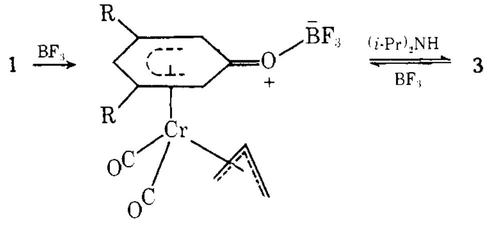
signal for both methyl groups and the single signal for both ring hydrogen atoms that are adjacent to the ring carbonyl group are consistent with the plane of symmetry which our proposed structure for **4** possesses. Moreover, the NMR spectra of both **3** and **4** show A_2M_2X patterns which are very similar to those described for π-allyl moieties of other π-allyl complexes.[9] The IR spectra of both **3** and **4** show an absorption at 1600 cm^{-1} which is almost as intense as those due to the metal-bound carbonyl groups. For this reason our proposed structures for **3** and **4** are ones that possess a ring carbonyl group.

In the presence of triethylamine the isomerization of arene-chelate **2** to **4** still occurred but in the presence of carbon monoxide **2** was converted to the corresponding (arene)tricarbonylchromium complex.

Treatment of arene-chelate **1** with boron trifluoride etherate in benzene resulted in the immediate formation of the BF_3 adduct of **3** (**5**).[10] Complex **5** could be converted to **3** by treatment with diisopropylamine. In a separate experiment **5** was obtained by treatment of **3** with boron trifluoride etherate.



5

The NMR spectrum of **5** is similar to that of **3** except that the ring hydrogens of **5** are deshielded compared to those of **3**, most likely a result of the electron withdrawing characteristics of the BF_3 moiety.[11] In comparing the π-allyl portion of the NMR spectrum of **3** to that of adduct **5** the chemical shifts of H_M (which are cis to H_X) and H_X of **5** are lower field than those of **3**, but the chemical shift of H_A of **5** is about the same as that of **3**. If these shifts are due to through space effects then the orientation of the π-bound allyl group is such that H_X is pointing toward the complexed ring in each complex.

The basicity of the ring carbonyl group of complexes **3** and **4** is further indicated by the formation of a stable hydrochloride salt (**6**)[12] of **4** prepared by treating **4** with dry HCl in an ether-benzene mixture.

The 6-oxocyclohexadienyl ligand is the middle member of the series of unsaturated ketones which includes cyclopentadienone and cycloheptadienone, and in fact complexes **3** and **4** appear to possess some properties which are similar to those of (cyclopentadienone)tricarbonyliron (**7**)[13] and (cycloheptatrienone)tricarbonylchromium (**8**).[14] For example all of these complexes can be protonated by mineral acids forming stable salts. The ring carbonyl group of neither complex **4** nor **8** will undergo nucleophilic attack by *n*-butyllithium and neither **4** nor **8** can be alkylated with methyl iodide.

The mechanism for the cleavage reaction catalyzed by the Lewis acid boron trifluoride probably involves initial complexation of the BF_3 with the ether oxygen atom followed by cleavage of the oxygen allyl bond. Apparently in the absence of a Lewis acid cleavage of the oxygen allyl bond occurs spontaneously.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Phillips Petroleum Foundation for support of this work.

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(2) W. S. Trahanovsky and R. A. Hall, *J. Organomet. Chem.*, **96,** 71 (1975).

(3) Compound **2:** mp 86–89 °C dec; IR (ether) 1924, 1869 cm^{-1}; NMR (C_6D_6) δ 5.08 (s, 1, *o*-ArH), 4.60–4.30 (m, 2, $-CH_2-$), 4.18 (s, 1, *o*-ArH), 3.70 (s, 1, *p*-ArH), 3.70–3.36 (m, 1, $-CH{=}CH_2$), 2.60 (d, J = 12.0 Hz, 1, *trans*-$CH{=}CHH$), 1.98 (s, 3, $-CH_3$), 1.88 (d, J = 9.0 Hz, 1, *cis*-$CH{=}CHH$), and 1.82 (s, 3, $-CH_3$); *m/e* (%) (70 eV) 271 (6.76), 270 (22.2), 242 (3.38), 214 (53.3), 173 (100), 122 (31.1); exact mass calcd for $C_{13}H_{14}CrO_3$: 270.0348, found: 270.0345 ± 0.0014.

(4) A solution of 0.91 mmol of **1**[2] and 0.76 mmol of triphenylphosphine in 10 mL of benzene was stirred under nitrogen at ambient temperatures for 93 h. The product mixture was rinsed into a separatory funnel with 50 mL of ether and the ethereal solution was extracted with two 50-mL portions of water. The solvent was removed from the combined, orange aqueous phase under reduced pressure providing an orange solid. This material was dissolved in 50 mL of benzene and the solution was dried and filtered and the solvent was removed under vacuum to give a 27% yield of **3**[5] as an orange crystalline solid.

(5) Compound **3:** mp 115 °C dec; IR ($CHCl_3$) 2875, 1972, 1909, 1582 cm^{-1}; IR (THF) 1957, 1899, 1597 cm^{-1}; NMR (acetone-d_6) δ 6.13–5.77 (m, 3), 4.73 (d, J = 7.0 Hz, 2, –CHCOCH–), 4.70–4.52 (m, 1, π-allyl X portion of A_2M_2X), 3.46 (d, J = 7.0 Hz, 2, π-allyl M_2 portion of A_2M_2X), and 1.39 (d, J = 12.0 Hz, 2, π-allyl A_2 portion of A_2M_2X). Anal. Calcd for $C_{11}H_{10}CrO_3$: C, 54.54; H, 4.17. Found: C, 54.19; H, 4.16.

(6) Compound **4:** mp 110 °C dec; IR ($CHCl_3$) 1960, 1897, 1573 cm^{-1}; IR (CCl_4) 1958, 1898, 1597 cm^{-1}; NMR (C_6D_6) δ 4.62 (s, 1), 4.60–4.32 (m, 1, π-allyl X portion of A_2M_2X), 4.19 (s, 2), 3.08 (d, J = 7.2 Hz, 2, π-allyl M_2 portion of A_2M_2X), 1.45 (s, 6, $-CH_3$), and 1.02 (d, J = 11.0 Hz, 2, π-allyl A_2 portion of A_2M_2X); *m/e* (%) (70 eV) 271 (7.68), 270 (18.0) 242 (11.8), 214 (78.0), 173 (100), 122 (98.0). Exact mass. Calcd for $C_{13}H_{14}CrO_3$: 270.03481, found: 270.03417 ± 0.00027. Anal. Calcd for $C_{13}H_{14}CrO_3$: C, 57.77; H, 5.23. Found: C, 57.69; H, 5.34.

(7) A solution of 0.091 mmol of **1** in 1.0 mL of benzene was purged with nitrogen and placed in the dark for 93 h. During this period changes were observed in the IR spectra corresponding to the gradual disappearance of 1 and formation of **3.** Workup provided a 43% yield of **3.**

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(10) Compound **5:** mp (dec) 140 °C dec; IR (THF) 1978, 1927, 1563 cm^{-1}; NMR (acetone-d_6) δ 6.90–6.50 (m, 2), 6.45–6.21 (m, 2), 5.96 (d, J = 6.5 Hz, 1, $-CHC{=}O$) 5.20–4.70 (m, 1, π-allyl X portion of A_2M_2X), 3.91 (d, J = 7.5 Hz, 2, π-allyl M_2 portion of A_2M_2X), and 1.36 (d, J = 10.0 Hz, 2, π-allyl A_2 portion of A_2M_2X). Anal. Calcd for $C_{11}H_{10}BCrF_3O_3$: C, 42.61; H, 3.26. Found: C, 39.30; H, 3.50.

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(12) Compound **6:** mp 148 °C dec; IR (KBr) 1976, 1922, 1551 cm^{-1}. Anal. Calcd for $C_{13}H_{15}ClCrO_3$: C, 50.90; H, 4.94; Cl, 11.56. Found: C, 50.68; H, 5.08; Cl, 11.56.

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Phototransposition of Carbon Atoms in Cyclopentadiene. Photoisomerization of Cyclopentadiene to Tricyclo[2.1.0.0^{2,5}]pentane

Sir:

Numerous five-membered heteroaromatic compounds are converted photochemically to ring-atom transposed isomers: indazole, for instance, is rearranged to benzimidazole;[1] 2-phenylthiophene gives 3-phenylthiophene;[2] and 3,5-diphenylisoxazole affords 2,5-diphenyloxazole.[3] Heteroatom-containing analogues of bicyclo[2.1.0]pent-2-ene and 3-vinylcyclopropene are the most commonly invoked intermediates responsible for these isomerizations; in some instances, such molecules have been detected and characterized.[4]

Phototransposition of carbon atoms has not been observed in the analogous hydrocarbon systems, for cyclopentadienes exhibit facile thermal[5] and photochemical[6] 1,5 shifts which would tend to obscure possible skeletal-atom permutations.

We have addressed this experimental problem through synthesis and photolysis of vicinal [$^{13}C_2$]cyclopentadiene: the phototransposition reaction does occur, and the previously

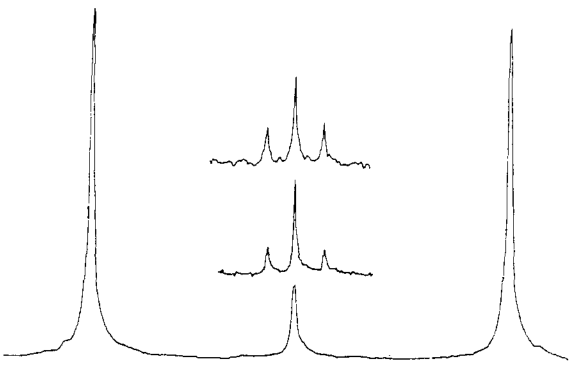


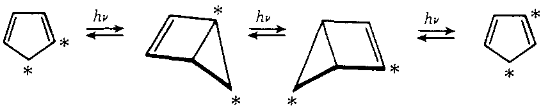
Figure 1. The C(5) ^{13}C NMR absorptions of cyclopentadiene. Bottom trace: [5-^{13}C]cyclopentadiene singlet at δ 42.5 flanked by [1,5-$^{13}C_2$] cyclopentadiene doublet, J = 38.5 Hz. Middle and top traces show new doublet, J = 5.2 Hz, from [2,5-$^{13}C_2$]cyclopentadiene.

undetected tricyclo[2.1.0.0^{2,5}]pentane has been found as a photoreaction product.

Barium [^{13}C]carbonate (29.4 g, 90% enriched; Mound Laboratory, Monsanto Research Corp.) was heated with 50 g of magnesium under an argon atmosphere to give labeled barium carbide.[7] Hydrolysis gave [$^{13}C_2$]acetylene which, upon reaction with acetic acid in the presence of a mercuric acetate catalyst, afforded [1,2-$^{13}C_2$]vinyl acetate.[8] Diels-Alder reaction of vinyl acetate and cyclopentadiene followed by catalytic hydrogenation gave [2,3-$^{13}C_2$]norborn-2-yl acetate as a 4:1 endo-exo mixture. The vicinal [$^{13}C_2$]cyclopentadiene was prepared by pyrolysis of the acetate mixture at 554 °C in a flow system.[9] Examination of the ethylene by-product from the pyrolysis by both ^1H NMR and ^{13}C NMR showed it had only natural-abundance level ^{13}C incorporation.

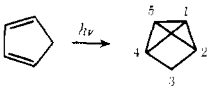
Detection of the photochemical carbon-skeletal rearrangement of cyclopentadiene was accomplished through careful observation of the C(5) ^{13}C NMR signals. Before photochemical isomerization, they showed a singlet at δ 42.5 for the [5-^{13}C]cyclopentadiene in the sample and a more intense doublet from the 1,5-$^{13}C_2$ substrate (J = 38.5 Hz); after photolysis, the presence of [2,5-$^{13}C_2$]cyclopentadiene was apparent from the new doublet, J = 5.2 Hz (see Figure 1). The total intensity of the central resonance(s) in starting material was 10.0% of all C(5) resonances in theory (for 90% enriched $BaCO_3$ and the synthetic sequence employed) and 9.9 ± 0.2% experimentally; after 6 h of irradiation with a 450-W Hanovia high-pressure lamp at −30 °C in Spectrograde decalin, the recovered dilabeled cyclopentadienes contained 6.2% (5.6 × 100)/90.1 = 6.2%) of the nonvicinal [$^{13}C_2$]cyclopentadienes (15.5% observed C(5) intensity in the central three-component absorption).

The bicyclo[2.1.0]pent-2-ene from photoisomerization of the vicinal [$^{13}C_2$]cyclopentadiene[10] contained *more* skeletally permuted, nonvicinal $^{13}C_2$ material than the recovered cyclopentadiene: the C(5) central absorption at 57.4 ppm ($J_{C(2)\ C(5)} < 1$ Hz) amounted to 20.2 ± 0.5% of the total formed by it and the doublet from $J_{C(1)\text{-}C(5)} = 15.1$ Hz.



A photochemical degenerate 1,3-carbon shift of bicyclo[2.1.0]pent-2-ene (λ_{max} 263 nm[11]), analogous to the process often postulated as occurring in unisolated and undetected heterocyclic [2.1.0] systems to account for the phototransposition reactions of some five-membered heteroaromatics, accommodates the facts; this mechanism in particular can rationalize the greater proportion of nonvicinal to vicinal $^{13}C_2$ label in bicyclopentene than in recovered cyclopentadiene.

The photolysis mixture also contained tricyclo[2.1.0.0^{2,5}]pentane, a previously undetected photoproduct of cyclopentadiene; the ^{13}C NMR spectrum consisted of signals at δ 20.8 (C(1), C(5)), 24.6 (C(2), C(4)), and 56.8 (C(3)) with the following couplings: $J_{C(2)\text{-}C(3)} = 34.0$; $J_{C(1)\text{-}C(2)} = 19.0$; $J_{C(1)\text{-}C(3)} = 3.5$ Hz. The cyclopentadiene:bicyclopentene:tricyclopentane proportions in the photolysis mixture were approximately 14:7:1.



It proved difficult to separate bicyclopentene and tricyclopentane by glc. A sample of nearly pure unlabeled tricyclo[2.1.0.0^{2,5}]pentane was secured by allowing a photolysis mixture from unlabeled cyclopentadiene to stand at −20 °C until the bicyclopentene had reacted with cyclopentadiene. The tricyclic isomer, isolated with low recovery by preparative glc, had proton absorptions at δ 3.46 (m, H(1,5), $J_{C(1)\text{-}H(1)} = 210$ Hz in the labeled case), 2.65 (m, H(3)), and 1.55 (s, H-(2,4)).[12]

This study establishes the phototransposition type of degenerate isomerization for cyclopentadiene, and suggests it may occur by way of a photochemical 1,3-carbon migration in the bicyclo[2.1.0]pent-2-ene valence isomer. Whether cyclopentadiene or bicyclopentene is the immediate precursor of tricyclopentane remains to be established. If the former possibility obtains, even s -cis conjugated dienes may be photoisomerized to bicyclo[1.1.0]butane derivatives.[13] The cyclopentadiene to tricyclopentane photoreaction would be analogous to the benzene to benzvalene conversion;[14] the aromatic character of cyclopentadiene[15] might facilitate such a photoisomerization.

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Thermal Isomerization of 5-Methylbicyclo[2.1.0]pent-2-enes and [1,5-$^{13}C_2$]Bicyclo[2.1.0]pent-2-ene

Sir:

The thermal isomerizations of 1- and 2-methylbicyclo[2.1.0]pent-2-enes give mixtures of both 1- and 2-methylcyclopentadienes in the gas phase at atmospheric pressure and in solution. 2-Methylbicyclo[2.1.0]pent-2-ene has been the most carefully investigated: the kinetically controlled 2- to 1-methylcyclopentadiene ratio from this substrate at 50 °C is 13:1 in hexane[1] and 10:1 in tetrahydrofuran;[2] in the gas phase it is reported to be 1.2:1 at 2 mm of substrate,[2] 1.3:1 at 760 mm of nitrogen as the bath gas,[3] and 1.5:1 at 900 mm of pentane.[2]

To explain these results,[1] two possibilities have been recognized. The first views the reaction as occurring with C(1)-C(4) bond cleavage to afford a vibrationally excited methylcyclopentadiene; 1,5-hydrogen shifts then compete with collisional deactivation of the "hot" product molecule, giving both 1- and 2-methylcyclopentadienes as observed initial products.[2,4] The second recognizes the possibility of C(1)-C(2)/C(4)-C(5) and C(3)-C(4)/C(5)-C(1) reaction modes.[1,3]

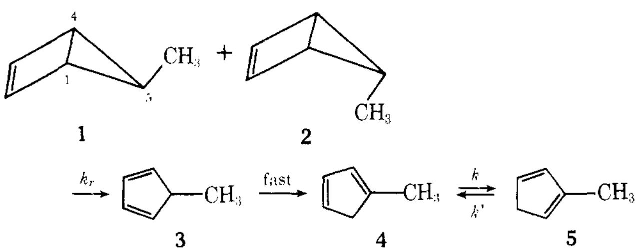
The strongest experimental evidence supporting the first possibility is the apparent pressure sensitivity of the product ratio in the gas phase.[2] Yet, formidable and unavoidable experimental difficulties have limited this line of clarification: the experimental errors associated with these product ratios are such that the ratio could well be constant from 2 mm (no bath gas) to 900 mm (in pentane). We calculate, assuming a 5% uncertainty in a twice-measured ratio of the rate constants compared, 90% confidence limits on these ratios of (1.2 ± 0.3):1 and (1.5 ± 0.4):1.[5]

Theoretical inclination toward the "hot molecule" mechanism comes from RRKM[2,4] and semiempirical molecular orbital[6] calculations. Fits between RRKM calculations and the relatively flat product ratio vs. pressure profile are not absolutely persuasive, since they incorporate a disposable parameter adjusted to obtain the fit, the efficiency of collisional deactivation.

We now report experiments which unambiguously demonstrate extensive "hot molecule" effects at an atmosphere of nitrogen and exclusive operation of the C(1)-C(4) bond cleavage mechanism in the parent hydrocarbon reaction, bicyclo[2.1.0]pent-2-ene to cyclopentadiene.

The *exo*- and *endo*-5-methylbicyclo[2.1.0]pent-2-enes (**1** and **2**) would give, through either C(1)-C(4) cleavage or C(1)-C(2)/C(4)-C(5) cycloreaction, 5-methylcyclopentadiene (**3**). The thermal isomerization of 5- to 1-methylcyclopentadiene (**4**) would be expected to be much faster than the other rearrangements in Scheme I;[7] thus both alternative mechanisms predict 1-methylcyclopentadiene as the observable primary product. Any 2-methylcyclopentadiene (**5**) found as a kinetically controlled product would unequivocally demonstrate a hot molecule effect in the rearrangement.

Scheme I



An approximately 1:1 mixture of 1- and 5-methylcyclopentadiene (25 mL) in 1 L of decalin was photolyzed with a 450-W Hanovia lamp at 5 °C for 5 h. The volatile material collected was treated with dimsyl anion in Me_2SO and vacuum transferred to give 0.5 ml of colorless liquid. Preparative GLC on a TCEP column separated this material into two fractions. The early-eluting fraction was shown by NMR to be 1-methylbicyclo[2.1.0]pentene.[3] The other fraction was a 4:1 mixture of *exo*- and *endo*-5-methylbicyclo[2.1.0]pentene contaminated with ~5% 2-methylbicyclo[2.1.0]pentene. The latter component could be removed by treatment of the mixture with dimsyl anion solution followed by GLC purification.[7]

exo-5-Methylbicyclopentene (**1**) had NMR absorptions at δ 6.18 (2 H, m), 2.54 (1 H, q of m, J = 6 Hz), 1.9 (2 H, m), 0.90 (3 H, d, J = 6 Hz). *endo*-5-Methylbicyclopentene (**2**) had NMR absorptions at δ 6.06 (2 H, m), 2.4 (1 H, m), 2.10 (2 H, d of d, J = 5, 2 Hz), and 1.32 (3 H, d, J = 6 Hz). Reduction of the crude photolysis product with diimide in THF gave a mixture (60%) of the four expected methylbicyclopentanes in about the same proportions as the corresponding bicyclopentenes.

Rearrangement of the *exo*- and *endo*-5-methylbicyclopentenes at 50 °C in the gas phase with 1-atm. pressure of nitrogen gave a kinetic 1- to 2-methylcyclopentadiene ratio of (1.20 ± 0.08):1 ($k_r = (6.91 \pm 0.11) \times 10^{-5}\ s^{-1}$), while in hexane the ratio increased to 60:1 ($k_r = (1.08 \pm 0.04) \times 10^{-4}\ s^{-1}$). The 60:1 ratio and its error limits are compatible with no formation of the 2-methyl isomer (**5**) in the kinetically controlled product mixture. The calculated rate for the 5- to 1-methylcyclopentadiene conversion at 50 °C is $2.61 \times 10^{-3}\ s^{-1}$;[8] the maximum concentration of 5-methylcyclopentadiene attainable is thus 4% in the solution runs. The formation of the large amounts of 2-methylcyclopentadiene, in the gas phase, which must arise from a hot-molecule reaction across two activation barriers, demonstrates the effect, but makes no distinction between the two alternative modes for the first step in the scheme.

Samples of bicyclo[2.1.0]pent-2-ene from the photolysis of vicinal [$^{13}C_2$]cyclopentadiene[9] were isomerized at 50 °C in pentane, and the product [$^{13}C_2$]cyclopentadiene was reexamined by ^{13}C NMR spectroscopy. The bicyclo[2.1.0]pent-2-ene had 20.2 ± 0.5% of the C(5) resonance ascribable to $^{13}C_1$ (9.9%) and $^{13}C_2$-2,5 (10.3%) species, with the balance, 79.8%, due to the $^{13}C_2$-1,5 isomer.[10] One run, in which the bicyclic and 12.5 mol % of [$^{13}C_2$]tricyclo[2.1.0^{2,5}]pentane were isomerized together, gave 22.0 ± 0.7% intensity in the central C(5) resonances of the cyclopentadiene produced. A calculated correction for the cyclopentadiene derived from the [$^{13}C_2$]tricyclo[2.1.0.0^{2,5}]pentene gave 20.7 ± 0.7% as the relative intensity of the central C(5) ^{13}C NMR absorptions of cyclopentadiene derived from bicyclopentene. Another run using tricyclopentane-free bicyclo[2.1.0]pentene gave 19.8 ± 0.5% as the relative intensity of the central C(5) absorptions in the cyclopentadiene formed. The three determinations of the sum of monolabeled and $^{13}C_2$-2,5-labeled hydrocarbons, one of starting bicyclopentene (20.2 ± 0.5%) and two of the cyclopentadiene derived thermally from that bicyclopentene in separate runs (20.7 ± 0.7% and 19.8 ± 0.5%) agree within