(osmometry in benzene)]: ir (Nujol) ν_{CO} 2035 cm^{-1}; pmr (CHCl$_3$) τ 8.67 (s).

Similarly using dibutylmethylcyclopropenium fluoroborate[8] yellow crystals of **3** are isolated: ir (Nujol) ν_{CO} 2038 cm^{-1}; pmr (CH$_2$Cl$_2$) τ 7.89 (s, 3 H), 8.78 (s, 18 H).

Stirring **2** with a stoichiometric amount of sodium cyclopentadienide in ethanol under nitrogen for 1 hr followed by addition of degassed water and sublimation of the product at 40° and 0.1 mm yields (h^5-C$_5$H$_5$)(h^3-C$_3$(t-C$_4$H$_9$)$_3$)Ni (**4**) as a yellow powder: mp 295° dec (*Anal.* Calcd for NiC$_{20}$H$_{32}$: Ni, 17.73; C, 72.63; H, 9.73. Found: Ni, 16.97; C, 72.98; H, 9.91); pmr (CS$_2$) τ 4.97 (s, 5 H), 8.97 (s, 27 H).

All three complexes are air stable as solids for a short period only and decompose rapidly in polar solvents when in contact with air.

These results strongly indicate that **2** and **3**, and probably Gowling and Kettle's compound, are monomeric. The mass spectrum of **2** at 100° (10 or 70 eV) shows no ions derived from CO-containing species but exhibits strong peaks corresponding to [h^3-C$_3$(t-C$_4$H$_9$)$_3$NiBr]$_2$.

Addition of carbon monoxide to a methylcyclohexane solution of **2** (ν_{CO} 2052 cm^{-1}) results in the rapid equilibria shown in eq 1 and 2. Carbonyl bands appear

$$C_3(t\text{-}C_4H_9)_3Ni(CO)Br + CO \rightleftharpoons C_3(t\text{-}C_4H_9)_3Ni(CO)_2Br \tag{1}$$

$$C_3(t\text{-}C_4H_9)_3Ni(CO)_2Br + 2CO \rightleftharpoons Ni(CO)_4 + C_3(t\text{-}C_4H_9)_3{}^+Br^- \tag{2}$$

at 2089 (s), 2060 (s), 2055 (s), and 2044 cm^{-1} (m). The two highest energy bands, which appear together, are assigned to tri-*tert*-butylcyclopropenium nickel dicarbonyl bromide (**5**). Nickel carbonyl is isolated from this solution by prolonged addition of carbon monoxide and trapping of the volatile components with a Dry Ice–acetone bath. The 2044-cm^{-1} band is due to Ni(CO)$_4$. The band at 2055 cm^{-1}, shifted slightly by overlap with adjacent bands, is assigned to **2**.

In nonhydrocarbon solvents **5** is formed from **2** through a slight amount of disproportionation. In chloroform ir CO bands are observed at 2054 (s) and 2096 cm^{-1} (w). Designation of the high energy band as arising from the dicarbonyl species, **5**, is based on the following observations. Addition of CO to a yellow chloroform solution of **2** in a closed vessel produces a colorless solution with an intense ir band at 2044 cm^{-1} due to nickel carbonyl, considerable enhancement of the band at 2096 cm^{-1}, and a shoulder of comparable intensity at approximately 2063 cm^{-1}. Removal of the CO atmosphere causes the nickel carbonyl spectrum to be displaced by the original band at 2054 cm^{-1} and instantaneous color change back to yellow. The band at 2096 cm^{-1} remains about three times more intense than before addition of CO; the lower energy band of the dicarbonyl is obscured by the intense band at 2054 cm^{-1}. The pmr spectrum of a CO saturated chloroform solution of **2** exhibits a new resonance at τ 8.31, inexplicably shifted from the τ 8.41 for [C$_3$(t-C$_4$H$_9$)$_3$]Br alone in chloroform.

Heating of **2** under vacuum at 80° for 20 hr results in loss of CO and formation of a very air-sensitive red-brown solid which we assume to be [h^3-C$_3$(t-C$_4$H$_9$)$_3$NiBr]$_2$, analog of the well-known allylnickel halide compounds. The solid dissolves in methylcyclohexane to yield a red solution which shows no ir CO band. Addition of CO to this solution results in ir spectra identical with those obtained on addition of CO to methylcyclohexane solutions of **2**.

These observations suggest that **2** behaves similarly to the analogous allyl–nickel complex[9] in those properties which allow it to remain trihapto. In contrast to the facile coupling reaction of methallylnickel bromide in the presence of carbon monoxide,[9] however, no cyclopropenium coupling products have been detected. The steric requirements of the *tert*-butyl groups in **2** could be accountable for the inability of the C$_3$ system to assume a monohapto configuration and thus to undergo coupling. On the other hand **3** seems equally stable in this respect.

Addition of [C$_3$(C$_6$H$_5$)$_3$]BF$_4$ to a methanolic solution of **2** yields analytically pure triphenylcyclopropenium nickel carbonyl bromide as a precipitate after 1 hr at room temperature.

Reaction of [C$_3$(t-C$_4$H$_9$)$_3$]BF$_4$ with NaMn(CO)$_5$ in THF at −15° results in the formation of air-sensitive orange crystals of [C$_3$(t-C$_4$H$_9$)$_3$]Mn(CO)$_5$ (**6**). The ir spectrum in the 2000-cm^{-1} region closely resembles that of Mn(CO)$_5{}^-$ and the pmr spectrum, (CD$_3$COCD$_3$) τ 8.38 (s), makes reasonable the assignment of **6** as ionic. At room temperature in THF solution the carbonyl ir spectrum is more complex, indicating formation of contact ion pairs or perhaps a monohapto interaction of the C$_3$ system with Mn(CO)$_5{}^-$. **6** decomposes rapidly in polar solvents to yield Mn$_2$(CO)$_{10}$ and [C$_3$(t-C$_4$H$_9$)$_3$]$_2$ and lesser amounts of C$_3$(t-C$_4$H$_9$)$_3$H. The same reaction with [C$_3$(C$_6$H$_5$)$_3$]BF$_4$ and NaMn(CO)$_5$ yields Mn$_2$(CO)$_{10}$ and [C$_3$(C$_6$H$_5$)$_3$]$_2$. Attempts to prepare the analogous trimethylcyclopropenium compounds have so far been unsuccessful, nor have the products of reductive coupling been clearly identified as yet.

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(9) E. J. Corey, M. F. Semmelhack, and L. S. Hegedus, *J. Amer. Chem. Soc.*, 90, 2416 (1968).

(10) Mobil Oil Foundation Fellow, 1969–1971.

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Antarafacial Allylic Participation in a Thermal 1,3-Sigmatropic Carbon Migration

Sir:

Orbital symmetry theory recognizes two thermally allowed 1,3-sigmatropic pathways for migration of an allylic moiety: inversion at the migrating carbon with suprafacial allylic utilization, and retention at the migrating carbon with antarafacial allylic participation.[1-4] This second allowed stereochemical combination has not been reported; it has been explicitly judged a difficult or perhaps impossible mode of reaction.[2,5]

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(1) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

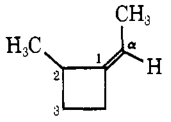
(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967); **92**, 1096 (1970).

(4) W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969).

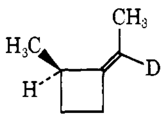
(5) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

We have synthesized optically active and deuterium-labeled samples of *syn*-1-ethylidene-2-methylcyclobutane (**1**) and determined the rate constants for racemization, k_α, and for deuterium scrambling, k_{ds}, which accompany and reveal the automerization reactions[6] of this system. Comparison of experimental findings with predictions based on a full range of mechanistic possibilities indicates that at least a prominent component, and possibly all, of the degenerate methylenecyclobutane rearrangement[7,8] proceeds with antarafacial participation of the allylic unit.

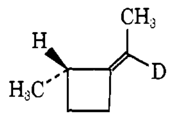


1

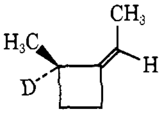
A chiral, deuterium-labeled structure such as **2a** might be converted to isomers **2b**, **2c**, and **2d** through various mechanisms.



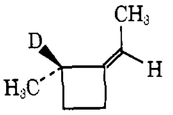
2a



2b

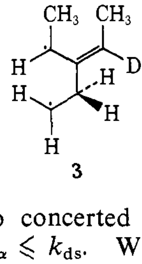


2c

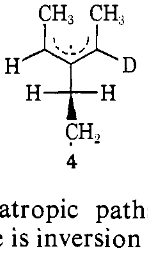


2d

Racemization without deuterium scrambling might occur through a Smith inversion[9] at C-2, or by way of a π-methylenecyclobutane[10] or a diradical intermediate such as **3** in which C-α and C-2 remain distinguished. Racemization and deuterium scrambling at equal rates would be predicted for rearrangements through a "diradical" species in which C-α and C-2 were indistinguishable, either instantaneously as in **4** or on a time-averaged basis, *whatever the stereochemical modes for generation or collapse of such intermediates.* Intermediates like **3** and **4**, then, may accommodate experimental results for the rearrangement of **2a** in which $k_\alpha \geqslant k_{ds}$.



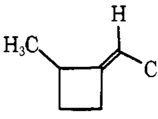
3



4

The two concerted 1,3-sigmatropic paths may rationalize $k_\alpha \leqslant k_{ds}$. When there is inversion at C-3 and suprafacial allylic participation,[11] $k_\alpha = k_{ds}$ (**2a** → **2d**); when there is retention at C-3 and allylic antarafation, the deuterium scrambling occurs without racemization (**2a** → **2c**).

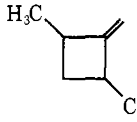
1-Ethylidene-2-methylcyclobutane was prepared as a mixture of syn and anti isomers (**1** and **5**) by the procedure of Bestmann and Kranz.[12] Thus, 2 equiv of methylenetriphenylphosphorane was allowed to react with 1.04 equiv of 1,3-dibromobutane to yield 2-methylcyclobutyltriphenylphosphonium bromide. This salt gave the isomeric olefins **1** and **5** by way of a standard Wittig reaction using acetaldehyde.[13] Deuterated analogs were prepared using α-deuterioacetaldehyde.[14]



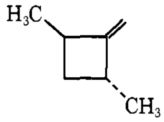
5

Optically active **1**, $[\alpha]^{27°}_{222\,\mathrm{nm}}$ − 8.70° in the gas phase, was prepared by the selective destruction of one enantiomer with diisopinocamphylborane.[15]

Gas-phase kinetic runs were made in a well-seasoned glass vessel at 332°. The syn isomer was isolated from isomeric rearrangement products **5**, **6**, and **7** and purified by preparative glpc, then scrutinized by nmr spectroscopy or polarimetry. The measured 95% confidence intervals of k_α and k_{ds} defined for approach to equilibrium were $4.93 \pm 1.13 \times 10^{-5}$ sec^{-1} and $8.15 \pm 0.60 \times 10^{-5}$ sec^{-1}, respectively.[16]



6



7

Deuterium scrambling without racemization by way of chiral *trans*-1-methylene-2,4-dimethylcyclobutane (**7**) was ruled out, since the rate constants $k(\mathbf{1} \rightarrow \mathbf{7})$ and $k(\mathbf{7} \rightarrow \mathbf{1})$ at 332° are only 0.145×10^{-5} and 0.36×10^{-5} sec^{-1}.[17]

At least the difference between k_α and k_{ds}, 3.22×10^{-5} sec^{-1} at 332°, must be attributed to a 1,3-sigma-

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[6] A. T. Balaban and D. Fărcasiu, *J. Amer. Chem. Soc.*, **89**, 1958 (1967).

[7] J. P. Chesick, *J. Phys. Chem.*, **65**, 2170 (1961).

[8] W. v. E. Doering and J. C. Gilbert, *Tetrahedron, Suppl.*, **No. 7**, 397 (1966).

[9] F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

[10] Compare π-cyclopropane proposals: R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

[11] Our molecular orbital calculations make this seem an unlikely possibility; J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forsch.*, **15**, 281 (1970).

[12] H. J. Bestmann and E. Kranz, *Chem. Ber.*, **102**, 1802 (1969).

[13] The nmr spectrum of **1** showed a doublet at δ 1.19 (3 H, J = 6.8 Hz, C-2–CH$_3$), and a multiplet at 1.49 (3 H, C-α–CH$_3$) in which the following coupling constants could be distinguished: 6.5 (to C-α–H), 1.5 (to C-2–H), and 2.0 Hz (to C-α–H$_2$). Other signals occurred at δ 2.06 (m, 2 H), 2.50 (m, 2 H), 2.98 (m, 1 H), and 5.01 (q of q, 1 H, J = 6.8 and 2.3 Hz). The gas-phase infrared spectrum showed bands at 2980, 1460, 1450, 1380, 1080, 940, and 810 cm^{-1}. The mass spectrum showed a parent molecular ion at *m/e* 96 and major fragment ions at *m/e* 81, 68, 67, 54, 53, 41, and 39. The anti isomer **5** had a doublet at δ 1.07 (3 H, J = 6.8 Hz, C-2–CH$_3$), a multiplet at 1.47 (3 H, C-α–CH$_3$) in which the following couplings could be distinguished (6.7 (to C-α–H), 2.1 (to C-2–H), and 1.5 Hz (to C-4–H$_2$)), a complex multiplet at 2.06 (2 H), another at 2.51 (2 H), another at 2.88 (1 H), and a symmetrical multiplet at 5.05 ppm (1 H).

[14] A. Murray and D. L. Williams, "Organic Synthesis with Isotopes," Vol. 2, Interscience, New York, N. Y., 1958, p 1360.

[15] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

[16] The less pertinent standard deviations were 0.26×10^{-5} and 0.14×10^{-5} sec^{-1} for k_α and k_{ds}; see, for example, T. Yamane, "Statistics: An Introductory Analysis," Harper and Row, New York, N. Y., 1967, p 418. Complete experimental details for these rate determinations were made available to the Editor and the referees of this manuscript in an eight-page document. The possibility that optically active **1** might be contaminated by (−)-α-pinene was excluded in several ways, including recognition of the fact that α-pinene loses optical activity with $k_1 \approx 7 \times 10^{-2}$ sec^{-1} at 332° [D. F. Smith, *J. Amer. Chem. Soc.*, **49**, 43 (1927); R. E. Fuguitt and J. E. Hawkins, *ibid.*, **69**, 319 (1947)].

[17] A complete account of the kinetics of the structural equilibrations among the hydrocarbons **1**, **5**, **6**, and **7** will be reported in due course.

tropic carbon migration with antarafacial allylic participation. Further experimentation will be needed to dissect the rate constant $k_\alpha = 2[k(\mathbf{2a} \rightarrow \mathbf{2b}) + k(\mathbf{2a} \rightarrow \mathbf{2d})]$ into its two components. If racemization should occur only through the process **2a** → **2b**, then the entire methylenecyclobutane automerization could occur with antarafacial allylic participation, **2a** → **2c**.

Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of the initial phase of this research, and to the Cities Service Oil Co. and the National Science Foundation for continuing financial aid. We thank Professor John Schellman for access to the Cary-60 spectrometer used for measuring gas-phase rotations.

(18) National Science Foundation Trainee, 1968–1971.

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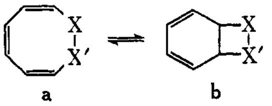
Cyclooctatriene–Bicyclooctadiene Equilibria. Effects of Additional Ring Fusions and Metal Binding

Sir:

The question of the relative stabilities of the mono- and bicyclic tautomers of C_8H_{10}, **1a** and **1b**, was first in-

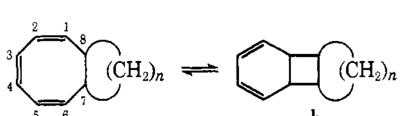


a **b**

1, X = X′ = CH_2

vestigated in these laboratories more than 20 years ago by Cope, *et al.*[1] The free energy difference was found to be small and the rate of interconversion slow at room temperature. More recently, Huisgen, *et al.*,[2] have examined the influence of variations in the X–X′ group on the position of equilibrium. This varies from a **b**/**a** ratio of ~0 for X–X′ = HC=CH, through 1/8 for H_2C–CH_2 to ≥100 for several cases. They examined two possible, simple explanations for the observed variation and found one (nonbonded repulsions) untenable and the other (hybridization effects) doubtful. The problem remains unsolved.

While we are not able to offer a general solution, we wish to report some new observations which are interesting and may be significant. Our first concern is with the effects of fusing saturated rings of different sizes across the C(7)–C(8) bond on the position of equilibrium. We have also employed the $Fe(CO)_3$ and $Mo(CO)_3$ groups (diene and triene seekers, respectively) to shift the equilibria and allow isolation of complexes of the isomeric olefins. The three systems **2a,b**, **3a,b**, and **4a,b** have been prepared (by reaction of $Li_2C_8H_8$ with $Br(CH_2)_nBr$, $n = 2, 3, 4$) and studied.[3,4] The size of the appended ring has been found to influence the position of the **a** ⇄ **b** equilibrium for **2**, **3**, and **4**.



a **b**

2, $n = 2$; **3**, $n = 3$; **4**, $n = 4$

Not surprisingly, for **2** ($n = 2$) the **b** (tricyclo) isomer is destabilized to the extent that it cannot be detected in the products of the preparative reaction. Pure **2a** is isolated from the preparative reaction. For **3** the situation is reversed. From the preparative reaction, mixtures of **3a** and **3b**, in comparable molar quantities, are obtained by distillation at 25° (0.01 mm). The rate and equilibrium of the reaction **3a** → **3b** have been studied[5] at 34 and 58°. Assuming a frequency factor of 10^{13}, the Arrhenius activation energy is 24 ± 1 kcal/mol, and the rate constants are 3.4×10^{-3} (58°), 4.2×10^{-5} (34°), and 1.6×10^{-5} sec^{-1} (20°, by extrapolation). The equilibrium ratio **3b**/**3a** at 58° is ~32 and $\Delta G°$ for the reaction is thus ~−2.0 kcal/mol. These values are comparable to those for several systems studied by Huisgen, *et al.*; for the C_8H_{10} system itself, **1** (X = X′ = CH_2), they found k_1 (20°) = 5.3×10^{-7} sec^{-1}, and both $\Delta G^{\ddagger}$ and $\Delta G°$ more positive by ~3 kcal/mol. While we cannot yet attempt to account quantitatively for the stabilizing influence of the fused five-membered ring on the tricyclodiene tautomer, the effect is qualitatively understandable. The most stable conformation of a cyclopentane ring causes C–H bonds from two adjacent carbon atoms to be coplanar. Presumably the cyclohexadiene ring in any bicyclo structure of type **b** imposes planarity upon the 4 ring. Thus any additional factor which also favors planarity of the 4 ring will enhance the relative stability of the **b** tautomer.

For **4**, the preparative procedure yields an approximately 7:3 mixture of **a** and **b**. Only at temperatures above 100° could significant changes in the relative amounts of the two be observed as a function of time; the equilibrium ratio **4a**/**4b** at 114° is approximately 1.0. Thus the fused cyclohexane ring is much less effective in stabilizing the **b** tautomer, presumably because fusion to a planar 4 ring forces the cyclohexane ring to adopt a half-chair conformation (or, less likely, a tub conformation).

In the three systems, 2, 3, and 4, the electronegativity and inductive effects must be substantially constant; steric and strain effects must be decisive. In order to examine these influences in detail later, accurate structural data will be required. Through the agency of metal carbonyl moieties which have particular affinities for 1,3-diene and 1,3,5-triene groups, it has been possible to sequester selectively the triene and diene tautomers as complexes of $Mo(CO)_3$, $Fe_2(CO)_6$, and $Fe(CO)_3$ moieties. The various complexes isolated,[6] all in the form of crystals suitable for X-ray study, are shown as **5–13**. All of these complexes have been

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[1] A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, 74, 4867 (1952).

[2] R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).

[3] All compounds discussed here have been characterized by satisfactory elemental analyses and spectra.

[4] The general preparative reaction is based on that reported for *cis*-bicyclo[6.4.0]deca-2,4,6-triene by S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, 92, 7612 (1970).

[5] These measurements were made by maintaining samples in an nmr tube in a constant temperature bath and periodically monitoring the concentrations by nmr.

[6] The metal carbonyl derivatives were all prepared by thermal reactions of the olefins with $Fe_2(CO)_9$ or $Mo(CO)_3(CH_3CN)$ and purified by sublimation or recrystallization.