$(CH_2)_5$; X = Br), 766-65-4; **2** ($R^1,R^2 = (CH_2)_5$; X = Cl), 766-66-5; **2** ($R^1,R^2 = (CH_2)_4$; X = Br), 822-85-5; **2** ($R^1,R^2 = (CH_2)_4$; X = Cl), 822-87-7; **2** ($R^1 = n\text{-}C_5H_{11}$; $R^2 = CH_3$; X = Br), 51134-60-2; **2** ($R^1,R^2 = (CH_2)_{10}$; X = I), 69381-33-5; **2** ($R^1 = n\text{-}C_5H_{11}$; $R^2 = CH_3$; X = I), 73746-49-3; **3** ($R^1,R^2 = (CH_2)_{10}$; R^3,R^4 = Me; X = Br), 73746-46-0; **3** ($R^1,R^2 = (CH_2)_{10}$; R^3,R^4 = Me; X = Cl), 73746-47-1; **3** ($R^1,R^2 = (CH_2)_5$; R^3,R^4 = Me; X = Br), 73746-48-2; **3** ($R^1,R^2 = (CH_2)_4$; R^3,R^4 = Me; X = Br), 1728-17-2; **3** ($R^3,R^1 = (CH_2)_3$; R^2 = H; R^4 = Me; X = Br), 5324-21-0; **3** ($R^3,R^1 = (CH_2)_3$; R^2 = H; R^4 = Me; X = Cl), 6581-61-9; **3** ($R^3,R^1 = (CH_2)_3$; R^2 = H; R^4 = Me; X = I), 67038-72-6; **3** ($R^3,R^1 = (CH_2)_3$; R^2 = H; R^4 = Et; X = Br), 39150-42-0; **3** ($R^3,R^1 = (CH_2)_3$; R^2 = H; R^4 = Pr; X = Br), 39150-11-3; **3** ($R^3,R^1 = (CH_2)_3$; R^2 = H; $R^4 = CH_2CH{=}CH_2$; X = Br), 73746-50-6; **3** ($R^3,R^1 = CH(OEt)CH_2CH_2$; R^2 = H; R^4 = Et; X = Br), 3149-11-9; **3** ($R^3,R^1 = CH_2CH_2CH(Me)$; R^2 = H; R^4 = Me; X = Br), 73746-51-7; **3** ($R^3,R^1 = CH_2CH_2$; R^2 = H; R^4 = Me; X = Br), 33691-61-1; **3** (R^3 = Et; R^1,R^2 = H; $R^4 = CH_2CH_2OMe$; X = Br), 73746-52-8; **3** (R^3 = Et; R^1,R^2 = H; $R^4 = CH_2CH_2OMe$; X = Cl), 73746-53-9; **3** (R^3 = Et; R^1,R^2 = H; $R^4 = CH_2CH_2OMe$; X = I), 73746-54-0; **4**, 73746-55-1; **5**, 73746-56-2; **6**, 73746-57-3; **7**, 73746-58-4; 1-octen-2-yl acetate, 26735-84-2; 2-(trimethylsiloxy)-1-octene, 55314-45-9; 1-bromo-2-octanone, 26818-08-6; 1-iodo-2-octanone, 63641-50-9.

Communications

Primary Tritium Isotope Effect on Hydride Transfer from Sodium Borohydride to Cyclopropenium Ion[‡]

Summary: Reduction of a cyclopropenium perchlorate with tritium-labeled sodium borohydride shows a primary kinetic isotope effect, suggesting that hydride transfer is at least partially rate-determining and thus demonstrating that formation of the encounter complex between cation and hydride is reversible.

Sir: The 1,2-disubstituted cyclopropene function occurs in the center of the fatty acid chain of lipids from plants belonging to the order *Malvales*. Cottonseed and kapok oils, which contain two of these unusual fatty acids, are consumed in large amounts by the world's population. Cottonseed flour finds increasing use as a source of protein for human consumption. These cyclopropenoid fatty acids are responsible for certain physiological disorders in farm and laboratory animals. Some of these disorders[1] are delayed sexual development in females, impaired reproduction, altered fat metabolism, pink discoloration in avian egg whites during storage, and liver damage.[2] More importantly, cyclopropenoid fatty acids have been reported to be potent cocarcinogens[3] and carcinogens in rainbow trout.[4]

There has been considerable interest in synthetic cyclopropenoid fatty acids, and in particular sterculic acid, a Δ^9-19-carbon acid. All of the synthetic procedures,[5] except for one,[6] utilize the special stability of the cyclopropenium ion which is reduced by hydride to the corresponding cyclopropene. Reduction appears to occur only at the 3-position; none of the above procedures[5] mention the occurrence or separation of an isomeric 1,3-disubstituted cyclopropene. We have reduced a series of seven 1,2-dialkylcyclopropenium perchlorates with sodium borohydride. The product contains no isomeric cyclopropenes, as indicated by the absence of vinylic cyclopropene proton resonance in the τ 2.99 region.[7]

Breslow and co-workers[7] report three equivalent propyl groups in the NMR spectrum of tripropylcyclopropenyl perchlorate, indicating that the positive charge is evenly distributed around the ring. Also, the propyl groups in the three cations tripropylcyclopropenyl, dipropylcyclopropenyl, and propyldiphenylcyclopropenyl perchlorate are relatively shifted to the same extent. Differences in chemical shift between the α- and β-methylene hydrogens are very similar for the propyl groups in each of these three cations. These data convincingly support the concept that each carbon of the cyclopropenyl cation has a similar charge structure, with essentially one-third of the charge at each ring carbon.

Long-lived carbonium ions have the ability to discriminate between nucleophiles. For example, triphenylmethyl cation, $pK_{R+} = -6.63$, has a competition factor, k_y/k_0, of 2.8×10^5 for azide ion in 50% aqueous acetone.[8] Although the competition factor has not been determined for the more stable dialkylcyclopropenium ions, $pK_{R+} = 2.7$,[9] one would expect it to be considerably more selective. As already mentioned, these cyclopropenium ions show a selectivity for site of reaction, allowing the less hindered positions to react more readily, rather than a combination dependent only upon their diffusion together. Ritchie[10] has documented the regularity of reactivity of anions with organic cations.

We are surprised to observe that cyclopropenium ions not only show a high degree of selectivity in their combination with hydride, but the reaction also exhibits a primary kinetic isotope effect. Sterculic acid was prepared by dropping the corresponding cyclopropenium perchlorate[7] into Me_2SO containing tritium-labeled sodium borohydride (26.7 mCi/mmol) at 5 °C. The product incorporated 6.8 times less label than was present in the sodium borohydride, or $k_H/k_T = 6.8$. Although this effect is smaller than the theoretical maximum for a primary kinetic isotope effect, it demonstrates that the reaction is not solely diffusion controlled. The cation–hydride approach must be somewhat reversible with hydride transfer at least partially rate determining.

Registry No. Sodium borohydride, 16940-66-2; cyclopropenium ion, 20829-57-6.

Norman E. Pawlowski,* Russell O. Sinnhuber
Department of Food Science and Technology
Oregon State University
Corvallis, Oregon 97331

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