and are uncorrected. Infrared spectra were obtained with a Beckman IR-7 apparatus, and visible and ultraviolet spectra with a Cary 15 spectrophotometer. NMR spectra were measured with a Varian XL-100 instrument using deuteriochloroform as solvent and with residual chloroform ($\delta$ 7.27) as an internal standard. Mass spectra were obtained using a CEC-21B-110 instrument set at 70 eV.

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

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**Abstract:** 2,2-Dimethylisoindene (**1**) is quite stable in solution at room temperature in the absence of oxygen. It can be prepared from the azoxy precursor **3** by irradiation in a glassy matrix or by room temperature deoxygenation with $Si_2Cl_6$, and from the dibromo precursor **4** by reaction with metals. The photochemical interconversion **1** $\rightleftarrows$ **2** is described; the activation energy for the facile thermal "forbidden" ring opening **2** → **1** is 18.9 kcal/mol. The NMR, UV, fluorescence, polarized excitation and emission, and MCD spectra of **1** are reported. Comparison with semiempirical calculations using singly and doubly excited configurations shows good agreement and suggests the presence of a low-energy "doubly excited" state, believed to be responsible for the photochemical reactivity of **1**.

## Introduction

The highly reactive *o*-xylylene[2,3] and its various simple derivatives[4,5] have been generated, trapped, and characterized spectroscopically, and some have been even isolated in solution. On the other hand, related simple isoindenes, although generated and trapped,[6,7] have eluded direct characterization until a short time ago.[8] In recent short communications,[9,10] two research groups have reported the isolation and spectral properties of solutions of 2,2-dimethyl-2*H*-indene (2,2-dimethylisoindene, **1**), and a full report on flash photolytic experiments which allowed the direct observation of several arylisoindenes by absorption spectroscopy has just appeared.[11] Similarly as other *o*-xylylenes,[2,5] **1** can be converted photochemically to the corresponding benzocyclobutene[9] (**2**). This highly strained tricyclic ring system is believed to have been first generated some time ago by Berson and Pomerantz[12] by addition of benzyne to a cyclopropene (they proposed the name pseudoindene). In the present paper, we describe the preparation and properties of both **1** and **2**, as well as their facile mutual interconversion.

## Results

We have found three methods useful for generation of **1** from easily accessible precursors. In the order of discovery as well as increasing convenience, these were (1) irradiation of the azoxy compound **3**[7] in an EPA glass matrix at 77 K, (2) deoxygenation of **3** with $Si_2Cl_6$ at room temperature with concurrent loss of $N_2$, (3) dehalogenation of the dibromo derivative **4** with metals at room temperature, all in the absence of oxygen.

The photochemical conversion **3** → **1** in rigid matrix can be accomplished both with a low-pressure mercury arc, which excites the benzene chromophore, and with a high-pressure mercury lamp using a $\lambda > 285$ nm filter, which excites primarily the azoxy chromophore. Only relatively low concentrations can be achieved by this method. Once produced, the solution of **1** is stable even at room temperature as long as no oxygen is present. However, room temperature or dry ice temperature irradiation of a fluid solution of **3** in EPA, ether, or ethanol ($\lambda > 285$ nm) produces only traces of **1**. The major product at −80 °C is a mixture of two species containing the benzene chromophore (UV) and stable for days at −80 °C but reconverting to **3** after several hours at −20 °C and faster at room temperature. The return to **3** was not affected by thorough removal of all gases present (freeze-pump-thaw), proving that the two new species still contain the elements of $N_2O$ and are isomeric with **3**. The NMR spectrum ($CD_3OD$) showed that the photoisomers were formed in a ratio of about 2.5:1. Both contribute to a narrow multiplet at $\delta$ 7.38 (4 H); the major isomer also has singlets at $\delta$ 4.64 (2 H), 1.50 (3 H), and 0.57 (3 H), and the minor one also has singlets at $\delta$ 4.81 (2 H), 1.44 (3 H), and 0.60 (3 H). Based on these data, we propose the structures of endo and exo oxadiaziridines **5a** and **5b** to these unstable products. There is good precedent for photocyclization of acyclic azoxy compounds to oxadiaziridines,[13] though cyclic (cis) azoxy compounds have apparently not been previously transformed in this fashion.

The deoxygenation of **3** with neat $Si_2Cl_6$[14] in the absence of oxygen proceeds smoothly at room temperature and provides much more concentrated yellow solutions of **1**. Unfortunately, the $Si_2Cl_6$ solvent interferes with some spectroscopic measurements and is difficult to remove. However, these solutions were suitable for chemical proofs of the structure of **1**. Treatment with HCl or with dimethyl maleate causes a rapid disappearance of the yellow color. Isolation yielded the chloroderivative **6** and the diester **7**, respectively. These were fully characterized and identified by comparison with authentic samples.

The dehalogenation of **4** with metals proceeds smoothly at room temperature. Zinc-copper couple and lithium amalgam are particularly suitable reagents. Absolute exclusion of oxygen is again essential. The reaction can be performed in volatile

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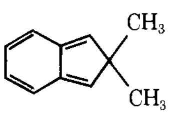
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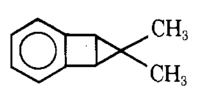
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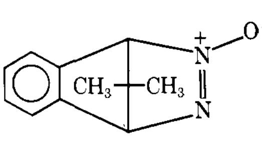
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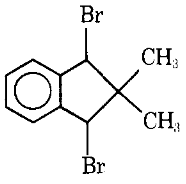
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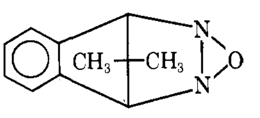
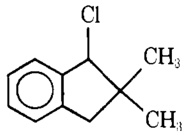

**5a**, endo
**b**, exo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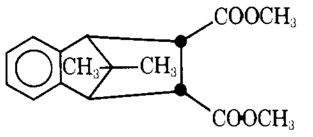
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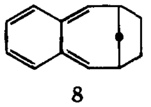
**8**


**9**

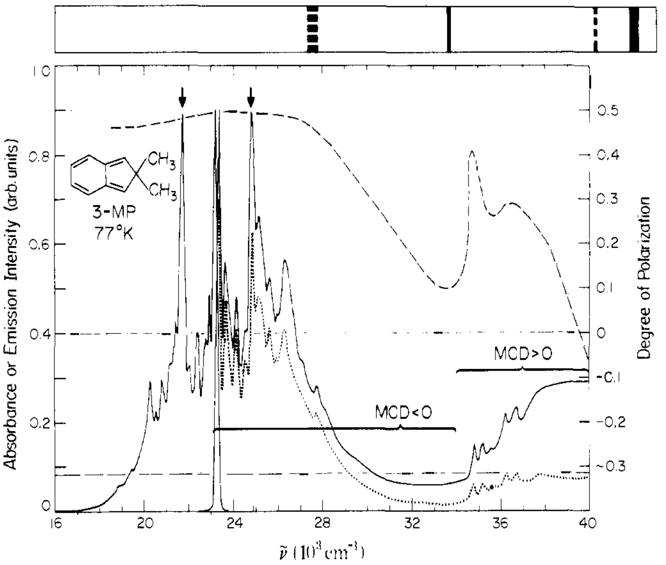

Figure 1. Spectra of 2,2-dimethylisoindene in 3-methylpentane glass at 77 K: solid lines, absorption and fluorescence (uncorrected); dotted line, corrected fluorescence excitation; dashed line, degree of polarization monitored at wavenumbers indicated by arrows). Room temperature MCD spectrum followed the absorption curve but was less resolved; the observed signs are shown. Calculated transitions are shown on top (line thickness indicates transition intensity; dashed line, short-axis; full-line, long-axis polarized).

solvents such as a hydrocarbon or in a nonvolatile solvent such as dibutyl phthalate, permitting removal of the volatile **1** by trap to trap distillation.

Even in quite concentrated solutions, **1** is stable at room temperature for many hours. Eventually, its yellow color is lost with concomitant formation of dimers and/or oligomers. The spectral behavior of **1** is fully in accord with the assigned structure. The absorption and fluorescence spectra are closely similar to those of the planar simple *o*-quinodimethane derivative **8** given in ref 5. They are presented in Figure 1, which also shows polarized excitation and emission spectra, magnetic circular dichroism (MCD), and results of semiempirical calculations employing configuration interaction with singly and doubly excited configurations. The NMR spectrum (100 MHz) showed a singlet at $\delta$ 1.16 (6 H) and vinylic multiplets at $\delta$ 6.08 (4 H) and 6.55 (2 H). No previous NMR data for a *o*-quinodimethane are available for comparison, and the closest analogues appear to be isoindole,[15] isobenzofuran,[16] and 1,2-(2,3-naphtho)-*o*-carborane,[17] whose spectra bear reasonable resemblance to that of **1**. The reported chemical shift for ring protons of *p*-xylylene[18] ($\delta$ 6.49) is indicative of a similar lack of aromaticity in molecules of *o*- and *p*-quinodimethane types.

In a rigid glass at 77 K, **1** is very stable to UV irradiation. In fluid solutions at higher temperatures, it fluoresces much less strongly, and undergoes a facile photochemical transformation. The product is thermally unstable and above 0 °C reverts easily to **1**. It does not fluoresce even at 77 K and can also be converted back to **1** photochemically. This reversal occurs even in a rigid glass at 77 K and the spectrum of **1** produced in this fashion is exactly identical with that of **1** produced in other ways, indicating that the photoproduct is formed by a unimolecular transformation and is not a dimer of **1**. This is confirmed by irradiation of a solution of **1** in a rigid glycerol glass at −60 °C, which leads to the same photoproduct. The spectral properties of the photoproduct are in accord with structure **2**: UV absorption only below 280 nm, compatible with the presence of a perturbed benzene chromophore, NMR singlets at $\delta$ 0.94 (3 H), 1.06 (3 H), and 2.54 (2 H), and a pair of symmetrical multiplets at $\delta$ 6.62 (2 H) and 6.82 (2 H). The singlet proton assigned to the bridgehead resonates at almost exactly the position which would be predicted from the chemical shifts of the benzylic protons of benzocyclobutene ($\delta$ 3.14),[19] the allylic protons of cyclobutene ($\delta$ 2.54),[20] and the bridgehead protons of bicyclo[2.1.0]pent-2-ene **9** ($\delta$ 2.0).[21]

The thermal rearrangement $\mathbf{2} \rightarrow \mathbf{1}$ in hexane solvent is strictly first order and proceeds with an activation energy of 18.9 ± 0.2 kcal/mol (frequency factor A = $10^{11.5\pm0.2}\ s^{-1}$), to be compared with 26.9 kcal/mol for the related **9**.[22]

## Discussion

The amazing thermal stability of the polycyclic *o*-quinodimethane **8**,[5] contrasting with the striking ease with which *o*-xylylene itself dimerizes,[2] is apparently due to the steric hindrance to dimerization as well as to product strain developed in the orbital symmetry preferred conrotatory closure. It is noteworthy that the much less sterically encumbered **1** is also quite stable; it would appear that very little steric hindrance is needed to suppress the extreme propensity of *o*-xylylene toward dimerization. Since even the parent isoindene appears to dimerize less eagerly,[6] it is tempting to speculate that the forced planarity of the conjugated system is partly responsible for the relative stability of the polycyclic *o*-quinodimethanes such as **1** compared with *o*-xylylene itself. If true, this then suggests that the reaction path for the dimerization of *o*-xylylene involves an out of plane twist of a vinylidene group. A need for this would be understandable if the dimerization proceeded via the triplet state of one of the components, since theory suggests that the energy of a twisted triplet should be a little lower than that of a planar triplet (cf. ref 2). However, at this time there is no other evidence for such a conjecture, and it should be noted that the addition reactions of *o*-xylylene with maleate and fumarate esters proceed with retention of stereochemistry in the usual Diels–Alder manner.[23a]

The thermal conversion $\mathbf{2} \rightarrow \mathbf{1}$ has a remarkably low activation energy for a "forbidden" disrotatory electrocyclic opening of a cyclobutene.[23b] Molecular models indicate that cyclic overlap of the atomic orbitals on the four centers involved is impossible to avoid during the reaction without unreasonable distortion of the $\sigma$ framework, so that this reaction certainly is pericyclic (concerted) even if the path of minimum energy involves a somewhat faster rotation of one of the termini. The low activation energy is undoubtedly related to the high ring strain in **2**. Comparison with **9**, which has similar strain, suggests that the additional conjugation with the six-membered ring stabilizes the "antiaromatic" transition state more than it stabilizes the starting material. As outlined in more detail elsewhere,[24] taking cyclobutadiene as the model of the transition state for the conversion of **9** and benzocyclobutadiene for the conversion of **2**, roughly the observed difference in activation energies is predicted by simple Hückel theory. The presence of methyl groups would appear to have little effect on the ring-opening process, since Baldwin has observed very little difference in rates for opening of bicyclo[2.1.0]pentene and various methyl derivatives, including the *exo*- and *endo*-5-methylbicyclopentenes.[25]

The photochemical conversions **1** → **2** and **2** → **1** have ample precedent. The former appears to require thermal activation, in accordance with the observed strong fluorescence of **1** which indicates the presence of a sizable well in the excited singlet surface near the starting geometry. Similarly as in the butadiene → cyclobutene conversion,[26] it is likely that the excited singlet state directly responsible for the reaction is the "doubly excited" covalent state calculated to occur a little above the fluorescent lowest excited singlet.

The spectroscopic data shown in Figure 1 are in very good agreement with results of standard $\pi$-electron calculations using systematically selected single and double excitations, except that all calculated transition energies are somewhat too high. The relatively strong lowest energy transition with origin at ~23 000 cm$^{-1}$, negative in MCD, is calculated to correspond to the HOMO → LUMO excitation and to be polarized in a direction perpendicular to the molecular axis of symmetry. The next obvious transition is observed near 35 000 cm$^{-1}$, is positive in MCD, and probably corresponds to the indistinct humps observed in this region for *o*-xylylene[2] and for **8**.[5] From the degree of fluorescence polarization, it is clearly polarized parallel to the lowest transition, and thus corresponds to the third calculated transition. The steady decrease of the degree of polarization in the region 28 000–34 000 cm$^{-1}$ is difficult to attribute to vibronic interactions within the first transition, particularly since its onset is rather abrupt and since no analogous decrease is seen in the polarization of fluorescence, which is a quite faithful mirror image of absorption. It appears much more likely that this decrease is due to a hidden transition located in this region and polarized perpendicular to the lowest transition. This hidden transition presumably corresponds to the second calculated transition, which contains a sizable contribution (~30%) from the doubly excited HOMO,HOMO → LUMO,LUMO state. Our hopes that this transition will be clearly revealed in the MCD spectrum have not been fulfilled. The MCD curve is very weak in this region and appears to follow approximately the shape of the absorption curve. As pointed out earlier,[2] the label "doubly excited" is only an inaccurate designation for this presumably present state which involves considerable configuration mixing. Similar low-energy "predominantly doubly excited" states have been detected in other biradicaloid hydrocarbons,[27,28] including long polyenes,[29] and high-energy doubly excited states have been assigned in several "ordinary" hydrocarbons.[30,31]

The decrease of the degree of polarization in the region of increasing absorption intensity beyond 38 000 cm$^{-1}$ probably corresponds to the onset of a fourth transition polarized perpendicular to the lowest one. Such a transition is indeed calculated to lie at somewhat higher energies.

Although we have not determined absolute polarizations experimentally, the agreement of relative polarizations with those calculated makes it highly likely that the calculated transition moment directions are correct, and that the first and third transitions are short-axis and the second and fourth transitions long-axis in-plane polarized.

## Experimental Section

**Instrumentation.** Solvent purification procedures and equipment[2] for photochemistry and absorption spectroscopy at 77 K as well as the spectrofluorimeter[32] used for polarized emission spectroscopy have been described. The MCD spectrum was measured at room temperature as in ref 33. Standard vacuum line techniques were used throughout.

**Calculations.** The calculations were of the PPP type and used 170 singly and doubly excited configurations selected automatically by the SECI-1 procedure of ref 34. The parameters were those appropriate for this extent of CI, and the ground-state energy was taken to be that of the SCF determinant, similarly as in ref 27. The parameters for the $(CH_3)_2C$ group were those proposed for methyl in ref 35. The calculated energies (10$^3$ cm$^{-1}$), oscillator strengths from dipole length and from dipole velocity, and polarizations follow: (1) 27.6, 0.17, 0.20, *y*; (2) 33.7, 0.01, 0.01, *z*; (3) 40.3, 0.001, 0.001, *y*; (4) 42.0, 0.23, 0.26, *z*; (5) 44.4, 0.007, 0.006, *y*; (6) 47.6, 0.43, 0.46, *z* (*z* is the long and *y* the short in-plane axis).

**Materials. 2,2-Dimethylisoindene (1).** The reaction vessel was comprised of a main compartment containing a Teflon-coated stir bar and a rotatable side-arm addition vessel from which liquids or solids could be added to the main vessel. The reaction vessel was loaded in a drybox with 20.0 g of Li(Hg) [prepared by swirling 0.5% by weight Li in Hg in a stoppered vessel until solution occurred (~40 min)] and 4 mL of pentane in the main compartment. The side arm was loaded with 0.508 g of 1,3-dibromo-2,2-dimethylindan[36] in 2 mL of pentane. The loaded vessel was removed and attached to a vacuum line and both pentane solutions were degassed four times. Then the contents of the side arm were added at room temperature over a period of 4 min to the stirred contents of the main compartment. After stirring for an additional 10 min, the volatile components of the reaction vessel were transferred to a storage vessel where the essentially pure pentane solution of **1** could be diluted for UV analysis or transferred as is to an NMR tube for analysis.

If dibutyl phthalate is used as reaction solvent, **1** may be transferred solvent free into whatever solvent is desired in the storage vessel.

**2,2-Dimethylisoindene (1) (from Azoxy Compound 3).** Working within a drybox, 36.7 mg of **3**[37] was placed in the main compartment of the above-described reaction vessel. In the side arm was placed 0.7 mL of hexachlorodisilane (Aldrich reagent). After the mixture was degassed four times the hexachlorodisilane was added to **3** at 40–45 °C and allowed to stir for 1.5 h. At that time the reaction mixture was vacuum transferred into an NMR tube for analysis.

Samples of **1** prepared in this manner were always contaminated by variable amounts of 1-chloro-2,2-dimethylindan (**6**) which was formed by addition of HCl to **1**. HCl was generally present as a contaminant in $Si_2Cl_6$ from traces of water and addition of $H_2O$ to the system or of HCl led to destruction of **1** and formation of **6**. **6** could also be synthesized independently by the reaction of *N*-chlorosuccinimide with 2,2-dimethylindan in refluxing $CCl_4$ with benzoyl peroxide. NMR of **6** ($CDCl_3$): $\delta$ 1.20 (s, 6 H), 2.68 (d, $J$ = 16.0 Hz, 1 H), 2.94 (d, $J$ = 16.0 Hz, 1 HO), 4.97 (s, 1 H), 7.16–7.48 (m, 4 H).

When an equivalent amount of dimethyl maleate was added to **1** in either $Si_2Cl_6$ or in pentane a high yield of Diels–Alder adduct **7** was obtained. NMR of **7** ($CDCl_3$): $\delta$ 0.72 (s, 3 H), 1.20 (s, 3 H), 3.05–3.15 (t, $J$ = 2.0 Hz, 2 H), 3.45 (s, 6 H), 3.68–3.72 (t, $J$ = 2.0 Hz, 2 H), 7.06–7.28 (m, 4 H).

**5,5-Dimethylbenzobicyclo[2.1.0]pent-2-ene (2).** A solution of **1** in various solvents (i.e., hexachlorodisilane, pentane, or $CCl_4$) was irradiated at −10 °C for 1 h with a 450-W medium-pressure mercury lamp to yield a quantitative yield of **2**. The sample was generally contained in a sealed Pyrex tube which was used directly for NMR analysis. Allowing the tube to stand at room temperature for 1 h gave rise to a complete reconversion to **1**.

**Kinetics of Thermal Conversion of 2 to 1.** A single sample of **1** in pentane was prepared at the proper dilution to give an absorbance of ~0.70 in a quartz UV cell which was sealed under vacuum. Photolysis of the cell at −20 °C for 1 h led to a total conversion of **1** to **2**, whence the sample was placed in the thermostated UV spectrometer for direct kinetic observation via change in absorbance. The spectrophotometer utilized was a Zeiss Model PMQII spectrometer. The wavelength observed was 403.9 nm. The temperature was measured using a

Chromel-Alumel thermocouple in conjunction with a Tinsley Model 3387F potentiometer. Temperatures were constant to ±0.1 °C. The measured values of the rate constants were [units of $10^{-2}\ s^{-1}$, temperature (°C) in parentheses] 8.99 ± 0.02 (12.3), 5.33 ± 0.02 (7.8), 3.41 ± 0.02 (4.25), 2.10 ± 0.003 (0.0), 1.19 ± 0.004 (−4.1), 0.642 ± 0.002 (−8.55). An Arrhenius plot of this data gave a good straight line with the frequency factor and energy of activation being calculated by the method of least squares, $\log A = 11.46 \pm 0.2$; $E_A = 18.9 \pm 0.2$ kcal/mol; at 275.1 K, $\Delta H^{\ddagger} = 18.4$ kcal/mol, $\Delta S^{\ddagger} = -8.0$ cal deg$^{-1}$, $\Delta G^{\ddagger} = 20.6$ kcal/mol.

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# Synthesis of Cyclopropane Derivatives from Olefins by the Reaction with Organic *gem*-Dihalides and Copper[1]

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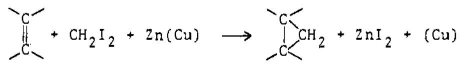
**Abstract:** A new, versatile, and convenient method for the synthesis of cyclopropane derivatives is reported and involves the reaction of olefins with organic *gem*-dihalides and copper powder in an aromatic hydrocarbon. The reaction is electrophilic and proceeds stereospecifically, i.e., cis and trans olefins afford cyclopropane derivatives whose configurations with respect to the olefin substituents are cis and trans, respectively. Moreover, ether functions controlled the stereochemistry of the cycloaddition; for example, *cis*-2-methoxybicyclo[4.1.0]heptane was exclusively obtained from 3-methoxycyclohexene. Isomeric olefins, which would be expected from the insertion of the corresponding free carbenes into C–H bonds, were generally not detected in the reaction mixture. The reaction appears to proceed via organocopper intermediates rather than free carbenes. The reaction with diiodomethane gave cyclopropane derivatives in good yields similar to the corresponding Simmons–Smith reaction. The reaction with trihalomethanes gave the corresponding monohalocyclopropane derivatives, and showed the syn stereoselectivity. The reaction with dibromoacetic esters, contrary to the reaction of diazoacetic esters with olefins, gave the corresponding alkoxycarbonylcyclopropane derivatives and showed syn stereoselectivity when steric repulsion between the alkoxycarbonyl group and the olefin substituents was not significant.

## Introduction



The reaction of olefins with organozinc reagent prepared from diiodomethane and zinc-copper couple is known as the Simmons–Smith reaction, and has proved to be a versatile and convenient method for the synthesis of cyclopropane derivatives.[2] The copper was reported to play no role other than ac-

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