that the diradical lifetimes are extremely short, since the diradical components are unquenched by up to 200 Torr of added oxygen. Liquid-phase DMCB photolyses support such a short lifetime.

A more quantitative and extensive investigation of this interesting diradical system is underway in order to study the energetics, rates, and mechanism.

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* Address correspondence to this author.

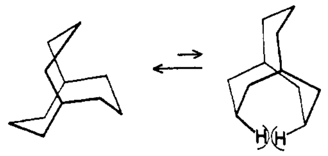
Howard A. J. Carless, Edward K. C. Lee*
Department of Chemistry, University of California
Irvine, California 92664
Received August 8, 1970

Synthesis and Characterization of Bicyclo[3.3.3]undecane and 1-Azabicyclo[3.3.3]undecane

Sir:

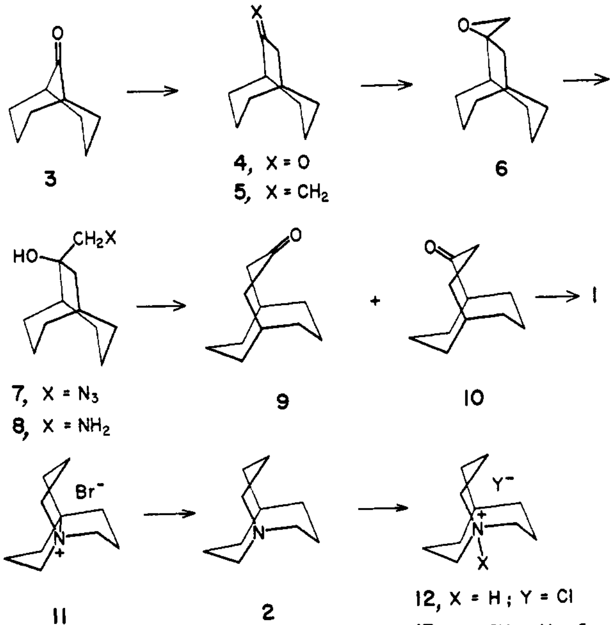
We wish to report the synthesis of two prototype compounds consisting of three eight-membered rings, namely, bicyclo[3.3.3]undecane (**1**) and 1-azabicyclo-[3.3.3]undecane (**2**). Compounds possessing this bridged ring system are of particular interest with regard to their possible conformations and their chemical reactivity in comparison with other multicyclic systems including adamantane.

Interest also stems from the conformational relationship to eight-membered rings[1] in the carbocyclic series,[2] when one or more ring atoms are replaced by heteroatoms,[3] and when the eight-membered ring has been constrained by a charge interaction,[4] or by a hydrocarbon bridge of one[5] or two[6] atoms. For unconstrained eight-membered rings, nmr[2e] and X-ray crystallographic[7] evidence has shown the boat–chair (BC), or twist forms thereof, to be the favored conformation. This is also the case for the charge-constrained system 5-methyl-1-thia-5-azacycloocten-1-oxide perchlorate.[4] For the bicyclo[3.3.1]nonane[8] and bicyclo[3.3.2]decane[6,9] systems, accumulated evidence suggests the boat–boat (BB) conformation for the eight-membered ring. Molecular models (Dreiding) of the BB conformation of the eight-membered ring indicate that the transannular H–H distance diminishes in going from the bicyclo[3.3.1]nonane to the bicyclo[3.3.2]decane system, and finally in the bicyclo[3.3.3]undecane system the transannular hydrogens are in contact when one of the eight-membered rings is in the boat–boat conformation (**1b**). On this basis we predict that in the bicyclo[3.3.3]undecane system the all-boat–chair conformation (**1a**) should be favored over the crown–BC–BB conformation (**1b**). Calculations based on the strain energy of the boat–chair, crown, and boat–boat conformations of cyclooctanes[2a] suggest that the all-BC form (**1a**) should be *at least* 6 kcal more stable than alternative conformations.[10]



1a
BC–BC–BC

1b
Crown–BC–BB



3

4, X = O
5, X = CH_2

6

7, X = N_3
8, X = NH_2

9

10

11

2

12, X = H; Y = Cl
13, X = CH_3; Y = I

The synthesis of bicyclo[3.3.3]undecane (**1**) was accomplished by lengthening the short bridge of a bicyclo-[3.3.1]nonane compound. Ring expansion of bicyclo-[3.3.1]nonan-9-one (**3**)[11] with methanolic diazomethane[12] afforded bicyclo[3.3.2]decan-9-one (**4**):[13] mp 177–179°; sublimed 60° (10 mm); 75% yield; ir ($CHCl_3$) 1690 cm^{-1}; nmr ($CDCl_3$) δ 2.85 (m, 1, CHCO), 2.50 (d, 2, $J = 6$ Hz, CH_2CO). This compound failed to react further with diazomethane under the same conditions, and numerous routes to the amino alcohol **8**

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were unsuccessful in our hands. The conversion was achieved *via* a modified Wittig reaction using the methylsulfinyl carbanion and methyl triphenylphosphonium bromide[14] to give 9-methylenebicyclo[3.3.2]decane (**5**): bp 67–69° (2.5 mm); ir (film) 3040, 1610 cm^{-1}; nmr ($CDCl_3$) δ 4.70 (q, 1, J_{AB} = 2.7 Hz, J_{AX} = 2 Hz), 4.57 (q, 1, J_{BA} 2.7 Hz, quartets collapsing to doublets, J = 2.7 Hz, on irradiation with the frequency of the signal for the two H_X protons). Epoxidation of **5** with *m*-chloroperbenzoic acid in chloroform (30 min) or monoperphthalic acid in ether (24 hr) at 0° afforded the epoxide **6**: mp 97–98°; sublimed 60° (5 min); nmr ($CDCl_3$) δ 2.62 (s, 2, OCH_2), 2.0 (m, 3, α-CH, α-CH_2), 1.65 (m, 13), which was cleaved by sodium azide in dimethylformamide containing a catalylic amount of boric acid[15] to the hydroxy azide **7**: ir (film) 3590, 3540, 2100 cm^{-1}. Reduction of **7** in ethanol with hydrogen and Adams' catalyst[16] gave 9-aminomethylbicyclo-[3.3.2]decan-9-ol (**8**), characterized as its hydrochloride salt: mp 241–242°; nmr (D_2O-DSS) δ_A 3.04, δ_B 3.22, J_{AB} = 13 Hz ($CH_2NH_3^+$). Demjanov–Tiffeneau expansion in aqueous acetic acid[17] yielded a mixture of the bicyclo[3.3.3]undecan-9- and 10-ones (**9**, **10**): ir 1685 cm^{-1}; nmr ($CDCl_3$) δ 2.9 (m, 0.62, CHCO in **10**), 2.60 (m, 2 × 0.62 + 4 × 0.38, CH_2CO). Wolff–Kishner reduction[18] of the ketone mixture (**9**, **10**) afforded bicyclo[3.3.3]undecane (**1**): mp 155–157°, sublimed 50° (10 mm); nmr ($CDCl_3$) δ 2.3 (m, 2, CH), 1.55 (18, CH_2's).

The implications of structure **1a**, with C_{3h} molecular symmetry, are of interest. All of the methylene bridges point in the same direction. The tertiary hydrogens may be susceptible to direct substitution,[19] and the 1-substituted bicyclo[3.3.3]undecanes would be dissymmetric (chiral), with the possibility of resolution depending upon the activation energy required for the flipping of the three methylene bridges.

1-Azabicyclo[3.3.3]undecane (**2**), with a C_3 axis, is of special interest in that it represents an *un*substituted [3.3.3] ring system capable of existing in enantiomeric forms if the conformational energy barrier is sufficiently large. The favored route to this compound proved to be remarkably simple. 1-Azoniatricyclo[3.3.3.0]undecane bromide (**11**), prepared by the method of Šorm and Beránek,[20] was treated with sodium in liquid ammonia[21] to give 1-azabicyclo[3.3.3]undecane (**2**): mp 150–152°, sublimed 35° (20 mm); nmr ($CDCl_3$) δ 2.85 (m, 6, α-CH_2), 2.57 (m, 1, CH), 1.60 (m, 6, β-CH_2), 1.57 (m, 6, γ-CH_2). The hydrochloride salt **12**, mp 305–307° dec, from ethanol, and the methiodide **13**, mp 273–275°, from ethanol, were prepared, and X-ray single-crystal determinations are in progress.

Further studies of the physical and chemical properties of the bicyclo[3.3.3]undecane compounds are continuing.

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* Address correspondence to this author.

Nelson J. Leonard,* John C. Coll
Department of Chemistry, School of Chemical Sciences
University of Illinois, Urbana, Illinois 61801
Received August 22, 1970

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Detection of a Secondary Isotope Effect on Partitioning of Benzhydryl Benzoate Ion Pairs

Sir:

Shiner's proposal that ion-pair intervention can influence secondary deuterium isotope effects in solvolytic processes[1] suggests that there should be isotope effects on partitioning of ion-pair intermediates. For example, in the solvolysis of *exo*-norbornyl brosylate,[2] which involves partitioning of intimate ion pair II (eq 1) between internal return and irreversible dissociation to III ($k_3 \gg k_{-2}$), the solvolytic rate constant

$$\underset{\text{I}}{\text{RX}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{II}}{\text{R}^+\text{X}^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{III}}{\text{R}^+\|\text{X}^-} \xrightarrow[\text{HOS}]{k_3} \underset{\text{IV}}{\text{ROS}} \qquad (1)$$

k_t is the product of the ionization rate k_1 and the fraction of ion pairs that dissociate, $F^{II} = k_2/(k_1 + k_2)$. The solvolytic isotope effect is given by eq 2 and $F_H{}^{II}/F_D{}^{II}$ by eq 3 (assuming $k_3 \gg k_{-2}$).[3] Any difference in total zero-point energy (ZPE) between the α-C–H bond in TS1 (Figure 1) and TS2 would make

$$(k_t{}^H/k_t{}^D) = (k_1{}^H/k_1{}^D)(F_H{}^{II}/F_D{}^{II}) \qquad (2)$$

$$F_H{}^{II}/F_D{}^{II} = \frac{(k_2{}^H/k_{-1}{}^H) + (k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H)}{(k_2{}^H/k_{-1}{}^H) + 1} \qquad (3)$$

$(k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H) \neq 1$ resulting in a partitioning isotope effect (PIE). If covalent bonding to the leaving group is greater in TS1 than TS2, $(k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H) > 1$ and $F_H{}^{II}/F_D{}^{II} > 1$. Since $k_2{}^H/k_{-1}{}^H$ is solvent dependent PIE's could cause solvent effects on *solvolytic* isotope effects, even though $(k_1{}^H/k_1{}^D)$ and $(k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H)$ are solvent independent.

To probe the existence of partitioning isotope effects we have measured the α-tritium isotope effect on partitioning of benzhydryl benzoate ion pair(s) generated from diphenyldiazomethane (DDM) and benzoic acid (HOBz–TOBz) in ethanol-*O*-*t* and in 90% acetone.[4] This reaction (Chart I) entails rate-determining proton transfer from monomolecular, undissociated HOBz giving diazonium benzoate ion pair that loses nitrogen to form what appears to be the same benzhydryl benzoate "ion pair or spectrum of ion pairs" as in solvolysis.[4,5] Except for the tracer (tritium, introduced as TOBz), the experimental conditions of Diaz and

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