic compounds is the widespread existence of multiple formal oxidation states for the metal ions and the general tendency of these ions to readily shuttle between oxidation states.[1] The situation is not so clear for organothorium and organouranium complexes, and by far the great bulk of known compounds contain the actinide ion in the +4 oxidation state.[2] The only low-valent (<IV) complexes of these metals reported to date are several uranium(III) complexes[3] and the deep violet $(C_5H_5)_3Th$.[4] The latter compound, prepared by reduction of $(C_5H_5)_3ThCl$, is especially noteworthy because few thorium(III) complexes of any type are known,[5,6] and because there is great current interest in the low oxidation state organometallics of the isoelectronic Ti, Zr, and Hf.[7] For these reasons we have initiated a study of new synthetic routes to low-valent organoactinides, and of the chemical and physicochemical properties of such species. In this communication we report an efficient, high-yield photochemical synthesis of two new thorium(III) complexes and some surprising observations on how $(C_5H_5)_3ThR$ photochemistry differs from the thermal chemistry.

It is known that $(\eta^5\text{-}C_5H_5)_3ThR$ compounds (e.g., R = *i*-propyl) thermolyze cleanly in toluene at 170 °C according to eq 1.[8]

$$2(C_5H_5)_3Th(i\text{-}C_3H_7) \xrightarrow[\Delta]{} \underset{\mathbf{1}}{[(C_5H_5)_2Th(C_5H_4)]_2} + 2C_3H_8 \quad (1)$$

Essentially no β-hydride elimination[9] is observed, but rather hydrogen is intramolecularly abstracted from a cyclopentadienyl ring to quantitatively yield propane and the $\eta^5{:}\eta^1$-cyclopentadienylthorium(IV) complex **1**.[10] In marked contrast, we find that irradiation (Hanovia 679A36 medium pressure mercury lamp) of benzene solutions (0.10–0.30 M) of $(C_5H_5)_3Th(i\text{-}C_3H_7)$ in quartz at 5 °C produces (within 1–2 h) a ≥ 92% yield of the highly air-sensitive, dark green microcrystalline complex **2a** as well as comparable quantities[11] of propane (53%) and propene (47%)

$$\underset{\substack{\mathbf{2a},\ R = H\\ \mathbf{2b},\ R = CH_3}}{(C_5H_4R)_3Th(i\text{-}C_3H_7)} \xrightarrow{h\nu} \underset{\mathbf{2}}{(C_5H_4R)_3Th} + \text{propane} + \text{propene} \quad (2)$$

In a similar manner, the methylated analogue, **2b**, can be prepared. Though different in properties from the abovementioned violet species,[4] the data at hand lead us to also formulate **2a** as $(C_5H_5)_3Th$. Anal. Calcd for $C_{15}H_{15}Th$: C, 42.12; H, 3.54. Found: C, 42.26; H, 3.77. The infrared spectrum (Nujol mull) of **2a** exhibits the characteristically simple pattern[8,12,13] of an $\eta^5\text{-}C_5H_5$ unit (as in the triscyclopentadienyl lanthanides[14]): 1261 w, 1065 w, 1008 m, 832 w, sh, 800 s, sh, 700 vs, 670 m, sh cm^{-1}. The laser Raman spectrum of **2a** (spinning sample, 5145 Å Ar$^+$ excitation) is also similar to the lanthanide triscyclopentadienyls[16] and other[8,12,17] $\eta^5\text{-}C_5H_5$ complexes: 1870 vw, 1866 vw, 1854 w, 1436 vw, 1136 w, 1121 s, 1068 vw, 1007 vw, 900 vw, 893 vw, 885 w, 840 s, 806 vw, 790 vw, 780 w, 615 w, 254 s, 234 s, 157 s cm^{-1}. No evidence for a metal hydride or any other non-$\eta^5\text{-}C_5H_5$ species is observed in these spectra or in those of the $(C_5D_5)_3Th$ analogue. The mass spectrum of **2a** exhibits a strong peak at $(C_5H_5)_3Th^+$; ions as high as $[(C_5H_5)_3Th]_2^+$,[18] which fragment by loss of C_5H_5, C_2H_2,[19] or C_3H_3[19] are also observed. Methanolysis of **2a** produces cyclopentadiene in greater than 95% yield. The