ng that the dienylic C–H dissociation energy in cyclopentadiene is very much larger (by *ca.* 50 kcal) than the activation energy for sigmatropic rearrangement. The former (70–75 kcal)[1c, 10a] has been estimated on the basis of the heat of formation of the cyclopentadienyl radical derived from mass spectroscopic studies involving the direct measurement of its ionization potential[1c, 2a] and the appearance potential of the cyclopentadienyl cation from nickelocene[1c] or cyclopentadiene.[10b]

In a few cases the rearrangement of **1** took an alternate course in deuteriochloroform. A red color developed, and the nmr spectrum was different from that of **3**. The nmr, uv, and ir spectra of the red product correspond to that reported[11] for 1,2-dihydrofulvalene (**4**) which has previously been obtained by the carefully controlled acid-catalyzed dehydration of 1-dicyclopentadienol.[11] We believe that the rearrangement of **1** to **4** was similarly catalyzed by traces of acid in the solvent. Indeed, deliberate addition of small quantities of trifluoroacetic acid to a dilute cold chloroform solution of **1** did lead to detectable amounts of **4**.

(10) (a) H. S. Hull, A. F. Reid, and A. G. Turnbull, *Inorg. Chem.*, **6**, 805 (1967); (b) F. Dorman, *J. Chem. Phys.*, **43**, 3507 (1965).

(11) K. V. Scherer, *J. Am. Chem. Soc.*, **85**, 1550 (1963).

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Low-Temperature Photolysis of Bicyclo[6.2.0]deca-2,4,6,9-tetraene and *trans*- and *cis*-9,10-Dihydronaphthalenes. Tetracyclo[4.4.0.0²,¹⁰.0⁵,⁷]deca-3,8-diene

Sir:

We have observed remarkable rearrangements of compounds **1**,[1] **2**,[1,2] and **3**.[3] Photolysis of all these

(1) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967). We have received many inquiries concerning the degenerate tautomerization of **1**. Because of theoretical significance of this problem, we describe briefly the observed results and answer the question whether or not this tautomerization is indeed occurring in this system. Over a range of −110 to 75° no line broadening of any nmr signals of **1** was observed. Therefore, the tautomerization, if it does proceed, must be slower than at least 10 sec⁻¹ below 75° because the spectrum is interpretable only on the basis of two allylic protons (τ 6.32), two olefinic protons of the cyclobutene (τ 3.98), and six other olefinic protons. Further, if a conformational change occurs, then this process must be fast even below −110°. Since **1** isomerizes to **2** ($\Delta H^{\ddagger}$ = 25 kcal/mol, $\Delta S^{\ddagger}$ = 0 eu) the range of experimentally observable rate of **1** is thus limited. We prepared monodeuterated **1′** (0.86 D/molecule), and its nmr spectrum clearly showed that deuterium was introduced solely at C-9 as evidenced by a 0.57 ± 0.03 ratio of intensity of signals at τ 3.98 and 6.32. This ratio remained unchanged for 10 days at 0° and an additional 5 days at 25°, during which time **1′** isomerized slowly to monodeuterated **2′**. Therefore, we conclude that the tautomerization demands an energy barrier of at least 25 kcal. There is good reason to believe that ΔF between the two conformers of **1** would be more than 10 kcal, mainly responsible for the absence of line broadening of the nmr signals of **1**. The ratio of intensities of olefinic to aliphatic protons in the spectrum of **2′** was 3.64 ± 0.05, supporting our previous proposal for this stereospecific transformation.

(2) (a) M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967); (b) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967). Compound **2** used in our work showed $\lambda_{max}^{methylcyclohexane}$ 276 mμ (ε 3850), $\lambda_{min}^{methylcyclohexane}$ 244 (1720), which differs vastly from that (λ_{max}^{MeOH} 231 mμ (no molar extinction coefficient)) reported by the latter group.[2b] The Dreiding model reveals that the diene system of **2** is nearly coplanar without any significant distortion of bond angles. Compound **2** was treated with a 300-fold molar excess of diimide (KCOON=NCOOK + AcOH) at room temperature repeatedly until no **2** was present in the reaction product, and then a mixture of partially hydrogenated **2** was catalytically hydrogenated with 10% Pd–C in methanol to provide *trans*-decalin in more than 90% yield. Since we found that thermolysis of **2**

compounds has provided in 65–70% yield the same, thermally unstable (CH)₁₀ hydrocarbon (**4**). Furthermore, we have proven that **4** is indeed tetracyclo-[4.4.0.0²,¹⁰.0⁵,⁷]deca-3,8-diene, an intermediate frequently discussed in many important isomerizations of (CH)₁₀ hydrocarbons.[4] Evidence for this structural assignment is now presented herein.

6: R = CH₂ - OAc
7: R = C₆H₅
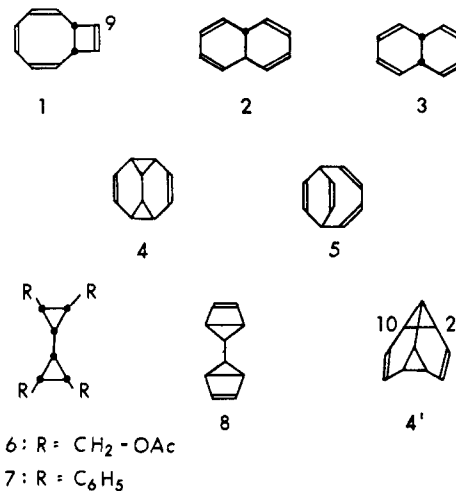
The light source employed in the present photolysis was a doubly coiled (3.5-cm diameter) low-pressure mercury lamp surrounded by a cylindrical reflection mirror (10 cm diameter).[5] A 0.25~0.5 M[6] solution of **1**, **2**, or **3** in tetrahydrofuran-d_8 was irradiated at −110 ± 10°, and the progress of the photolysis was followed by 100-MHz nmr spectra taken at −70° at intervals. Initial rates of disappearance of these compounds were rapid (half-lives of **1**, **2**, and **3** were approximately 30, 60, and 30 min, respectively), and in *all* cases the product distribution reached within 2.5 hr a *similar* composition (the yield of each component deviated within 5% from those given below) which was essentially unaffected by further irradiation. As shown in Figure 1 in the case of the photolysis of **3**, for instance, the photolysate consisted of **2**! (19% yield), **3**

proceeded partly as a parallel *second*-order reaction [to provide naphthalene, 1,2-dihydronaphthalene, hydrogen, and a hydronaphthalene (minor) (S. Masamune, unpublished)], it was nearly impossible to prepare a substantial amount of neat **2** by ordinary workup techniques including preparative glpc. We prepared a solution of **1** in deuterated methylcyclohexane (known concentration) and converted it to **2** (quantitative, *first* order). Nmr spectra showed no impurities.

One of the referees requested us to record an nmr spectrum of our sample employed throughout our work, and it is shown in Figure 3. In view of thermal behavior of **2** (*vide supra*), very likely some of the room-temperature (2 min) photoproducts of their *trans*-9,10-dihydronaphthalene[2b] are thermal products of **2** (*e.g.*, naphthalene and 1,2-dihydronaphthalene) and were present in their starting material, because we could not detect these compounds in our photolysis of **2** under similar conditions.

(3) Prepared according to the procedure reported by W. von E. Doering, *et al.*, *Tetrahedron*, **23**, 3943 (1967). We thank Mr. K. Hojo for the preparation.

(4) First proposed by G. Schröder, *Chem. Ber.*, **97**, 3140 (1964), and appeared in ref 2a; W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966); W. von E. Doering and J. W. Rosenthal, *Tetrahedron Letters*, 349 (1967); G. Schröder and J. F. M. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 414 (1967); G. Schröder, "Cyclooctatetraen," Verlag Chemie, GmbH, Weinheim, 1965; S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Am. Chem. Soc.*, **90**, 2727 (1968).

(5) The lamp was constructed by Mr. C. Shott of this department and connected with a Jefferson Luminus Tube Outdoor Type transformer (Catalog 721-561, primary 115 V, secondary 5000 V). The total stretched length of the lamp is 1.8 m. A diagram of this photoapparatus is available upon request.

(6) The concentration must be kept in the range specified in order to obtain the reproducible distribution of the photoproducts.
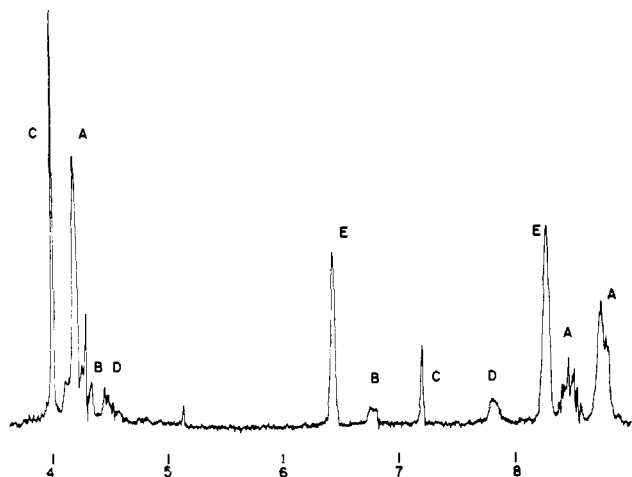
Figure 1. Nmr spectrum of the photolysate of 3 taken at −70° (see text): (A) signals of 4; (B) 3; (C) 2; (D) bullvalene; (E) partially deuterated THF

(8%), bullvalene (7%), and a new compound (65%) which showed the following nmr signals: a broad singlet at τ 4.20 and two multiplets centered around τ 8.47 and 8.77 with a relative intensity of *ca.* 2:1:2. Irradiation at τ 8.77 collapsed the first signal (τ 4.20) to the line width of 1 Hz at half-height. The second signal (τ 8.47) was unaffected by irradiation at τ 4.20.

Figure 2 is a spectrum taken after warming the same sample to room temperature and then cooling it to −60° (in order to confirm the presence of bullvalene).[7] It shows clearly that all the signals attributed to 4 have disappeared and that those of tricyclo[4.2.2]deca-2,4,7,9-tetraene (5) are discernible.[2a] Gas chromatography identified 5 (65%) in addition to 2, 3, and bullvalene (19, 8, and 7%, respectively). Photolysis of 2 or 3 under similar conditions except with Corex-filtered light (200-W, high-pressure, Osram GmbH) changed to some extent the final composition of photolysates in which the amount of 2 was negligible (*cf.* the uv spectra of 2 and 3).[2] Room-temperature photolyses of 1–3 were also performed (very rapid, 5 min), and the results are readily interpretable by further photoisomerization of 5 and other minor products.

Thermal isomerization of 4 to 5 was quantitative to the sensitivity of the spectrometer and provided the following kinetic data: $k_{-14.9°} = 1.25 \times 10^{-4}$ sec^{-1}, $k_{-29.9°} = 9.5 \times 10^{-6}$ sec^{-1}. A constant-temperature liquid bath was employed to control the temperatures, and the integration of nmr signals was performed at −80°.

Ozonolysis of 4 at −80° followed by sodium borohydride reduction and acetylation provided in 35% over-all yield a C_{10}-tetraol tetraacetate (6), mp 82.5–83.5°; calcd mass for $C_{18}H_{23}O_6$ (M − $C_2H_3O_2$), 311.1495; found, *m/e* 311.1493; calcd mol wt, 370; found, 370 (osmometer); nmr, multiplet (τ 5.75, 4 H), singlet (7.93, 6 H), multiplets (8.55 and 9.05, 2 H and 1 H). *Anal.* Calcd for $C_{18}H_{26}O_8$: C, 58.37; H, 7.08. Found: C, 58.24; H, 7.07. Compound 6 was also obtained from a known compound as outlined below.

Catalytic hydrogenation of 3,3-bis(Δ^1-1,2-diphenylcyclopropenyl)[8] with 10% palladium-on-carbon catalyst

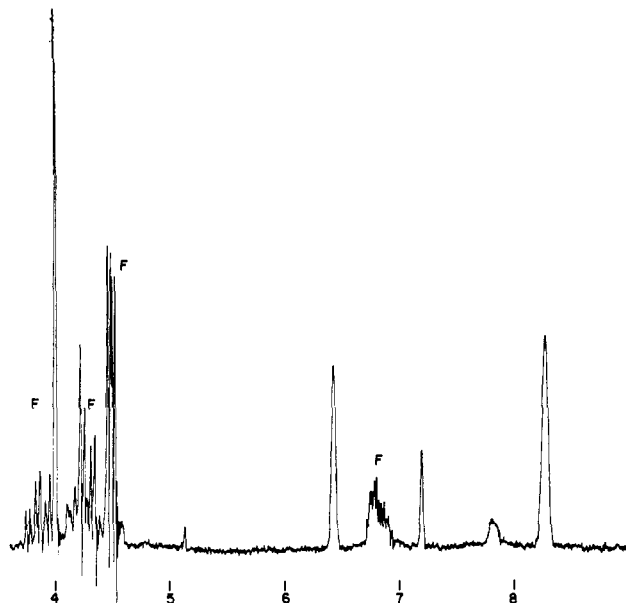(7) R. Merenyi, J. F. M. Oth, and G. Schröder, *Ber.*, **97**, 3150 (1964).

Figure 2. Nmr spectrum taken after warming the photolysate of 3 to room temperature and then cooling it to −60°: (F) signals of 5.

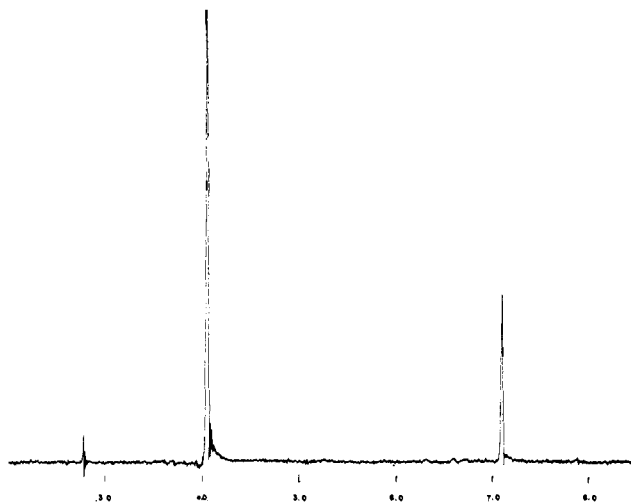Figure 3. Nmr spectrum (100 MHz) of 2 in CDCl₃.

in tetrahydrofuran provided the corresponding saturated 1,1′-bicyclopropyl (7), mp 201°, which was ozonized (oxidative workup) to afford a tetracarboxylic acid (tetramethyl ester mp 151°). Successive treatment of this acid with diazomethane, lithium aluminum hydride, and finally acetic anhydride provided a tetraacetate which was identical in every respect with that obtained from 4. Therefore compound 6 must be 2,-2′,3,3′-tetraacetoxylmethyl-1,1′-bicyclopropyl (IUPAC A-52.1) with stereochemistry specified in 6.[9]

Only two (CH)₁₀ structures, 4 and 8, are compatible with the ozonolysis experiments. 8, however, is excluded, because the formation of 8 from 3 and thermal rearrangement of 8 to 5 are extremely unlikely. The absorption of the allylic protons of 4 at τ 8.77 is no longer exceptional to the current knowledge of chemical shifts. Therefore, the chemical and spectral evidence

(8) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965).

(9) This structure proof was added in a revision received on June 19, 1968.

presented above removed any reasonable doubts as to the correctness of the structure proposed for compound **4**. It is pleasing to learn that the Woodward–Hoffmann selection rule[10] uniquely applies to the present system; in particular, the thermal conversion of **4** into **5** (reverse Diels–Alder reaction) but not into **3** in spite of the geometry of the C-2–C-10 bond of **4** disposed favorably to form the allylic radical (see **4'**).[11]

The significance of **4** is evident as it has been often cited in the recent literature of (CH)$_{10}$ hydrocarbons,[4] and we do not elaborate here in this respect. However, we mention that formation of **4** from **1** and **2** *was* surprising indeed. Minor products **2** and **3** in these photolyses are strongly suggestive of the species[12] (of either ground state or excited state) which may be involved in the processes leading to the ultimate formation of **4**. Investigations directed toward this aspect and the fate of electronically excited **4** will be described in future publications.[13,14]

(10) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(11) We have attempted to reduce **4** with dimide at −20 or −40° to obtain tetracyclo[4.4.0.0^{2,10}.0^{5,7}]decane. However, apparently due to the low reactivity of the reducing reagent toward this type of compound at these temperatures, we isolated only bicyclo[4.2.2]decane and its partially unsaturated compounds even with 200-fold molar excess of potassium azodicarboxylate for 48 hr (*cf.* half-lives of **4**). In fact, reduction of bullvalene under similar conditions proceeded only to 50% completion.

(12) In ref 2b the authors reported that photolysis of **2** at a somewhat lower temperature than ours, followed by diimide reduction at −70° and/or higher temperatures, provided ∼40% over-all yield of cyclodecane.

(13) We are grateful to the National Research Council of Canada for financial support and to Badische Anilin- und Soda-Fabrik AG for a generous gift of cyclooctatetraene.

(14) During the process of refereeing, E. Balad, D. Ginsburg, and M. B. Rubin reported that photoirradiation of 12-oxa[4.4.3]propella-2,4,7,9-tetraene afforded 12-oxapentacyclo[4.4.0.0^{2,10}.0^{5,7}]trideca-3,8-diene (*Tetrahedron Letters*, 2361 (1968)).

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Stereochemistry of Chlorobis(acetylacetonato)cyclopentadienylzirconium

Sir:

Nuclear magnetic resonance studies[1-4] of a considerable number of higher coordination number metal β-diketonate complexes have not yet provided stereochemical information for this important class of compounds in solution. In general, the lack of progress can be attributed to the lability of the complexes investigated. Among the zirconium acetylacetonate[5] complexes, for example, seven-coordinate Zr(acac)$_3$Cl and eight-coordinate Zr(acac)$_4$, as well as six-coordinate Zr(acac)$_2$Cl$_2$, give single methyl proton resonance lines at temperatures even as low as −130°, because of rapid intramolecular configurational rearrangement processes which average the expected nonequivalent methyl group environments.[4] We wish to report here that the higher coordination number zirconium complex (π-C$_5$H$_5$)-

(1) A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 228 (1966).
(2) T. J. Pinnavaia and R. C. Fay, *ibid.*, **5**, 233 (1966).
(3) F. A. Cotton, P. Legzdins, and S. J. Lippard, *J. Chem. Phys.*, **45**, 3461 (1966).
(4) T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **7**, 502 (1968).
(5) CH$_3$COCHCOCH$_3^-$; abbreviation, acac.

Zr(acac)$_2$Cl is sufficiently stereochemically rigid at room temperature to observe nonequivalent environments for methyl and –CH= protons on the chelate rings.

(π-C$_5$H$_5$)Zr(acac)$_2$Cl was prepared following the method of Freidlina, Brainina, and Nesmeyanov.[6] The product was recrystallized twice from benzene and dried *in vacuo* at 80°: mp 189–190° (sealed capillary); lit.[6] 188–190°. *Anal.* Calcd for C$_{15}$H$_{19}$O$_4$ClZr: C, 46.20; H, 4.91. Found: C, 46.01; H, 5.00. Since the compound is readily hydrolyzed in solution, all solutions were prepared and subsequently handled under anhydrous conditions.

In nitrobenzene solution the compound is monomeric and a very weak electrolyte: mol wt 390 calcd *vs.* 407 found; Λ <0.014 ohm^{-1} cm^2 mole^{-1} at a concentration of 7.3 × 10^{-3} M. A band due to a symmetric carbonyl stretching vibration is observed near 1595 cm^{-1} in CDCl$_3$ solution. No bands are found in the region 1626–1695 cm^{-1} where ketonic carbonyl modes have been reported for silicon(IV)[7] and platinum(II)[8-11] acetylacetonates containing uncoordinated carbonyl groups. These data indicate that the chlorine atom and all four carbonyl groups are coordinated to the zirconium atom in solution.

The proton nmr spectrum of (π-C$_5$H$_5$)Zr(acac)$_2$Cl in benzene solution is presented in Figure 1. The resonance line at τ 3.50 is assigned to protons on the cyclopentadienyl ring. The remaining six lines are due to –CH= and methyl protons on the acetylacetonate ligands. The two –CH= lines at τ 4.75 and 4.82 have relative intensities 1:1.03 ± 0.03. Four methyl lines occur in the region τ 8.31 to 8.45. Relative to the line at τ 8.31, the two lines of equal intensity at τ 8.37 and 8.38 have a combined intensity of 2.03 ± 0.05, and the line at τ 8.45 has an intensity of 0.99 ± 0.03. The intensities were determined by planimetric integration of five spectra; errors are estimated at the 95% confidence level.

The nmr data cannot be interpreted in terms of an equilibrium mixture of compounds of different stoichiometries arising from disproportionation of the complex. Equal molar mixtures of (π-C$_5$H$_5$)Zr(acac)$_2$Cl and Zr(acac)$_2$Cl$_2$, Zr(acac)$_3$Cl, Zr(acac)$_4$, H(acac), or (π-C$_5$H$_5$)$_2$ZrCl$_2$ give spectra characteristic of the two compounds initially mixed. That is, the relative intensities of resonance lines found in the spectrum of a solution containing only (π-C$_5$H$_5$)Zr(acac)$_2$Cl are not altered by varying the ligand composition. Therefore, it must be concluded that the observed methyl and –CH= proton resonances result from nonequivalent environments for these groups in the (π-C$_5$H$_5$)Zr(acac)$_2$Cl molecule. The existence of a single, sharp cyclopentadienyl resonance is attributed to rapid rotation of the ring about the metal–ring axis.

The simplest configuration which places each of the methyl and –CH= groups in nonequivalent environments is based on an octahedron with the C$_5$H$_5$ ring at

(6) R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR, Chem. Sect.*, **138**, 628 (1961).
(7) R. West, *J. Amer. Chem. Soc.*, **80**, 3246 (1958).
(8) B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, R. J. Pauling, and G. B. Robertson, *Nature*, **195**, 1278 (1962).
(9) R. A. D. Wentworth and C. H. Brubaker, *Inorg. Chem.*, **3**, 1472 (1964).
(10) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).
(11) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 440 (1967).