Calcd for C₁₅H₂₁NOS: C, 68.40; H, 8.04; N, 5.32. Found: C, 68.10; H, 8.20, N, 5.00. IR (KBr) 2960, 2930, 2870, 1690, 1615, 1465, 1395, 1360, 1315, 1210, 1160, 1065, 885, 865, 760, 700 cm⁻¹. ¹H NMR (CDCl₃) δ 0.77-2.06 (t, s, m, 14 H), 3.16-4.23 (m, 2 H), 5.48 (s, 1 H), 7.23-7.90 (m, 4 H). EIMS (70 eV), m/e (relative intensity) 207 (M - isobutylene, 19), 174 (M - SC(CH₃)₃, 100), 132 (M - $SC(CH_3)_3$ - propylene, 47).

Acknowledgment. This work was supported in part by NIH Grant CA-09242 from the National Cancer Institute and is taken in part from the Doctoral Thesis by John F. Stobaugh entitled "Chemical Studies in the Fluorogenic Reaction of o-Phthalaldehyde with Primary Amines", University of Kansas, 1982.

Registry No. 1c, 64807-91-6; 2, 33125-70-1; 3, 5323-50-2; 4, 66161-45-3; 5, 91948-93-5; 6, 4122-56-9; OPA, 643-79-8; PrNH₂, 107-10-8; t-BuSH, 75-66-1; 3-chlorophthalide, 6295-21-2; phthalic anhydride, 85-44-9.

Trifluoroacetic Acid Catalyzed Allylic Phenylation of α -Methylallyl Acetate, α -Methylallyl Trifluoroacetate, and α -Methylallyl **Alcohol with Benzene**

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Received April 25, 1984

In a previous paper we have reported that the reaction of allyl esters with benzene in the presence of $Pd(OAc)_2$ and CF₃COOH gives cinnamaldehyde derivatives via the acyl–O bond fission–phenylation.¹ In connection with this reaction we have found that CF_3COOH without palladium salts causes phenylation of allylic esters and alcohol with benzene. This paper reports the CF₃COOH-catalyzed allylic phenylation of allyl compounds like α -methylallyl acetate, α -methylallyl trifluoroacetate, and α -methylallyl alcohol with benzene to give trans-1-phenyl-2-butene (1) in fair to good yields.



R . H, COCH3, COCF,

Allylic phenylation takes place by stirring the mixture of the allylic compound, CF₃COOH, and benzene at 80 °C. For example, the reaction of α -methylallyl trifluoroacetate with benzene in the presence of CF_3COOH at 80 °C gives 1 in a 78% yield together with 1-phenyl-1-butene (2) (3%)and 3-phenyl-1-butene (3) (1%) (run 5). The results are listed in Table I.

As is apparent from Table I, the trifluoroacetate (runs 3 and 5) is more reactive than the corresponding acetate (runs 1 and 2) and alcohol (run 6). In the case of α -methylallyl trifluoroacetate, the reaction proceeds even at room temperature (run 4). Substitution of CH₃COOH resulted in no reaction.

The role of CF₃COOH appears to be to convert the allylic acetate or alcohol to the trifluoroacetate and may further assist in dissociation to an allyl cation 4.² Elec-

Table I. Allylic Phenylation with Benzene^a

run	allylic compd, mmol	CF ₃ COOH, mL	temp, °C	time, h	yield of 1, ^b %
1	α -methylallyl	1.3	80	4	33°
2	acetate, 2.1 α -methylallyl acetate, 2.0	0.5	80	8	21 ^d
3	α -methylallyl trifluoroacetate, 1.6	1.3	80	8	64 ^e
4	α -methylallyl trifluoroacetate, 1.6	1.3	\mathbf{rt}^i	53	16 [/]
5	α-methylallyl trifluoroacetate 1.5	0.8	80	8	78 ^s
6	α -methylallyl	0.5	80	8	21^{h}

^aBenzene, 5 mL. ^bBased on the starting allyl compound and determined by GLC. ^cA 1% yield of 3 and a trace amount of 2 were also formed. d A 1% yield of 3 was also formed. A 2% yield of 2 and a 1% yield of 3 were also formed. ^fTrace amounts of both 2 and 3 were also formed. #A 3% yield of 2 and a 1% yield of 3 were also formed. ^hA 1% yield of 3 was also formed. ⁱRoom temperature.



trophilic attack of 4 at C_1 (path a) or C_3 (path b) to benzene gives 1 or 3, respectively (Scheme I).³ The almost exclusive formation of the 1-isomer may be due to the less sterically crowded position at C_1 in 4 and the less reactive nonpolar benzene substrate as compared to the usual solvolysis conditions. Addition of $Pd(OAc)_2$ to this reaction gave similar results.¹

The reaction described here is the first example of the allylic phenylation of allylic compounds with benzene by the catalysis of CF₃COOH and provides a very convenient route to 1.

Experimental Section

General Methods. NMR spectra were obtained with a Hitachi R-24S spectrometer using Me₄Si as an internal standard. The starting trifluoroacetate was prepared by treatment of α -methylallyl alcohol with trifluoroacetic anhydride: ¹H NMR (CCl₄) δ 1.46 (d, J = 7 Hz, 3 H, methyl), 5.10–6.20 (m, 4 H, allylic and olefinic).

General Method for Allylic Phenylation. Into a 50-mL centrifuge tube containing a magnetic stirring bar were added benzene (5 mL), the allyl compound, and CF₃COOH (see Table I), and the tube was sealed under air with a serum cap. Then the mixture was heated with stirring at 80 °C. After the usual workup, the products were analyzed and separated by GLC (Apiezon L, 1.5 m) to give 1 with 2 and 3 as byproducts. The identities of the products were proved by IR, NMR, and retention time comparison with samples prepared from dehydrations of 4-phenyl-2-butanol (compound 1) and 1-phenyl-1-butanol (compound 2) and from crotyl chloride and phenylmagnesium bromide (compound 3).⁴ 1-Phenyl-2-butene (1): ¹H NMR (CCl₄) δ 1.50-1.81 (d, J = 5 Hz, 3 H, methyl), 3.08-3.40 (m, 2 H, allylic), 5.22-5.68 (m, 2 H, olefinic), 6.83-7.31 (m, 5 H, Ar). 1-Phenyl-1-butene (2): ¹H NMR (CCl₄) δ 1.10 (t, J = 7 Hz, 3 H, methyl), 2.10 (m, 2 H, allylic), 6.08-6.32 (m, 2 H, olefinic), 7.18 (s, 5 H, Ar).

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⁽¹⁾ Fujiwara, Y.; Yoshidomi, M.; Kuromaru, H.; Taniguchi, H. J. Or-ganomet. Chem. 1982, 226, C36.
(2) Brown, H. C.; Wirkkala, R. A. J. Am. Chem. Soc. 1966, 88, 1441.

⁽³⁾ Byproduct 2 would be formed by acid-catalyzed isomerization of 1.

⁽⁴⁾ Hayashi, T.; Konishi, M.; Yokota, K.; Kumada, M. J. Chem. Soc., Chem. Commun. 1981, 313.

Registry No. 1, 935-00-2; 2, 824-90-8; CH₃C(O)OCH(CH₃)-CH=CH₂, 6737-11-7; CF₃C(O)OCH(CH₃)CH=CH₂, 37729-50-3; CH₃CH(OH)CH=CH₂, 598-32-3; CF₃CO₂H, 76-05-1; benzene, 71-43-2.

A Near Perfect Complementarity of Equilibrium Isotope Effects. A Corrected Value for a Recently Published Equilibrium Constant Derived for the 2-Norbornyl- $h_{10}d_1$ Cation

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Received April 18, 1984

Several years ago, we initiated a study of the 2-norbornyl- h_1d_{10} cation (and others) in an attempt to measure primary isotope rate constant ratios $(k_{\rm H}/k_{\rm D})$ for typical intramolecular hydride shifts in carbocations.¹ This NMR line-broadening analysis required a prior knowledge of the equilibrium isotope effects, the one of major interest for a 6,2(1)-hydride(deuteride) shift being that shown in eq 1.



Saunders and Kates, A'/B'= 2.14 at -105 °C

Recently, Saunders and Kates (S-K)² have reported equilibrium isotope data for the isotopically complementary system, the 2-norbornyl- $h_{10}d_1$ cation, as shown in eq 2, and one notes a large discrepancy in the two sets of data (compared to the "no effect" result of K = 1, our data are about 25% larger compared to over 100% for the S-K result). In discussion with S-K, it was apparent that neither of our data was subject to much experimental error and so it initially appeared to us that the expected isotopic



complementarity³ was being seriously violated in this case.⁴ In any event, we have now undertaken a complete reinvestigation of the whole problem in order to try and resolve the matter.

Results and Discussion

The h_1d_{10} cation was synthesized as shown in Scheme I. Mass spectrometric analysis shows $83\% d_{11}$ and 17% h_1d_{10} compounds in the starting material, and this ratio is carried through in the synthesis without significant change (giving 83% h_1d_{10} and 17% h_2d_9 cations). The proton in the $h_1 d_{10}$ cation becomes rapidly and randomly scrambled into all positions, resulting in a set of either six or eleven different cations, depending on whether one views the cation as being symmetrical or not.⁶ In the temperature range -40 to -100 °C, the 6.2(1)-deuteride shift is rapid but the 3.2-deuteride shift is slow, resulting in three observable ¹H NMR peaks, the same number found in the h_{11} cation. The lowest field ¹H peak in the spectrum is the averaged proton from structures A and B, and K can be calculated from a knowledge of the "frozen-out" positions for the hydrogen in the A and B structures. These in fact can be obtained at -140 °C, resulting in the K value given in eq 1. The averaged peak for $A \rightleftharpoons B$ is slightly temperature dependent, as expected, and shifts to higher fields at lower temperatures. This calculation of K is straightforward and there is very little possible error involved.

⁽¹⁾ The strategy for obtaining these ratios envisaged using 1:10 mixtures of the h_{11} and h_1d_{10} species in the same solution. Measurements in the same solution at the same instant and region of the NMR tube are needed in order that temperatures for $k_{\rm H}$ and $k_{\rm D}$ will be exactly the same. The need to use the h_1d_{10} species in our studies occurs because one cannot fix isotope labels in the 2-norbornyl cation, all hydrogen atoms being rapidly scrambled on a normal time scale over all possible positions, except at very low temperatures. However, when one observes ¹H NMR in an $h_1 d_{10}$ species, we can be positive that line-broadening phenomena will only be caused by deuterium migrations. Considering the low temperatures involved and the possibility of tunneling, values for $k_{\rm H}/k_{\rm D}$ > 10 for a 6,2(1)-hydride(deuteride) shift would not have been surprising to us. Such rate differences would have allowed the slower rate system to clearly decoalesce under lowering temperature conditions whereas the faster rate system would still have given a single peak, thereby allowing both k's to be very accurately analyzed. In any event, these $k_{\rm H}/k_{\rm D}$ ratios turned out to be much smaller than expected ($\lesssim 2$ at -130 °C) and not amenable to accurate analysis by our projected technique

⁽²⁾ Saunders, M.; Kates, M. R. J. Am. Chem. Soc. 1983, 105, 3571.

⁽³⁾ Saunders and Kates² have argued, quite reasonably, that the preference for A' over B' is a consequence of a nonclassical structure for $\dot{A}'-B'$ (as indeed we have written these), i.e., that a hypervalent C_6-H bond is weaker than a "normal" $\mathrm{C_{l}\text{-}H}$ bond and therefore, using standard arguments, that the $h_{10}d_1$ cation, wishing to maximize bonding, will preferentially locate the deuterium in the stronger bond (C-1). An analogous argument applies to our data, i.e., the h_1d_{10} cation, also wishing to maximize bonding, will preferentially locate the proton in the weaker bond (C-6). There seems little reason why these preferences should not normally have been approximately equal and opposite; i.e., one might have expected similar K values for B/A and A'/B'.

⁽⁴⁾ The divergent results suggested to us that the structures of A-B and A'-B' might be quite different, i.e., that the overall presence of ten proton or ten deuterium atoms makes a very significant structural change in the cation. The most recent ab initio calculations⁵ on the 2-norbornyl cation substantiate the idea that, regardless of what the ground-state structure is, the potential energy surface is extremely "mushy". Thus it would not be entirely unreasonable for one to find such large structural

changes in this particular case. (5) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F., III. J. Am. Chem. Soc. 1983, 105, 5915.

⁽⁶⁾ For simplicity of presentation only, we write a symmetrical structure for the 2-norbornyl cation. The alternate assumption of two ture for the 2-norbornyl cation. classical" structures interconverted by a very rapid Wagner-Meerwein shift leads to similar conclusions.