**Registry No.**—Ferrocenylmethyl acetate 12300-24-2; ferrocenylmethyl butyrate, 12300-27-5; ferrocenylmethyl propionate, 12300-25-3; ferrocenylmethyl valerate, 12300-29-7; ferrocenylmethyl caproate, 12300-30-0; ferrocenylmethyl heptanoate, 12300-32-2; ferrocenyl methyl benzoate, 12300-31-1; ferrocenylmethyl 3-hydroxybutyrate, 12300-28-6; ferrocenylmethyl isopropyl ether, 12300-26-4.

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## Conformational Analysis. XI.[1,2] 2-Carbomethoxy-7-oxabicyclo[2.2.1]heptane and 2-Carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene

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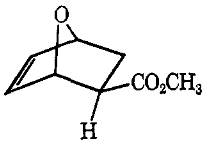
In recent years, the question of the effective size of lone-pair electrons relative to the bonded hydrogen atom has been of interest.[3] While there is some evidence that lone-pair electrons have larger spatial requirements than the bonded hydrogen atom,[4] there is considerable evidence to the contrary.[5] Recently Eliel[6] reported some important observations on the conformational preferences of alkyl groups in the 1,3-dioxane ring system. However, there is little data available with which to extrapolate to systems containing polar groups attached to a heterocycle such as 1,3-dioxane.[7]

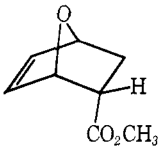
The concept of effective steric size of lone-pair electrons is at best a nebulous one. Solvents may solvate one heterocyclic conformation more effectively than an alternate conformation. The problem then develops into one of separating differential steric requirements and solvent stabilization of conformations. A second problem resides in the variation of the nonbonded electron density of a heteroatom as a function of the hybridization of attached bonds. Incorporation of a heteroatom into rings of varying size should change the spatial requirements of the lone-pair electrons. Therefore, conclusions derived from a particular ring system may not be applicable to other heterocycles.

In order to study the possible effects of solvents and hybridization on the conformations of substituents attached to heterocycles, we have chosen the 7-oxabicyclo[2.2.1]heptene and 7-oxabicyclo[2.2.1]heptane ring systems. These rings eliminate the possibility of nonidealized conformations such as might exist in monocyclic compounds. Only the change in position of a substituent as a result of direct equilibration need be considered. The ring system also provides an oxygen atom in a strained configuration which could lead to lone-pair spatial requirements differing from those determined in other studies.

The equilibration of the isomeric 2-carbomethoxy-7-oxabicyclo[2.2.1]heptenes was accomplished by taking advantage of the relative instabilities of Diels–Alder adducts from furan with dienophiles.[8] Equal volumes of furan and methyl acrylate were sealed in nmr tubes and maintained at 75°. The $\tau$ 6 region of the nmr spectrum of the mixture was monitored. The three-proton methyl singlet at $\tau$ 5.90 gradually decreased with time relative to two high-field singlets which began to develop. A resonance at $\tau$ 5.99 appeared first and increased in intensity while a second resonance at $\tau$ 5.92 appeared at a slower rate. After 2 days the $\tau$ 5.99 resonance maximized and started to decrease, whereas the $\tau$ 5.92 resonance continued to increase. After approximately 5 days the relative intensities of the $\tau$ 5.92 and 5.99 resonances remained constant. The $\tau$ 5.92 and 5.99 resonances were assigned to the methyl singlets of the *exo* and *endo* adducts I and II, respectively. This assignment was based on the known thermal behavior of the Diels–Alder adducts of furan and established by chemical conversion into known derivatives. Mixtures of nonequilibrium composition were reduced by hydrogen over palladium on charcoal, and the isomeric saturated esters were separated from a 12-ft, 25% DEGS on Chromosorb W column. The individual esters were reduced by lithium aluminum hydride to the known saturated primary alcohols.[9]



I



II

The equilibrium constant (*exo/endo*) was calculated to be 0.98 ± 0.06 at 75° from the integrated areas of the $\tau$ 5.92 and 5.99 resonances. The total yield of adduct was approximately 10% at the temperature examined. The reversibility of the equilibrium and the cleanness of the reaction were demonstrated by allowing equilibration to occur at 63° and then reequilibrating these samples at 75° and *vice versa*. At 63° a 14% yield of adduct results after 20 days. The equilibrium constant at 63° is 0.98 ± 0.06. Thus, while no apparent change in the value of the equilibrium constant is observed, the mole fraction of both adducts increases with decreasing temperature and *vice versa*.

A 10% solution by volume of the mixture of reacting diene and dienophile in dimethyl sulfoxide was studied

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(1) Conformational Analysis. X: R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, **32**, 2394 (1967).

(2) The authors acknowledge a grant from the Petroleum Research Fund of the American Chemical Society in support of this research.

(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, p 245.

(4) J. B. Lambert and R. G. Keske, *J. Amer. Chem. Soc.*, **88**, 620 (1966).

(5) R. J. Bishop, L. E. Sutton, D. Dineen, A. Y. Jones, and A. R. Katritzky, *Proc. Chem. Soc.*, 257 (1964); K. Brown, A. R. Katritzky, and A. J. Waring, *ibid.*, 257 (1964); N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 1227 (1965); N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *ibid.*, **87**, 1232 (1965); M. J. T. Robinson, *Tetrahedron Lett.*, 1153 (1968); R. W. Baldock and A. R. Katritzky, *ibid.*, 1159 (1968).

(6) E. L. Eliel and Sr. M. C. Knoeber, *J. Amer. Chem. Soc.*, **88**, 5347 (1966); **90**, 3444 (1968).

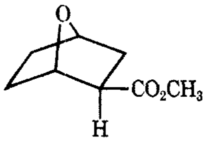
(7) F. G. Riddell, *Quart. Rev.* (London), **21**, 364 (1967).

(8) R. B. Woodward and H. Baer, *J. Amer. Chem. Soc.*, **70**, 1161 (1948); J. A. Berson and R. Swidler, *ibid.*, **75**, 1721 (1953).

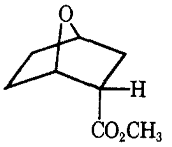
(9) M. P. Kunstmann, D. S. Torbell, and R. L. Autrey, *ibid.*, **84**, 4115 (1962).

using the same technique as for the neat liquids. The lower concentrations decreased slightly the sensitivity of the analytical method. The equilibrium constant (*exo/endo*) is 1.01 ± 0.08. The equilibrium was examined in methanol as solvent, and the equilibrium constant is 1.3 ± 0.1. The slightly higher error limit is a reflection of a partial overlap of the resonances of methyl acrylate and the *exo* Diels–Alder adduct in methanol as solvent.

The saturated esters III and IV were equilibrated by sodium methoxide in methanol as previously reported for 2-carbomethoxybicyclo[2.2.1]heptane.[10] The equilibrium constant (*exo/endo*) was determined to be 3.05 ± 0.10 at 75°. In Table I the equilibrium values determined for the oxabicyclic compounds at 75° are listed along with the previously determined values for the carbocyclic compounds.[10]

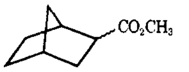
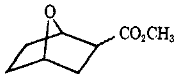
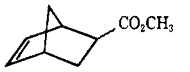
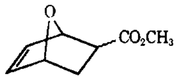


III



IV

TABLE I

| Compound | K (*exo/endo*) | Solvent |
|---|---|---|
|  | 2.35 ± 0.10 | Methanol[a] |
|  | 3.05 ± 0.10 | Methanol |
|  | 1.05 ± 0.02 | Methanol[b] |
|  | 0.98 ± 0.06 | Neat |
| | 1.01 ± 0.08 | Dimethyl sulfoxide |
| | 1.3 ± 0.1 | Methanol |

[a] A value of 2.30 at 90° has been reported by other workers: A. C. Cope, E. Ciganek, and N. A. LeBel, *J. Amer. Chem. Soc.*, **81**, 2799 (1959). [b] See ref 10.

There are small, but experimentally significant, differences between the equilibrium constants of the carbobicyclic compound and their 7-oxa analogs. Oxygen could be considered to be of smaller effective steric size than a methylene group. However, there are several other structural contributions that could give rise to the observed differences in the equilibrium constant. The smaller C–O bond distance (1.43 Å) compared with the normal C–C bond distance (1.54 Å) requires that the bicyclic ring systems be modified when oxygen replaces methylene. The distance separating the carbomethoxy group and the π electrons in the unsaturated compound and the *endo*-6 proton in the saturated compound should be smaller in the oxa derivative. This should lead to a destabilization of the *endo* isomer in the oxa compounds compared with the *endo* isomer of the carbobicyclic compounds. Some and perhaps all of the increased amount of the *exo*-oxa compound at equilibrium could be due to this difference.

Dipole–dipole repulsion should destabilize the *exo*-oxa compounds relative to the *endo* isomers. However, such contributions cannot be properly evaluated with a single ring system. The determination of the equilibrium constants for a polar group such as carbomethoxy in a ring system such as 1,3-dioxane will be needed in order to determine the magnitude of dipole–dipole repulsion between an ether oxygen and a carbomethoxy group. The near equivalence of methylene and oxygen and the difference between this conclusion and those of Eliel may involve hybridization changes. In a strained system the decreased ether bridge angle should increase the s character of the lone-pair electrons. While the hybridization of the methylene carbon–hydrogen bond also should be of increased s character, the shorter carbon–oxygen bond requires a larger hydridization change for oxygen. The change in the directional character of the lone-pair electrons of the oxygen bridge with increasing s character should decrease the distance to the carbomethoxy substituent. Therefore, the effective steric size of the lone pairs of oxygen in our compounds may be larger than in 1,3-dioxane. However, many additional substituents in both the oxabicyclic and 1,3-dioxane ring systems will have to be examined before an established model can be presented.

## Experimental Section

**2-Carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene.**—Furan (25 g) and methyl acrylate (32 g), both stabilized with hydroquinone, were mixed and maintained at 40° for 1 month. Evaporation of unreacted material under reduced pressure at 0° yielded 10 g of a colorless oil. Attempted analysis of the product by vapor phase chromatography was unsuccessful as complete cracking occurred. Reduction of the reaction mixture as detailed in the following section followed by vpc analysis indicated that equimolar amounts of the *exo* and *endo* isomers were present.

**2-Carbomethoxy-7-oxabicyclo[2.2.1]heptane.**—A mixture of the isomeric unsaturated esters (2 g) was hydrogenated in 95% ethanol using palladium on charcoal (5%, 100 mg) as the catalyst. Cessation of hydrogen uptake occurred after 2 hr. The ethanol was removed by distillation, and the product was obtained as a colorless oil (65° at 8 mm). The isomers were separated on a 10 ft × 1/4 in., 20% DEGS on Chromosorb W column. The *exo* isomer had the longer retention time. The assignment of configuration was based initially on the composition of hydrogenated mixtures derived from unsaturated esters which were obtained by shorter reaction times as the *endo* isomer should be formed initially. With increasing lengths of time for the Diels–Alder reaction, the percentage of the *exo* isomer increased until at equilibrium, and *exo* and *endo* isomers were in a 1:1 ratio. Assignment of configuration was confirmed by nmr. The resonance of the 2 proton of the saturated *exo* isomer appears as a quartet at τ 7.45, while the corresponding resonance of the *endo* isomer appears as a pentuplet at 7.08.

*Anal.* Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found for *exo:* C, 61.33; H, 7.65. Found for *endo*: C, 61.70; H, 7.70.

**Equilibration of *endo*- and *exo*-2-Carbomethoxy-7-oxabicyclo[2.2.1]hept-5-enes.**—Equimolar amounts of furan and methyl acrylate were sealed in nmr tubes. The tubes were placed in water baths maintained at 63 and 75°. At various times, the nmr spectra were determined at the same temperature as that employed for equilibration. The methyl protons in methyl acrylate, *endo*-2-carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene, and *exo*-2-carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene appear at τ 5.90, 5.99, and 5.92, respectively. The initial ratio of *endo* to *exo* product was approximately 5:2 but gradually changed to 1:1 with time. The times necessary for equilibration at 63 and 75° were approximately 15 and 4 days, respectively.

**Equilibration of *endo*- and *exo*-2-carbomethoxy-7-oxabicyclo[2.2.1]heptanes.**—Equilibrations were carried out according to procedures previously described.[10] A 10 ft × 1/4 in., 20% DEGS on Chromosorb W column was employed for analysis.

**Registry No.**—I, 17791-32-1; II, 17791-33-2; III, 17791-34-3; IV, 17791-35-4.

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(10) R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **30**, 423 (1965).