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Reactions of Carbocations with Unsaturated Hydrocarbons: Electrophilic Alkylation or Hydride Abstraction?

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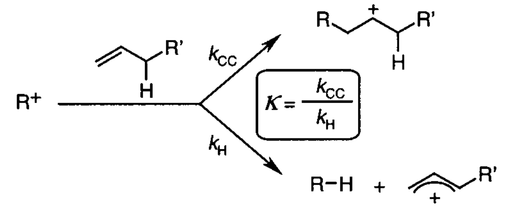
Abstract: Benzhydryl cations were used as reference electrophiles to determine the hydride donor reactivities of unsaturated hydrocarbons. The kinetics of the reactions were followed by UV−vis spectroscopy and conductivity measurements, and it was found that the second-order rate constants for the hydride transfer processes were almost independent of the solvents or counterions employed. The rate constants correlate linearly with the previously published empirical electrophilicity parameters E of the benzhydrylium ions. Therefore, the linear free energy relationship $\log k(20\ °\mathrm{C}) = s(E + N)$ could be employed to characterize the hydride reactivities of the hydrocarbons by the nucleophilicity parameters N and s. The similarity of the slopes s for hydride donors and π-nucleophiles allows a direct comparison of the reactivities of these different functional groups based on their nucleophilicity parameters N. Since nucleophilicity parameters of $-5 < N < 0$ have been found for a large variety of allylic and bisallylic hydride donors, a rule of thumb is derived that hydride transfer processes may compete with carbon−carbon bond-forming reactions when carbocations are combined with olefins of π-nucleophilicity $N < 0$.

Introduction

Electrophilic alkylations of alkenes and arenes are often accompanied by hydride transfer processes, and the success of carbon−carbon bond-forming reactions as shown on the top of Scheme 1 depends on the magnitude of the competition constant κ.

For that reason, the rational design of synthetic transformations via carbocationic intermediates requires knowledge of the rate constants shown in Scheme 1. The value of the competition constant κ is also crucial for the course of carbocationic polymerizations, since the ratio of propagation (k_{CC}) and hydride transfer constants (k_H) is an important factor controlling the molecular weights of macromolecules.[1]

Scheme 1



Our previous work allows one to predict rate constants for the reactions of a large variety of π-nucleophiles with carbocations (k_{CC}).[2−5] To determine the complementary values for hydride transfer processes (k_H), we have now studied the kinetics of the reactions of CH-hydride donors with benzhydryl cations, that is, the same class of carbocations recommended as reference electrophiles for the characterization of π-nucleophiles.[5] In this way, a direct comparison of σ- and π-nucleophiles should become possible.

Previous kinetic investigations of hydride transfer reactions have often used tritylium ions as hydride abstractors.[6−25] Generally, these reactions follow second-order kinetics,[7,8,10,12−16,18,19,21−23] and the rate constants depend only slightly on the nature of the negative counterion[17,18,23] or the solvent,[24,25] though a comparison of data from different sources sometimes proved to be problematic. Only a few studies were addressed

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(1) (a) Kennedy, J. P.; Maréchal, E. *Carbocationic Polymerization*; Wiley: New York, 1982. (b) *Cationic Polymerizations: Mechanism, Synthesis, and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996.

(2) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990−1010; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957.

(3) Mayr, H.; Kuhn, O.; Gotta, M. F.; Patz, M. *J. Phys. Org. Chem.* **1998**, *11*, 642−654.

(4) Mayr, H.; Patz, M.; Gotta, M. F.; Ofial, A. R. *Pure Appl. Chem.* **1998**, *70*, 1993−2000.

(5) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512. See also: http://www.cup.uni-muenchen.de/oc/mayr.

(6) Giese, G.; Heesing, A. *Chem. Ber.* **1990**, *123*, 2373−2380.

(7) Karabatsos, G. J.; Tornaritis, M. *Tetrahedron Lett.* **1989**, *30*, 5733−5736.

(8) Jerkunica, J. M.; Traylor, T. G. *J. Am. Chem. Soc.* **1971**, *93*, 6278−6279.

(9) Hannon, S. J.; Traylor, T. G. *J. Org. Chem.* **1981**, *46*, 3645−3650.

(10) Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651−3656.

(11) Ishikawa, M.; Fukuzumi, S.; Goto, T.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3754−3756.

(12) Penczek, S. *Makromol. Chem.* **1974**, *175*, 1217−1252.

(13) Washburne, S. S.; Szendroi, R. *J. Org. Chem.* **1981**, *46*, 691−693.

(14) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **1995**, *14*, 4031−4033.

(15) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137.

(16) Cheng, T.-Y.; Bullock, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3150−3155.

(17) Chojnowski, J.; Fortuniak, W.; Stańczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776−7781.

(18) Chojnowski, J.; Wilczek, L.; Fortuniak, W. *J. Organomet. Chem.* **1977**, *135*, 13−22.

(19) McDonough, L. M. Ph.D. Thesis, University of Washington, Seattle, WA, 1960.

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to the evaluation of a quantitative relationship between the structure and the reactivity of hydride donors and hydride acceptors.[15,16,19,22,26−36]

Preparative Investigations. Solutions of the benzhydrylium ions $1a^+$−$1d^+$ in dichloromethane were generated by mixing the corresponding benzhydryl chlorides **1**-Cl and Lewis acids (BCl_3, $TiCl_4$, or trimethylsilyl triflate). Hydride transfer occurred when these carbocations were mixed with the hydrocarbons **2**−**12** (Table 1) as shown in Scheme 2. Whereas the diarylmethanes (**1a**−**1d**)-H could be isolated in 81−99% yield in all instances, the identification of the oxidation products was not always possible.

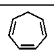
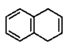
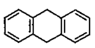
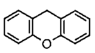
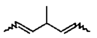
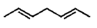
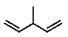
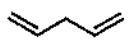
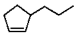
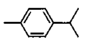
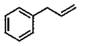
While the tropylium ion 2^+ could be directly identified as the oxidation product of **2** by ^1H NMR spectroscopy, the generation of benzene, naphthalene, and anthracene from **3**, **4**, and **5**, respectively, was proven by gas chromatographic analysis of the reaction mixtures after aqueous workup. Oxidation of **6** gave the xanthylium ion 6^+, the hydrolysis product of which (9-xanthenol) was identified by ^1H NMR spectroscopy. The carbocations 7^+−12^+ generated from **7**−**12** gave complex consecutive reactions, and we have not been able to isolate the resulting products.[37]

While products arising from electrophilic attack of the benzhydrylium ions at the double bonds of **2**−**12** could not be detected, C−C bond formation as well as hydride transfer took place in the reaction of $1d^+$ with allylbenzene **13** (Scheme 3). The analogous reaction of $1d^+$ with 4-allyltoluene led to a slight increase in the yield of the hydride transfer product (at −78 °C, 16% **1d**-H, determined by ^1H NMR).

Kinetic Investigations. As indicated in Scheme 2, the reactions of the benzhydrylium ions 1^+ with the hydride donors **2**−**12** occur with decolorization of the solutions, and it was possible to follow the kinetics with the workstation described previously.[38]

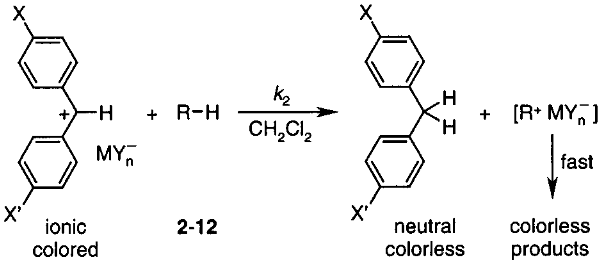
The second-order rate constants listed in Table 1 are those directly measured or extrapolated from the Eyring equation and are not corrected for statistical factors. Because in reactions of carbocations with symmetrical π-systems the statistical corrections depend on the assumed nature of the transition states (symmetrical or unsymmetrical), we generally omit statistical corrections to avoid ambiguity.

Table 1. Second-Order Rate Constants (CH_2Cl_2, 20 °C) and Eyring Parameters for Hydride Abstractions by Benzhydrylium Ions

Hydride Donor		Hydride Acceptor	k_2, L mol^{-1} s^{-1}	$\Delta_rH°$(AM1)[a], kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
	**2**	$1a^+$	3.18	−29.5	39.3 ± 1.2	−101 ± 4
	**3**	$1a^+$	1.22	40.8	38.9 ± 1.1	−110 ± 4
		$1b^+$	3.47×10^1	29.5	30.7 ± 0.5	−111 ± 2
		$1c^+$	1.40×10^2	21.5	25.8 ± 0.7	−116 ± 3
	**4**	$1a^+$	8.32×10^{-1}	26.8	–	–
		$1c^+$	1.36×10^2	7.5	31.4 ± 0.5	−96.7 ± 2.0
		$1d^+$	4.65×10^3	1.4	29.5 ± 1.2	−74.0 ± 5.5
	**5**	$1a^+$	1.46×10^{-1}	15.8	–	–
		$1c^+$	1.85×10^1	−3.5	43.1 ± 0.7	−73.5 ± 2.5
		$1d^+$	3.01×10^2	−9.6	33.3 ± 1.5	−83.6 ± 6.3
	**6**	$1a^+$	4.18	−21.6	–	–
	**7**[b]	$1d^+$	(6.47×10^2)	–	(17.5 ± 0.4)	(−132 ± 2)
	**8**	$1b^+$	4.90	22.1	32.4 ± 1.2	−121 ± 4
		$1c^+$	2.61×10^1	14.1	30.7 ± 0.6	−113 ± 2
		$1d^+$	6.88×10^2	8.0	25.2 ± 0.6	−105 ± 3
	**9**	$1d^+$	3.39	29.8	30.2 ± 0.9	−132 ± 4
	**10**	$1d^+$	4.13	52.9	34.7 ± 1.3	−115 ± 5
	**11**	$1a^+$	1.43×10^{-1}	50.0	–	–
		$1c^+$	1.63×10^1	30.7	32.0 ± 0.4	−112 ± 2
		$1d^+$	3.65×10^2	24.6	24.3 ± 0.9	−113 ± 4
	**12**	$1d^+$	6.43	5.8	41.6 ± 0.8	−87.4 ± 3.5
	**13**	$1d^+$	3.33×10^{-1} [c]	13.0	–	–

[a] $\Delta_rH°$ for Scheme 2; the AM1 gas-phase calculations were carried out with Gaussian 98 software (ref 39). [b] Mixture of (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-isomers (isomeric ratio = 8/5/1). Because of the eventual change of the isomer ratio during the reaction, the rate constants and activation parameters should be interpreted with caution. [c] Calculated from k_{exp} = 1.11 L mol^{-1} s^{-1} by assuming 30% hydride transfer.

Scheme 2



$1a^+$, X = X' = OMe **1a**-H
$1b^+$, X = OMe, X' = Me **1b**-H
$1c^+$, X = OMe, X' = H **1c**-H
$1d^+$, X = X' = Me **1d**-H
$1e^+$, X = X' = H **1e**-H

As shown in Table 2, the second-order rate constants are almost independent of the nature of the negative counterions, as previously observed for other reactions of carbocations with neutral nucleophiles.[2,38] The neglect of the counterions in the listing of Table 1 is thus justified. The reasons for this phenomenon have been discussed for related reactions.[38,40−42]

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(20) (a) Adolph, S.; Spange, S.; Zimmermann, Y. *J. Phys. Chem. B* **2000**, *104*, 6429−6438. (b) Spange, S.; Eismann, U. *Macromol. Chem. Phys.* **2001**, *202*, 900−905.
(21) Washburne, S. S.; Simolike, J. B. *J. Organomet. Chem.* **1974**, *81*, 41−44.
(22) Uglova, E. V.; Makhaev, V. D.; Reutov, O. A. *J. Org. Chem. USSR (Engl. Transl.)* **1975**, *11*, 1−4; *Zh. Org. Khim.* **1975**, *11*, 3−7.
(23) Panayotov, I. M.; Manolova, N. E.; Velichkova, R. S. *Polym. Bull.* **1981**, *4*, 653−660.
(24) Kabir-ud-Din; Plesch, P. H. *J. Chem. Soc., Perkin Trans. 2* **1978**, 937−938.
(25) Jedlinski, Z.; Lukaszczyk, J.; Dudek, J.; Gibas, M. *Macromolecules* **1976**, *9*, 622−625.
(26) Müller, P.; Joly, D. *Helv. Chim. Acta* **1983**, *66*, 1110−1118.
(27) Funke, M. A.; Mayr, H. *Chem.-Eur. J.* **1997**, *3*, 1214−1222.
(28) Bethell, D.; Hare, G. J.; Kearney, P. A. *J. Chem. Soc., Perkin Trans. 2* **1981**, 684−690.
(29) For a preliminary report on some of the results in this article, see: Mayr, H.; Roth, M.; Lang, G. In *Cationic Polymerization, Fundamentals, and Applications*; Faust, R., Shaffer, T. D., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1997; Vol. 665, pp 25−40.
(30) Sarker, N.; Bruno, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 2174−2180.
(31) Lee, I.-S. H.; Ostović, D.; Kreevoy, M. *J. Am. Chem. Soc.* **1988**, *110*, 3989−3993.
(32) Kreevoy, M. M.; Ostović, D.; Lee, I.-S. H.; Binder, D. A.; King, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 524−530.
(33) Kim, D.; Lee, I.-S. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 1889−1894.
(34) Kreevoy, M. M.; Kotchevar, A. T. *J. Am. Chem. Soc.* **1990**, *112*, 3579−3583.
(35) Kim, Y.; Truhlar, D. G.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 7837−7847.
(36) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1997**, *119*, 2722−2728.
(37) The reaction of **12** with the *tert*-amyl cation in sulfuric acid was reported to yield 1,1,3,5-tetramethyl-3-(*p*-methylphenyl)indane: Ipatieff, V. N.; Pines, H.; Olberg, R. C. *J. Am. Chem. Soc.* **1948**, *70*, 2123−2128.
(38) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446−4454.

Scheme 3

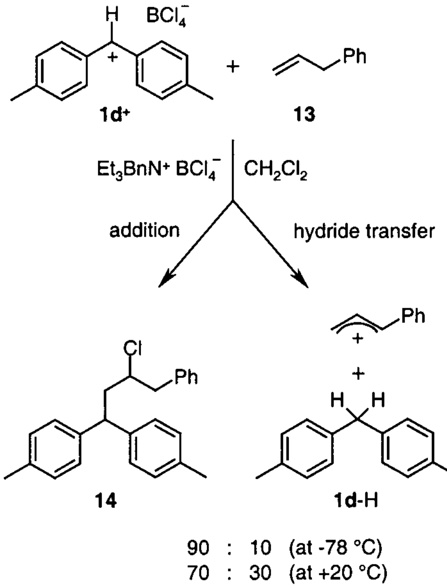


Table 2. Counterion Dependence of the Rate Constants of the Reactions of Benzhydrylium Salts with Hydride Donors (in CH_2Cl_2)

hydride donor	**1**-MY$_n$	*T*, °C	k_2, L mol^{-1} s^{-1}
1,4-cyclohexadiene (**3**)	**1a**-BCl_4	20	1.19
	1a-OTf	20	1.12
p-cymene (**12**)	**1d**-BCl_4	−30	1.32×10^{-1}
	1d-$TiCl_5$	−30	1.25×10^{-1}
	1d-$GaCl_4$	−30	1.73×10^{-1}

The independence of the observed rate constants on the nature of MY_n^- furthermore reveals hydride transfer as the rate-determining step of the reaction sequence outlined in Scheme 2. In the case of a reversible hydride transfer, the rate of decomposition of $R^+MY_n^-$, which must involve the complex counterion, would have an influence on the overall rate.

Previously we have argued that solvent polarity has only a small influence on the rates of the reactions of carbocations with uncharged nucleophiles, since charge is neither destroyed nor created in the rate-determining step.[2,43] The same arguments can now be used to explain why the reaction of the bis(*p*-anisyl)-carbenium ion **1a**$^+$ with 1,4-cyclohexadiene **3** is only slightly affected by solvent polarity (Scheme 4).

Scheme 4

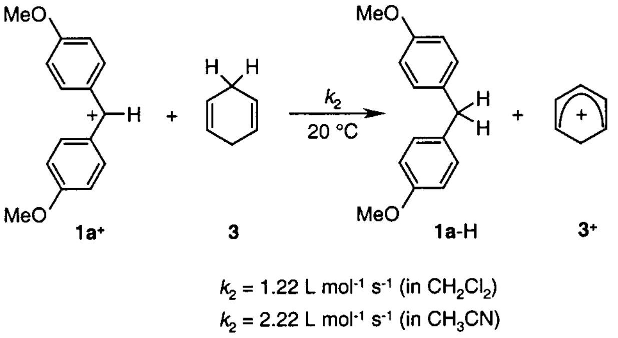
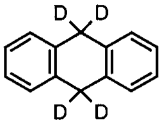


Table 3. Kinetic Isotope Effects for the Reactions of Benzhydrylium Ions **1**$^+$ with 9,10-Dihydroanthracenes **5** (k_H) and **5-D$_4$** (k_D)[a]

1$^+$	k_H, L mol^{-1} s^{-1}	k_D, L mol^{-1} s^{-1}	k_H/k_D
1a$^+$	1.46×10^{-1}[b]	3.70×10^{-2}	3.9
1a$^+$	competition experiment[c]		3.9
1c$^+$	1.85×10^{1}[b]	4.19	4.4
1d$^+$	3.01×10^{2}[b]	7.60×10^{1}	4.0
1e$^+$	competition experiment[c]		3.0

[a] In dichloromethane at 20 °C. [b] From Table 1. [c] Details are given in Table 8.

Kinetic isotope effects have been determined for the reactions of benzhydrylium ions with 9,10-dihydroanthracene **5**. While k_H/k_D for the reactions of **1a**$^+$, **1c**$^+$, and **1d**$^+$ with **5** and its deuterated analogue **5-D$_4$** could be obtained from the ratio of the directly measured rate constants (Table 3), the corresponding isotope effect for the reaction with the unsubstituted benzhydrylium ion **1e**$^+$ has only been derived from a competition experiment, since this reaction is too fast to be followed directly with our kinetic methods. The internal consistency of these two methods is shown by the fact that direct rate measurements and competition experiments gave the same ratio k_H/k_D for the reaction of **1a**$^+$ with **5** and **5-D$_4$** (Table 3).



5-D$_4$

Discussion

Benzhydryl cations have recently been recommended as reference electrophiles for comparing reactivities of a wide variety of nucleophiles based on eq 1.[5] An analogous procedure shall now be used to compare the hydride donating abilities of **2**−**13**.

$$\log k(20\ °\mathrm{C}) = s(N + E) \qquad (1)$$

where *E* is the electrophilicity parameter, *N* is the nucleophilicity parameter, and *s* is the nucleophile-dependent slope parameter.

Figures 1 and 2 show that the rate constants of the reactions of hydride donors with benzhydrylium ions **1**$^+$ correlate linearly with the electrophilicity parameters *E* of these cations which have been derived from the reactions of **1**$^+$ with π-systems.[5] From the slope (*s*) and the intercept (*sN*) of these correlations, the *N* and *s* parameters for the hydride donors **3**, **4**, **5**, **8**, and **11** can be calculated (Table 4).

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(39) (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. G.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(40) (a) Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.* **1992**, *114*, 3060−3066. (b) Mayr, H.; Basso, N. *Angew. Chem.* **1992**, *104*, 1103−1105; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1046−1048.

(41) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954−4961.

(42) Burfeindt, J.; Patz, M.; Müller, M.; Mayr, H. *J. Am. Chem. Soc.* **1998**, *120*, 3629−3634.

(43) (a) Mayr, H. *Angew. Chem.* **1990**, *102*, 1415−1428; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1371−1384. (b) Mayr, H. In *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 51−136.

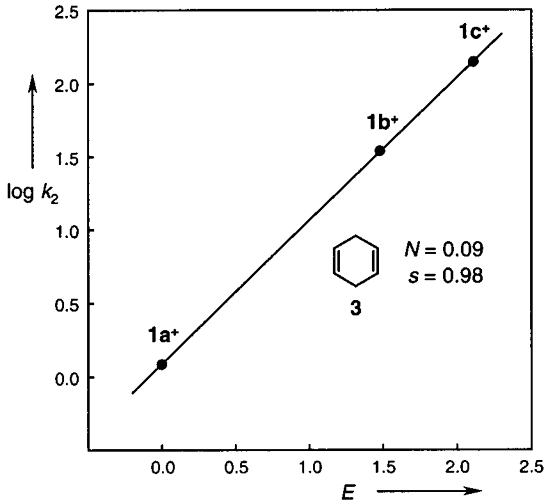

Figure 1. Determination of the nucleophilicity of 1,4-cyclohexadiene **3** from a plot of log k_2 vs E of the benzhydrylium ions $\mathbf{1}^+$ (CH_2Cl_2, 20 °C).

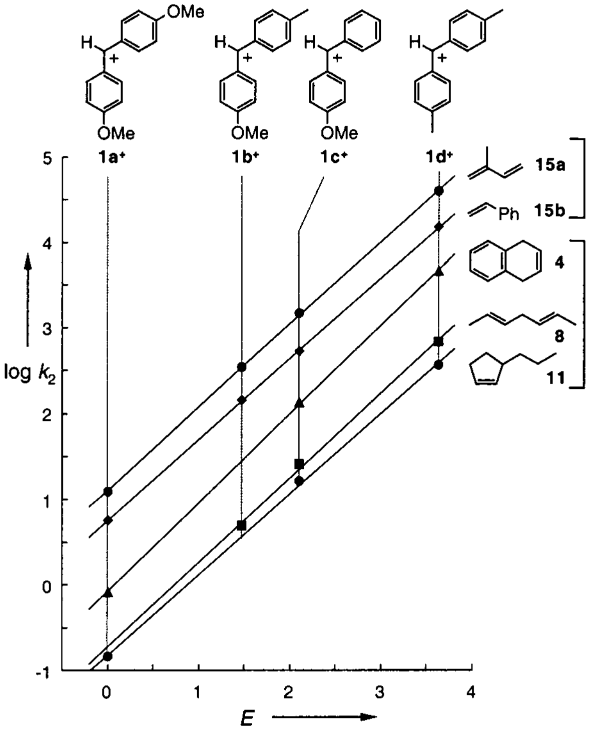

Figure 2. Comparison of the reactions of benzhydrylium ions $\mathbf{1}^+$ with hydride donors and π-nucleophiles (CH_2Cl_2, 20 °C).

The similarity of the slope parameters s implies that a variation of the electrophiles affects the rates of the reactions of different hydride donors to similar extents; that is, the relative reactivities of the hydride donors appear to be almost independent of the nature of the hydride abstractor. In accord with these findings, the kinetic isotope effect **5**/**5-D$_4$** was also found to be almost constant ($k_H/k_D = 4$, Table 3), indicating that **5** and **5-D$_4$** would also give rise to almost parallel correlation lines in Figure 2. The magnitude of k_H/k_D indicates rate-determining cleavage of the CH bond.[44]

Assuming that the averaged slope ($s = 0.97$) also holds for the other hydride donors investigated in this work (Table 1), it is possible to estimate N-parameters on the basis of eq 1 also for those hydride donors, which were studied with respect to only a single carbocation. A semiquantitative comparison of relative hydride activities can now be based on the reactivity parameters N given in Table 4.

Table 4. Nucleophilicity Parameters for Hydride Donors

hydride donor	N	s
cycloheptatriene (**2**)	0.52	(0.97)[a]
1,4-cyclohexadiene (**3**)	0.09	0.98
1,4-dihydronaphthalene (**4**)	−0.07	1.03
9,10-dihydroanthracene (**5**)	−0.86	0.92
xanthene (**6**)	0.64	(0.97)[a]
4-methyl-2,5-heptadiene[b] (**7**)	−0.73	(0.97)[a]
(*E*,*E*)-2,5-heptadiene (**8**)	−0.74	0.99
3-methyl-1,4-pentadiene (**9**)	−3.08	(0.97)[a]
1,4-pentadiene (**10**)	−2.99	(0.97)[a]
3-propylcyclopentene (**11**)	−0.88	0.94
p-cymene (**12**)	−2.80	(0.97)[a]
allylbenzene (**13**)	−4.12[c]	(0.97)[a]

[a] Values in parentheses indicate that $s = 0.97$ (average value) was assumed when hydride transfer has only been studied to a single carbocation. [b] Mixture of (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-isomers (isomeric ratio = 8/5/1). [c] Hydride reactivity; N(addition) = −3.74.

Remarkably, the slopes for the reactions of the hydride donors are almost identical to those for π-nucleophiles with terminal double bonds (Figure 2); that is, in both reaction series the rate constants are similarly affected by variations of the electrophilicities of the carbocations.

3-Propylcyclopentene (**11**), for example, like styrene (**15b**), reacts 10^3 times faster with the bis(p-tolyl)carbenium ion $\mathbf{1d}^+$ than with the bis(p-anisyl)carbenium ion $\mathbf{1a}^+$; that is, in hydride abstractions such as in C−C bond-forming reactions, two-thirds of the change in reaction enthalpy caused by variation of the electrophile ($\Delta\Delta_rH°$, Table 1) is reflected as $\Delta\Delta G^\ddagger$(20 °C). Consequently, the relative reactivities of π-nucleophiles and hydride donors are almost independent of the nature of the benzhydrylium ions. Figure 2, therefore, not only provides a comparison of reactivities of different hydride donors with each other, but also a direct comparison between π- and hydride reactivities, which is inaccessible by intuition.

Comparison of **7** with **9** and of **8** with **10** shows an increase of reactivity due to the two extra methyl groups by approximately a factor of 100. This ratio can be explained by the stabilization of the pentadienyl cations generated from **7** and **8** by two terminal methyl groups. From $\Delta\Delta_rH°$ of the reaction of $\mathbf{1d}^+$ with **8** and **10** (Table 1), one derives a difference in driving force of 45 kJ mol^{-1}, indicating that one-fourth of this effect is found in $\Delta\Delta G^\ddagger$(20 °C).

Since one-third of the positive charge is formally localized at the central position of the dienylium ion, one might also expect **7** to be more reactive than **8**, and diene **9** to be more reactive than **10**. The surprising observation that methyl groups in the central position of this system have almost no influence on reactivity (Tables 1 and 4) is partially due to a compensation of enthalpic and entropic effects (Table 1). As expected, the enthalpy of activation ($\Delta H^\ddagger$) is smaller for the abstraction of the tertiary hydrogen from **7** and **9** than for the abstraction of the secondary hydrogen from **8** and **10**, respectively. However, the abstraction of the tertiary hydrogen from **7** and **9** proceeds with a more negative entropy of activation ($\Delta S^\ddagger$). As a consequence, the relative reactivities **7**/**8** and **9**/**10** decrease with

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(44) Kinetic isotope effects of comparable size have been reported for analogous hydride transfer reactions: (a) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **2001**, *123*, 7492−7496. (b) Stewart, R.; Toone, T. W. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1243−1248. (c) Reference 6. (d) Reference 28.

Table 5. Relative Hydride Reactivities toward Different Hydride Abstractors

hydride donor	$\mathbf{1a}^+$	Ph_3C^+	DDQ[a]
cycloheptatriene (**2**)	2528[b]	9538[c]	6907[d]
1,4-cyclohexadiene (**3**)	970[b]	769[c]	1856[d]
3-methyl-1,4-pentadiene (**9**)	0.82[e]		4[d]
1,4-pentadiene (**10**)	1[e]	1[c]	1[d]

[a] DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone. [b] In dichloromethane at 20 °C, this work. [c] In acetonitrile at 25 °C, from ref 46. [d] In acetic acid at 25 °C, from ref 47. [e] Calculated from eq 1 with $E(\mathbf{1a}^+) = 0.00$.

Table 6. Relative Rate Constants for the Reactions of Dihydroarenes with Different Hydride Abstractors

	1,4-cyclohexadiene (**3**)	1,4-dihydronaphthalene (**4**)	9,10-dihydroanthracene (**5**)
k_{rel} ($\mathbf{1a}^+$)	8.4[a]	5.7[a]	1.0[a]
k_{rel} (Ph_3C^+)	67[b]	7.8[b]	1.0[b]
k_{rel} (BQ[c])	6.7[d]	3.8[d]	1.0[d]
	9.1[e]	3.9[e]	1.0[e]
k_{rel} (DDQ[f])	1.6[g]	3.8[g]	1.0[g]
	1.0[h]	2.9[h]	1.0[h]

[a] In dichloromethane at 20 °C, this work (see Table 1). [b] In acetonitrile at 25 °C, from ref 26. [c] BQ = benzoquinone. [d] In 1,4-dioxane at 80 °C, from ref 53. [e] In anisole at 60 °C, from ref 26. [f] DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone. [g] In acetic acid at 25 °C, from ref 26. [h] In acetic acid at 25 °C, from ref 50.

increasing temperature. However, only a small fraction (1/5) of the calculated difference in reaction enthalpy caused by variation of the hydride donor is found as $\Delta\Delta H^{\ddagger}$ (cf. reactions of $\mathbf{1d}^+$ with **9** and **10**, Table 1).

1,4-Cyclohexadiene **3**, which produces a cyclic pentadienyl cation in which the methylene group connects both termini, is approximately seven times more reactive than its acyclic analogue **8** in contrast to the relative order of $\Delta_r H°$ (Table 1) which does not indicate an extra stabilization of the benzenium ion.[45] It is remarkable that cycloheptatriene **2** is only slightly more reactive than 1,4-cyclohexadiene **3** (ca. a factor of 3) or 2,5-heptadiene **8** (ca. a factor of 18), though hydride abstraction from **2** yields the highly stabilized aromatic tropylium ion which is considerably more exothermic than the formation of $\mathbf{3}^+$ or $\mathbf{8}^+$ (Table 1). The astonishingly small preference of hydride abstraction from cycloheptatriene **2** as compared to that of other bisallylic hydrides has previously been observed with other hydride acceptors (Table 5). The values of k_{rel} in Table 5 again confirm that the *relative rates* of hydride abstraction depend little on the electrophile.

Related orders of hydride abstraction rates from the dihydroarenes **3**, **4**, and **5** (Tables 1 and 4) have also been found in their reactions with other hydride acceptors (Table 6). It should be noted, however, that for the reactions of dihydroarenes with quinones the possibility of concerted didehydrogenation with direct formation of arenes has been discussed.[26,46−52]

The similarities of the slopes for the hydride donors **8** and **11** on one side and the dihydroarenes **3**−**5** on the other side indicate the operation of analogous reaction mechanisms and thus provide an argument against concerted didehydrogenation of **3**−**5** under the conditions of this work.

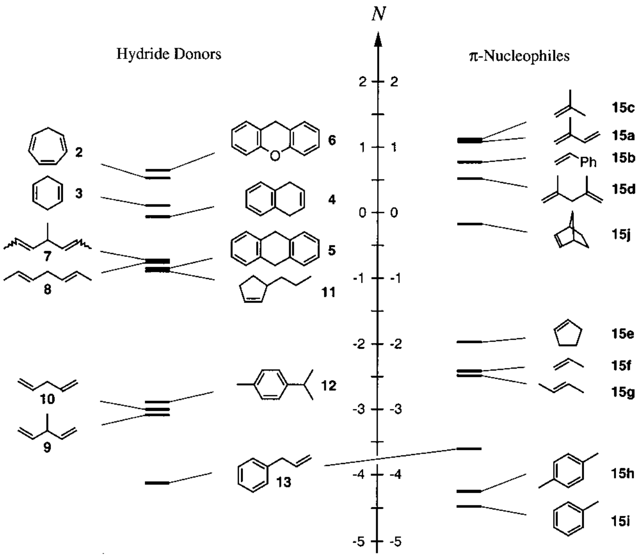

Figure 3. Comparison of the reactivities of hydride donors and π-nucleophiles toward carbenium ions.

In the discussion of Figure 2, we had already mentioned that the similarities of the slopes for π-nucleophiles and hydride donors provide a direct comparison of the two classes of compounds. Figure 3 now answers the title question on the preferred reaction pathways by listing compounds which undergo hydride transfer on the left and compounds which undergo electrophilic alkylation on the right.

To draw general conclusions from the information given in Figure 3, let us first compare the reactions of the 1,4-dienes **7**−**10** and **15d** with benzhydryl cations. While **15d** is attacked at the double bond to give a tertiary carbenium ion,[54a] compounds **7**−**10** do not react analogously because now electrophilic addition to the π-system would produce secondary carbenium ions (Scheme 5).

For these hydrocarbons, hydride transfer with formation of pentadienylium ions is faster. The corresponding hydride abstraction from **15d**, however, would yield a pentadienyl cation with the methyl groups located at the noncharged 2- and 4-positions of the π-system. The stabilization of the 2,4-dimethylpentadienyl cation is comparable to that of the unsubstituted pentadienyl cation, and for that reason the rate of hydride abstraction from **15d** can be expected to be similar to that of **10** ($N = -2.99$), that is, considerably lower than its actually observed π-reactivity ($N = 0.54$).[54]

Figure 3 shows that the π-nucleophiles isoprene (**15a**), styrene (**15b**), and isobutylene (**15c**) are more reactive than the most active hydride donors of this series. For that reason, one can conclude that electrophilic alkylations of nonaromatic π-systems are generally preferred over hydride transfer processes when the electrophilic attack at the double bond gives rise to the formation of tertiary or better stabilized carbocations.

The π-nucleophiles **15e**−**g**, which give secondary carbenium ions by electrophilic attack at the double bond, are positioned

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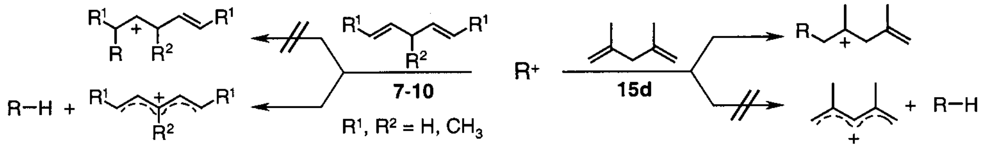
(45) Sorensen, T. S. *J. Am. Chem. Soc.* **1969**, *91*, 6398−6403.
(46) Müller, P. *Helv. Chim. Acta* **1973**, *56*, 1243−1251.
(47) Stoos, F.; Roček, J. *J. Am. Chem. Soc.* **1972**, *94*, 2719−2723.
(48) Müller, P.; Roček, J. *J. Am. Chem. Soc.* **1972**, *94*, 2716−2719.
(49) Müller, P.; Joly, D.; Mermoud, F. *Helv. Chim. Acta* **1984**, *67*, 105−112.
(50) Thummel, R. P.; Cravey, W. E.; Cantu, D. B. *J. Org. Chem.* **1980**, *45*, 1633−1637.
(51) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415−2434.
(52) Brock, M.; Hintze, H.; Heesing, A. *Chem. Ber.* **1986**, *119*, 3727−3736.
(53) Braude, E. A.; Jackman, L. M.; Linstead, R. P. *J. Chem. Soc.* **1954**, 3564−3568.
(54) (a) Irrgang, B.; Mayr, H. *Tetrahedron* **1991**, *47*, 219−228. (b) The nucleophilicity parameter *N* of **15d** was calculated with the assumption $s(\mathbf{15d}) = 1.0$.

Scheme 5



between the dienes **9**, **10** and **7**, **8** in Figure 3. The question arises why **9** and **10** undergo hydride transfer and do not behave as π-nucleophiles though their hydride reactivity is lower than the π-nucleophilicity of propene and 2-butene.

The comparison of **15d** and isobutylene (**15c**) shows that the inductive effect of the second double bond reduces the π-nucleophilicity by a factor of 4. Analogously, one would expect the π-reactivity of **9** and **10** to be lower than that of **15f**. However, the deactivation by the second double bond must be even larger in these systems to account for the observation that these dienes do not act as π-nucleophiles.

The significant reduction of the π-nucleophilicity by a second π-system can also be seen in the comparison of propene (**15f**) with allylbenzene (**13**), which shows ambient reactivity and behaves as a π-nucleophile and as a hydride donor. From the partial rate factors one can derive that **13** is an 18-fold weaker π-nucleophile than propene (Figure 3, right) and a 13-fold weaker hydride donor than **10** (Figure 3, left). Since phenyl is usually more efficient in stabilizing carbocations than vinyl, the comparison of **10** with **13** ($\Delta\Delta_r H° = 40$ kJ mol^{-1}, Table 1) again indicates that hydride transfer rates are not predominantly controlled by the stabilization of the carbocations produced during this reaction.

Careful analysis of the products obtained from the reaction of cyclopentene **15e** with **1d**$^+$ reveals the formation of 2% of **1d**-H by hydride transfer;[55] that is, the hydride reactivity of **15e** is around $N \approx -3.6$. The propyl group in **11** can, therefore, be derived to raise the hydride reactivity of cyclopentene by three units of *N*, surprising in view of the small methyl effect in the comparison of **9** with **10** and of **7** with **8** (see above).

The acceleration of hydride transfer by α-methyl groups can also be seen in the comparison of *p*-xylene (**15h**) with *p*-cymene (**12**). Because hydride transfer was not accompanying the Friedel−Crafts reactions of benzhydryl cations with **15h**,[56] the hydride reactivity of **15h** must be below $N < -6$ (assuming a detection limit of 1% for the hydride transfer products). The exclusive reaction of **12** as a hydride donor, therefore, implies that the two extra methyl groups in **12** (*i*Pr instead of Me) raise the hydride reactivity by more than 3−4 orders of magnitude.

In previous work, it has been demonstrated that linear free enthalpy relationships as shown in Figure 2 hold for numerous classes of electrophiles but fail for systems with strong steric demand.[2−5] Because of this restriction, the relative hydride and π-reactivities shown in Figure 3 will not hold for reactions with tritylium ions. Since front strain retards the reactions of tritylium ions with π-systems to a greater extent than the corresponding reactions with hydride donors, one can expect hydride abstractions by tritylium ions also from those hydrocarbons which are indicated to be slightly better π- than hydride donors by Figure 3.

Conclusion

The small alkyl effects and the unusual substituent effects (phenyl < vinyl) indicate that hydride abstractions, unlike the related S_N1 reactions, are not predominantly controlled by the stabilization of the carbocations generated during hydride transfer. One reason is the small range of hydride reactivity covered by hydride donors.

The *N*-scale for the hydride donors in Figure 3 extends over only five units, corresponding to $\Delta\Delta G^{\ddagger}(20\ °C) = 28$ kJ mol^{-1}, though the stabilities of $\mathbf{2}^+{-}\mathbf{13}^+$ differ dramatically in the gas phase ($\Delta\Delta_r H°$, Table 1) as well as in solution. While tropylium chloride is ionic in polar organic solvents,[57] barriers of 87 and 82 kJ mol^{-1} have to be overcome in the S_N1 solvolysis reactions of *p*-methylcumyl chloride (90% acetone, 25 °C)[58] and 1-phenylallyl chloride (96% ethanol, 30 °C)[59] to give $\mathbf{12}^+$ and $\mathbf{13}^+$, respectively. This comparison shows that hydride transfer rates are much less affected by variation of the substituents in the hydride donor than analogous S_N1 reactions, and it is not surprising that the small differences in reactivity are due to a manifold of factors which are difficult to assign. In the succeeding article,[60] we will analyze the reason for the small size of the substituent effects in detail.

For practical applications, the small magnitude of the substituent effects on the reactivity of hydride donors has an interesting consequence. Since most typical bisallylic and allylic hydride donors can be expected to possess *N*-values between −5 and 0, one can predict that hydride abstractions do not occur whenever 1,1-dialkylated or higher alkylated ethylenes, styrenes, or 1,3-dienes, that is, structural units with a π-reactivity of $N > 0$, are present. Hydride transfer processes may become dominant, however, in reactions with monoalkylated or 1,2-dialkylated ethylenes since the π-reactivities of these compounds are of the same order of magnitude ($-3.5 < N < -2$). Competing hydride transfer reactions, therefore, may account for the observation that aliphatic Friedel−Crafts type reactions can successfully be performed with 1,1-dialkylated and higher alkylated ethylenes, as well as with styrenes, 1,3-dienes, and related compounds,[43] but tend to give side reactions with monoalkylated and 1,2-dialkylated compounds.[61]

Experimental Section

General Considerations. All reactions were carried out under dry, oxygen-free nitrogen. Dichloromethane (Merck, p.a.) was stirred over

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(55) In dichloromethane at −78 °C; boron trichloride was used for the ionization of **1d**-Cl. The hydride transfer product **1d**-H (t_R 3.6 min) was identified by HPLC analysis of the crude product (column, Nucleosil RP-C_{18} 100/7 μm; eluent, acetonitrile:water = 95:5; flow rate, 1.0 mL/min).

(56) Mayr, H.; Bartl, J.; Hagen, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1613−1615.

(57) Kessler, H.; Feigel, M. *Acc. Chem. Res.* **1982**, *15*, 2−8. See also: Harmon, K. M. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1973; Vol. 4, pp 1579−1641.

(58) Brown, H. C.; Brady, J. D.; Grayson, M.; Bonner, W. H. *J. Am. Chem. Soc.* **1957**, *79*, 1897−1903.

(59) Valkanas, G.; Waight, E. S.; Weinstock, M. *J. Chem. Soc.* **1963**, 4248−4256.

(60) Würthwein, E.-U.; Lang, G.; Schappele, L. H.; Mayr, H. *J. Am. Chem. Soc.* **2002**, *124*, 4076−4092.

(61) (a) Mayr, H.; Klein, H.; Kolberg, G. *Chem. Ber.* **1984**, *117*, 2555−2579. (b) Mayr, H.; Will, E.; Heigl, U. W.; Schade, C. *Tetrahedron* **1986**, *42*, 2519−2522.

sulfuric acid for 3 days, then washed with water, aqueous $NaHCO_3$ solution, and again with water, dried over $CaCl_2$, and freshly distilled from CaH_2 prior to use. Acetonitrile was distilled from P_2O_5, and diethyl ether was distilled from sodium/benzophenone before use. Titanium tetrachloride (Fluka) was distilled and stored under nitrogen.

1,4-Dihydronaphthalene (**4**),[62] (*E*,*E*)-2,5-heptadiene (**8**),[63] 4-allyltoluene,[64] benzhydryl chlorides **1**-Cl,[65] and the tetrafluoroborate salt **1a**-BF_4[66] were prepared as described in the literature. Other hydride donors are commercially available; 3-methyl-1,4-pentadiene (**9**), 1,4-pentadiene (**10**), allylbenzene (**13**), and cyclopentene (**15e**) were used without further purification, whereas 1,4-cyclohexadiene (**3**) and *p*-cymene (**12**) were distilled before use. Cycloheptatriene (**2**) was distilled from $LiAlH_4$, 9,10-dihydroanthracene (**5**) was recrystallized from dry ethanol, and xanthene (**6**) was sublimed before use. Traces of moisture in the commercial samples get deactivated by the excess of Lewis acid used for the ionization of the benzhydryl chlorides.

^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H 0.00) or to the solvent signal (δ_C 77.0), respectively. DEPT-135 experiments were used to obtain information about the multiplicities of ^{13}C resonances.

The reactions of the colored benzhydrylium ions $\mathbf{1}^+$ with the hydride donors gave rise to colorless products, and the rates of the reactions were determined photometrically (Schölly KGS III photometer with band-pass filters by Corion) as described in ref 38. The temperature of solutions during the kinetics studies was maintained within ±0.2 °C by using circulating bath cryostats (water glycol bath for $T > -10$ °C, ethanol bath for $T < -10$ °C) and monitored with a thermocouple probe that was inserted into the reaction mixture.

Hydride donor concentrations (10^{-3} to 10^{-2} mol L^{-1}) at least 10 times higher than the benzhydryl cation concentrations (10^{-5} to 10^{-4} mol L^{-1}) were usually employed, resulting in pseudo-first-order kinetics with an exponential decay of the benzhydryl cation concentration. Second-order rate constants k_2 were calculated from $k_2 = k_{1\Psi}/[\text{hydride donor}]_0$. Details of the individual kinetic experiments are given in Tables S1−S26 in the Supporting Information.

9,9,10,10-Tetradeuterio-9,10-dihydroanthracene (5-D_4).[67] In a carefully dried two-necked 100-mL round-bottom flask equipped with a reflux condenser, a solution of sodium (1.70 g, 73.9 mmol) in ethanol-d_1 (60 mL, 99.5% D) was prepared under an atmosphere of dry nitrogen. After the addition of 9,10-dihydroanthracene **5** (3.00 g, 16.6 mmol), the mixture was heated to reflux for 10 h and then allowed to cool to ambient temperature. Excess ethanol-d_1 was distilled off to obtain a solid residue which was hydrolyzed with D_2O (10 mL) and extracted with dichloromethane (2 × 50 mL). The combined dichloromethane phases were dried ($MgSO_4$), and the solvent was evaporated in vacuo. Kugelrohr distillation (150 °C/0.31 mbar) of the residue yielded **5-D_4** (2.96 g) as a colorless solid with a degree of deuteration of 97.5% (^1H NMR). Repetitive treatment of this sample with NaOEt/EtOD gave **5-D_4** (2.26 g, 75%) with >99% deuteration; mp 106−107 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, <0.04 H, 9-H, 10-H), 7.15−7.20, 7.25−7.30 (2 m, 2 × 4 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 35.4 (weak m, CD_2), 126.1, 127.4 (2 d, Ar), 136.6 (s, Ar).

4-Methyl-2,5-heptadiene (7). 4-Methyl-2,5-heptadiene (**7**) was obtained as a mixture of (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-isomers with an isomeric ratio of 38/48/14 (determined by GC), respectively, from 1-ethoxyprop-1-ene and trimethyl(1-methyl-2-butenyl)silane by following a procedure described for the synthesis of analogous 1,4-dienes.[68] To increase the content of the (*E*,*E*)-isomer, the mixture of 1,4-dienes was combined with 1.6 equiv of dichloroketene[69] which preferentially attacks CC double bonds with a (*Z*)-configuration. Distillation of the crude product gave a fraction (54−56 °C/150 mbar) which contained the (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-isomers in a ratio of 58/35/7 (determined by GC). NMR signals assigned to **(*E*,*E*)-7**, ^1H NMR (300 MHz, $CDCl_3$): δ 0.97 (d, $J = 6.9$ Hz, 3 H, 4-CH_3), 1.58 (dd, $J = 4.6$ Hz, $J = 0.9$ Hz, 6 H, 1-H), 2.63−2.73 (m, 1 H, 4-H), 5.11−5.41 (m, 4 H, 2-H and 3-H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.0 (q, C-1), 20.6 (q, 4-CH_3), 39.6 (d, C-4), 123.1, 136.1 (2 d, C-2 and C-3).

Table 7. Reactions of the Hydride Donors **2**−**12** with Benzhydrylium Ions $\mathbf{1}^+$ (in CH_2Cl_2)

nucleophile	$\mathbf{1}^+$	reaction conditions	yield, %	products
2	$\mathbf{1a}^+$	−[a], 20 °C, 16 h	88	**1a**-H + $C_7H_7^+$ [b]
3	$\mathbf{1a}^+$	TMSOTf, −78 °C, 1.5 h	92	**1a**-H + benzene[c]
3	$\mathbf{1b}^+$	BCl_3, −78 °C, 5 h	98	**1b**-H
3	$\mathbf{1c}^+$	BCl_3, −78 °C, 3 h	98	**1c**-H
4	$\mathbf{1c}^+$	BCl_3, 20 °C, 2 h	81	**1c**-H + naphthalene[d]
5	$\mathbf{1a}^+$	BCl_3, 20 °C, 12 h	85	**1a**-H + anthracene[d]
6	$\mathbf{1c}^+$	BCl_3, 20 °C, 12 h	89	**1c**-H + xanthen-9-ol[d]
7	$\mathbf{1d}^+$	$TiCl_4$, 20 °C, 15 h	87	**1d**-H
8	$\mathbf{1b}^+$	BCl_3, −78 °C, 14 h	90	**1b**-H
8	$\mathbf{1c}^+$	BCl_3, −78 °C, 12 h	91	**1c**-H
8	$\mathbf{1d}^+$	$TiCl_4$, −78 °C, 4 h	96	**1d**-H
9	$\mathbf{1d}^+$	$TiCl_4$, 20 °C, 3 h	89	**1d**-H
10	$\mathbf{1d}^+$	$TiCl_4$, −78 °C, 4.5 h	98	**1d**-H[e]
11	$\mathbf{1d}^+$	$TiCl_4$, −78 °C, 3 h	81	**1d**-H[e]
12	$\mathbf{1d}^+$	$TiCl_4$, −78 °C, 3 h	99	**1d**-H

[a] The tetrafluoroborate salt of $\mathbf{1a}^+$ was used. [b] The ^1H NMR signal of the tropylium ion was detected in a sample taken from the reaction mixture before the workup. [c] Detected in a sample of the crude product by GC analysis. [d] Detected in a sample of the crude product by ^1H NMR spectroscopy. [e] HPLC analysis of a sample of the crude product revealed that only the hydride transfer product **1d**-H (t_R 3.6 min) was formed.

3-Propylcyclopentene (11).[70,71] A carefully dried two-necked 250-mL round-bottom flask equipped with a reflux condenser and a dropping funnel was filled with freshly grinded magnesium turnings (6.08 g, 250 mmol) and diethyl ether (50 mL). A solution of 1-bromopropane (30.7 g, 250 mmol) in diethyl ether (50 mL) was then added slowly to keep the reaction mixture gently boiling. After the addition was finished, the Grignard solution was heated to reflux for another 30 min, before it was cooled to 0 °C. A solution of 3-chlorocyclopentene (17.9 g, 175 mmol) in diethyl ether (50 mL) was then added dropwise within 1 h. After another 2 h of stirring at ambient temperature, the reaction mixture was carefully hydrolyzed with water (30 mL) and 6 M hydrochloric acid (30 mL). Separation of the phases, drying of the organic phase ($MgSO_4$), and evaporation of the solvent yielded the crude product which was distilled to give **11** (8.07 g, 42%) as an unpleasant smelling, colorless liquid; bp 71−73 °C/125 mbar. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88−0.93 (m, 3 H, CH_3), 1.21−1.43 (m, 5 H, 1′-H_2, 2′-H_2, and 4-H), 1.97−2.08 (m, 1 H, 4-H), 2.19−2.39 (m, 2 H, 5-H_2), 2.59−2.68 (m, 1 H, 3-H), 5.65−5.71 (m, 2 H, 1-H and 2-H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.3 (q, C-3′), 21.1 (t, C-2′), 29.9, 32.0 (2 t, C-4 and C-5), 38.5 (t, C-1′), 45.4 (d, C-3), 129.9, 135.4 (2 d, C-l and C-2).

As a byproduct, [3,3′]bicyclopent-1-enyl[72] was isolated from the residue of the distillation.

Reaction of the Hydride Donors 2−12 with Benzhydrylium Salts $\mathbf{1}^+$. General Procedure. Colored solutions of benzhydrylium salts $\mathbf{1}^+$ were produced by mixing benzhydryl chlorides **1**-Cl (2−5 mmol) and

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(62) Hückel, W.; Bretschneider, H. *Liebigs Ann. Chem.* **1939**, *540*, 157−189.
(63) Chin, S. K.; Golding, B. T.; Pierpoint, C. *J. Chem. Res. (S)* **1985**, 71; *J. Chem. Res. (M)* **1985**, 946−953.
(64) Martin, M. M.; Gleicher, G. J. *J. Am. Chem. Soc.* **1964**, *86*, 233−238.
(65) Schneider, R.; Mayr, H.; Plesch, P. H. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 1369−1374.
(66) Arnett, E. M.; Venimadhavan, S.; Amarnath, K. *J. Am. Chem. Soc.* **1992**, *114*, 5598−5602.
(67) Gerst, M. Dissertation, Universität Freiburg, 1994.
(68) Ohm, S.; Bäuml, E.; Mayr, H. *Chem. Ber.* **1991**, *124*, 2785−2790.
(69) Generated in situ from dichloroacetyl chloride and triethylamine: Montaigne, L. G. R.; Roussel, A.; Vanlierde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615−633.
(70) Crane, G.; Boord, C. E.; Henne, A. L. *J. Am. Chem. Soc.* **1945**, *67*, 1237−1239.
(71) Roth, M. Dissertation, Technische Hochschule Darmstadt, 1996.
(72) Adam, W.; Finzel, R.; Walther, B. *Chem. Ber.* **1993**, *126*, 2137−2141.

2−4 equiv of Lewis acid in dry CH_2Cl_2. Next 2−3 equiv of a solution of the nucleophile in a small amount of CH_2Cl_2 was added. The reaction mixture was stirred until the color of the reaction mixture had almost faded. For hydrolysis, aqueous NH_4OH solution (30 mL) was added. The resulting mixture was filtered through a layer of Celite. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic fractions were dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product mixture was then analyzed by ^1H NMR spectroscopy and in part by HPLC (column, Nucleosil RP-C_{18} 100/7 μm; eluent, acetonitrile:water = 95:5; flow rate, 1.0 mL/min) or GC (SE 30 column). Diarylmethanes **1**-H were separated from the crude product by Kugelrohr distillation or column chromatography (silica gel 60, *n*-hexane:ethyl acetate = 10:1).

Details and results of the preparative studies are displayed in Table 7.

Bis(4-methoxyphenyl)methane (1a-H).[73] ^1H NMR ($CDCl_3$, 300 MHz): δ 3.75 (s, 6 H), 3.85 (s, 2 H), 6.78−6.83, 7.05−7.10 (2 m, 2 × 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 40.1 (t), 55.2 (q), 113.8, 129.7 (2 d), 133.7, 157.9 (2 s).

(4-Methoxyphenyl)(4-methylphenyl)methane (1b-H). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.19 (s, 3 H), 3.62 (s, 3 H), 3.76 (s, 2 H), 6.67−6.72 (m, 2 H), 6.92−7.03 (m, 6 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 20.9 (q), 40.5 (t), 55.1 (q), 113.7, 128.6, 129.0, 129.7 (4 d), 133.4, 135.3, 138.4, 157.8 (4 s).

(4-Methoxyphenyl)phenylmethane (1c-H).[71,74,75] ^1H NMR ($CDCl_3$, 300 MHz): δ 3.74 (s, 3 H), 3.90 (s, 2 H), 6.79−6.83, 7.06−7.11 (2 m, 2 × 2 H), 7.14−7.29 (m, 5 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 41.0 (t), 55.2 (q), 113.8, 125.9, 128.4, 128.8, 129.8 (5 d), 133.2, 141.5, 157.9 (3 s).

Bis(4-methylphenyl)methane (1d-H).[73] ^1H NMR ($CDCl_3$, 300 MHz): δ 2.30 (s, 3 H), 3.89 (s, 2 H), 7.03−7.12 (m, 8 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.0 (q), 41.1 (t), 128.7, 129.1 (2 d), 135.4, 138.3 (2 s).

Reaction of 1d-BCl$_4$ with Allylbenzene (13). A solution of bis(4-methylphenyl)methyl chloride **1d**-Cl (671 mg, 2.91 mmol) and benzyltriethylammonium chloride (663 mg, 2.91 mmol) in dichloromethane (30 mL) was cooled to −78 °C. Boron trichloride gas (150 mL, 6.70 mmol) and allylbenzene **13** (400 μL, 356 mg, 3.01 mmol) were then added, and the reaction mixture was stirred for 18 h at −78 °C. For hydrolysis, aqueous NH_4OH solution (8 M, 30 mL) was added. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic fractions were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was filtered through a short column of silica gel to remove ammonium salts before it was analyzed by NMR spectroscopy and HPLC (column, Nucleosil RP-C_{18} 100/7 μm; eluent, acetonitrile:water = 95:5; flow rate, 1.0 mL/min; t_R, 3.6 min, **1d**-H; 4.4 min, **14**). In the crude product a 10:90 ratio of **1d**-H and **14** was determined by ^1H NMR spectroscopy.

The hydride transfer product **1d**-H (58 mg, 10%) was separated by Kugelrohr distillation (130−140 °C/1 × 10^{-3} mbar). The distillation residue was recrystallized from pentane to yield 1,1-bis(4-methylphenyl)-3-chloro-4-phenylbutane **14** (802 mg, 79%) as a colorless solid; mp 74−75 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.19, 2.21 (2 s, 2 × 3 H, Me), 2.12−2.22, 2.31−2.45 (2 m, 2 H, 2-H_2), 2.90−3.04 (m, 2 H, 4-H_2), 3.76−3.85 (m, 1 H, 3-H), 4.20 (dd, J = 11.1 Hz, 4.5 Hz, 1 H, Ar_2CH), 6.90−7.23 (m, 13 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.9, 21.0 (2 q, 2 × Me), 43.4, 45.2 (2 t, C-2 and C-4), 47.1 (d, C-1), 61.5 (d, C-3), 126.7, 127.4, 127.9, 128.3, 129.1, 129.3, 129.4 (7 d, Ar), 135.7, 135.9, 137.6, 139.7, 141.8 (5 s, Ar). Anal. Calcd for $C_{24}H_{25}Cl$ (348.92): C, 82.62; H, 7.22. Found: C, 82.87; H, 7.30.

Table 8. Relative Reactivities of 9,10-Dihydroanthracene (**5**) and 9,9,10,10-Tetradeuterio-9,10-dihydroanthracene (**5-D$_4$**) toward the Benzhydrylium Ions **1a**$^+$ and **1e**$^+$ (CH_2Cl_2, 20 °C)

1-Cl, g (mmol)	Lewis acid, mL (mmol)	**5**, g (mmol)	**5-D$_4$**, g (mmol)	[**1**-H]/[**1**-D]	k_H/k_D
1a-Cl, 0.127 (0.483)	BCl_3, 25 (1.12)	0.270 (1.50)	1.57 (8.50)	0.66[a]	3.9
1e-Cl, 0.115 (0.567)	$TiCl_4$, 0.20 (1.82)	0.227 (1.26)	0.314 (1.70)	1.95[b]	3.0
1e-Cl, 0.130 (0.641)	$TiCl_4$, 0.20 (1.82)	0.150 (0.832)	0.268 (1.45)	1.41[b]	3.0
1e-Cl, 0.132 (0.651)	$TiCl_4$, 0.20 (1.82)	0.215 (1.19)	0.195 (1.06)	2.79[b]	2.9

[a] Determined from the ratio of the NMR integrals at δ 3.81 (t, J = 2.1 Hz, CHD) and 3.83 (s, CH_2). [b] Determined from the ratio of the NMR integrals at δ 3.93 (t, J = 2.1 Hz, CHD) and 3.95 (s, CH_2).

Reaction of 1d-BCl$_4$ with 4-Allyltoluene. A solution of **1d**-Cl (598 mg, 2.59 mmol) and benzyltriethylammonium chloride (590 mg, 2.59 mmol) in dichloromethane (30 mL) was cooled to −78 °C. Boron trichloride gas (200 mL, 8.90 mmol) and 4-allyltoluene (397 mg, 3.00 mmol) were then added, and the reaction mixture was stirred for 18 h at −78 °C. Workup as described above for the analogous reaction of **13** yielded a 84:16 mixture of 3-chloro-1,1,4-tris(*p*-tolyl)butane and **1d**-H (determined by ^1H NMR spectroscopy) as a yellowish oil (838 mg) which was analyzed by HPLC (column, Nucleosil RP-C_{18} 100/7 μm; eluent, acetonitrile:water = 95:5; flow rate, 1.0 mL/min; t_R, 3.6 min, **1d**-H; 4.9 min, 3-chloro-1,1,4-tris(*p*-tolyl)butane). From the NMR spectra of the crude product the following signals were assigned to 3-chloro-1,1,4-tris(*p*-tolyl)butane. ^1H NMR (300 MHz, $CDCl_3$): δ 2.15, 2.17, 2.20 (3 s, 3 × 3 H, 3 × Me), 2.33−2.42 (m, 2 H, 2-H_2), 2.82−2.96 (m, 2 H, 4-H_2), 3.72−3.81 (m, 1 H, 3-H), 4.18 (dd, J = 11.1 Hz, 4.5 Hz, 1 H, Ar_2CH), 6.86−7.21 (m, 12 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.9, 21.0, 21.1 (3 q, 3 × Me), 43.4, 44.7 (2 t, C-2 and C-4), 47.1 (d, Ar_2CH), 61.7 (d, C-3), 127.4, 127.9, 129.1, 129.2 (4 d, Ar), 134.5, 135.4, 135.6, 135.9, 141.8, 144.5 (6 s, Ar).

Determination of Kinetic Isotope Effects by Competition Experiments. The benzhydryl chloride **1**-Cl and a mixture of the 9,10-dihydroanthracenes **5** and **5-D$_4$** were dissolved in dry dichloromethane (20 mL) at 20 °C. After the addition of the Lewis acid, the reaction mixture was stirred for 1 h. Aqueous NH_4OH solution was then added, and the mixture was filtered through Celite. The layers were separated, and the aqueous layer was extracted with dichloromethane. The organic fractions were combined and dried ($MgSO_4$). After the evaporation of the solvent in vacuo, the residue was analyzed by ^1H NMR spectroscopy.

In a first competition experiment, a mixture of **5** and **5-D$_4$** was reacted with **1a**$^+$ (generated from **1a**-Cl and BCl_3) to give k_H/k_D = 3.9 (Table 8),[76] in good agreement with the reactivity ratio determined from direct kinetic measurements (Table 3). With the method thus confirmed, the competition experiment **5**/**5-D$_4$** + **1e**$^+$ (generated from **1e**-Cl and $TiCl_4$) was performed. An averaged reactivity ratio of k_H/k_D = 3.0 was calculated[76] from three independent experiments (Table 8).

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Supporting Information Available: Details of the kinetic experiments (concentrations, rate constants at variable temperatures, and activation parameters) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[73] Makioka, Y.; Uebori, S.-y.; Tsuno, M.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *J. Org. Chem.* **1996**, *61*, 372−375.

[74] Akiyama, T.; Hirofuji, H.; Ozaki, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1932−1938.

[75] Nakai, Y.; Takabayashi, T.; Yamada, F. *Org. Magn. Reson.* **1980**, *13*, 94−96.

[76] Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1949**, 575−581.