eq 2. (Approximately 5–10% of excess BCl_3 was used

$$LiBH_4 + 3BCl_3 + 4Et_2O \longrightarrow 4BHCl_2:OEt_2 + LiCl \downarrow \quad (2)$$
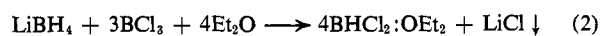
to ensure that the product was free of BH_2Cl.) The mixture was stirred for 2 hr at 0° and kept overnight in a cold room (0–5°). The solution was then decanted or filtered from precipitated lithium chloride. The excess ether was removed at room temperature with a water aspirator (30 mm) until constant weight of the contents was realized (6–8 hr). The $BHCl_2:OEt_2$ thus obtained is a clear liquid. It is not stable at room temperature for more than 2 days, but can be stored in a cold room (0–5°) for 2 or so weeks without difficulty. The reagent was analyzed by hydrolyzing aliquots—the hydrogen gas evolved gave the hydride content and the hydrochloric acid formed gave the chloride content. The preparation used contained 4–6% excess $BCl_3:OEt_2$. The neat reagent is 6.6 M in $BHCl_2:OEt_2$.

The following procedure for the synthesis of cyclopentyldichloroborane and dimethyl cyclopentylboronate is representative. A dry 300-ml round-bottom flask kept under nitrogen was charged with 100 mmol (8.8 ml) of cyclopentene, 100 mmol of BCl_3 in pentane (50 ml), and 127 ml of dry pentane. The mixture was cooled in an ice bath and 100 mmol of $BHCl_2:OEt_2$ (15.1 ml) was slowly added over a period of 15 min, while vigorously stirring the contents of the flask. The stirring was continued for 15 min at 0°. Then the reaction mixture was brought to room temperature and stirred for another 15 min. The contents of the flask were cooled to 0° and the pentane solution was siphoned into another flask through a glass tube fitted with a fritted disk under a positive pressure of nitrogen. The $BCl_3:OEt_2$ in the reaction flask was washed twice with pentane at 0°, and the washings were collected along with the main solution. The pentane was then removed using a water aspirator. Cyclopentyldichloroborane was obtained in 79% yield by distillation at 136–138° (751 mm). The purity of the product was checked by methanolysis and analysis of the dimethylboronate by pmr.

For the synthesis of dimethyl cyclopentylboronate, the above procedure was followed. After stirring at room temperature for 15 min, the reaction mixture was cooled to 0° and 50 ml of methanol was added slowly while stirring. Stirring was continued for 0.5 hr at 0°. The solvent, HCl, and $B(OCH_3)_3$ were removed using a water aspirator and the dimethyl cyclopentylboronate was distilled at 76–78° (40 mm). The product was obtained in 76% yield. The material was identified by pmr and comparison with an authentic sample.

The conventional methods for the synthesis of $RBCl_2$ are the exchange reactions of BCl_3 and BR_3 in the presence of boron hydrides at elevated temperature,[6,7] the reaction of trialkylboroxines with BCl_3,[8] and the reaction of tetraalkyltin compounds with BCl_3.[9] These are time consuming multistep syntheses and generally the overall yields are low. More seriously, the exchange

reaction often causes considerable isomerization involving migration of the boron atom.[7] The procedure reported here is much simpler and possesses the enormous advantage in that the $RBCl_2$ is obtained in pure form in pentane solution. Thus, these reagents can be used directly in pentane solution,[2] without isolation, or they can be easily isolated from such solution in the pure state.

The syntheses of trialkylboranes and dialkylboron derivatives *via* hydroboration have been previously accomplished.[1,10] The present development provides an exceptionally simple hydroboration procedure for the general synthesis of monoalkylboron derivatives. Thus, we are now in a position to synthesize tri-, di- and monoalkylboron compounds *via* hydroboration under mild conditions.

(10) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972.
(11) Graduate Assistant on Research Grant DA-31-124 ARO(D) 453, supported by the U. S. Army Research Office, Durham.

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Solvolysis of 1-Aryl-1-cyclopropyl-1-ethyl p-Nitrobenzoates. Evidence for Major Increases in Electron Supply by the Cyclopropyl Group with Increasing Electron Demand at the Cationic Center

Sir:

Increasing the electron demand at the carbonium ion center by varying the substituent on the aryl group results in major increases in rates of solvolysis of the p-nitrobenzoates of 1-aryl-1-cyclopropyl-1-ethyl as compared to the corresponding 2-aryl-3-methyl-2-butyl derivatives. This result is attributed to major increases in the electron supply by the cyclopropyl moiety, in contrast to that of the isopropyl groups, under the increasing demand by the cationic center. This result is in marked contrast to the behavior of the 2-aryl-2-*exo*-norbornyl p-nitrobenzoates, where the exo:endo rate ratios reveal no significant change in electron supply with increasing electron demand at the cationic center.

In the study of neighboring group effects, it has been postulated that the more stable the carbonium ion center, the less demand that center will make upon neighboring groups for additional stabilization through participation.[1] Gassman and Fentiman have shown that this postulate is valid for π participation in the 7-norbornenyl derivatives.[2] The ability of the π electrons in 7-aryl-7-*anti*-norbornenyl p-nitrobenzoates (I) to stabilize the developing carbonium ion center increases as a function of the electron demand of that center. Thus, the relative rate of I increases from 3.4 for p-anisyl to over 10^5 for 3,5-bis(trifluoromethyl)-phenyl in comparison to the corresponding 7-aryl-7-norbornyl derivatives (II).[2]

This postulate has never been tested for σ participation in carbon systems not containing π electrons. Therefore, we decided to examine the effect of increasing electron demand on the rates of solvolysis of the

(6) R. Köster and M. A. Grassberger, *Justus Liebigs Ann. Chem.*, **719**, 169 (1968).
(7) H. C. Brown and A. B. Levy, *J. Organometal. Chem.*, **44**, 233 (1972).
(8) P. A. McCusker, E. C. Ashby, and H. S. Makowski, *J. Amer. Chem. Soc.*, **79**, 5182 (1957).
(9) W. Gerrard, E. F. Mooney, and R. G. Rees, *J. Chem. Soc.*, 740 (1964).

(1) S. Winstein, B. K. Morse, E. Grunwald, K. C. Shreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).
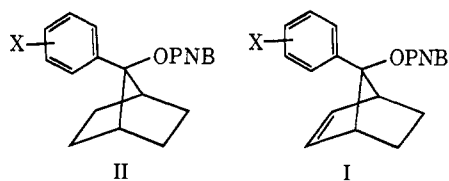(2) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2549 (1970).

X		
p-CH$_3$O	1.0	3.4
p-H	1.0	41.5
p-CF$_3$	1.0	34,500
m,m'-(CF$_3$)$_2$	1.0	255,000

2-aryl-3-methyl-2-butyl (III) and 1-aryl-1-cyclopropyl-1-ethyl p-nitrobenzoates (IV) in 80% acetone. It was observed that with increasing electron demand at the cationic center the rate of solvolysis of the cyclopropyl derivative (IV) increases enormously, as compared to the isopropyl derivative (III).[3,4] Thus, the postulate is
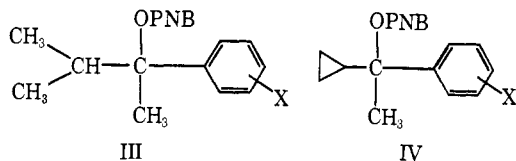
X		
p-CH$_3$O	1.0	505
p-H	1.0	25,300
p-CF$_3$	1.0	285,000
m,m'-(CF$_3$)$_2$	1.0	1,210,000

valid for electron supply from the carbon–carbon bonds of the cyclopropane ring. The data are summarized in Table I.

Table I. Rates of Solvolysis of 1-Aryl-1-cyclopropyl-1-ethyl and 2-Aryl-3-methyl-2-butyl p-Nitrobenzoates in 80% Acetone at 25.0°

Substituent[a]	System[b]	$k_1 \times 10^6$,[c] sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-CH$_3$O	III[d]	65.3[e]		
	IV[f]	33,000[g]		
p-H	III[h]	9.51 × 10^{-3}	26.7	−5.7
	IV[i]	241[e]	20.8	−5.5
p-CF$_3$	III[j]	1.36 × 10^{-5}	31.4	−2.8
	IV[k]	3.88	22.9	−6.4
m,m'-(CF$_3$)$_2$	III[l]	2.61 × 10^{-7}	34.8	0.4
	IV[m]	0.315	23.6	−9.1

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] III, 2-aryl-3-methyl-2-butyl; IV, 1-aryl-1-cyclopropyl-1-ethyl. [c] Calculated from rates at higher temperatures, except where otherwise indicated. [d] Mp 90.4–91.0° dec. [e] Rate constant measured at 25°. [f] This ester was too unstable to isolate. [g] Because of synthetic difficulties, this rate constant was obtained by extrapolation of the log k–σ^+ plot from the other derivatives. [h] Mp 75.0–76.2°. [i] Mp 76.5° dec. [j] Mp 122.7–123.6°. [k] Mp 115.8–116.1°. [l] Mp 95.6–96.3°. [m] Mp 71.3–72.3°.

(3) Rate enhancements of 100–1000 have been reported for the substitution of one cyclopropyl group for an isopropyl group: H. Hart and J. M. Sandri, J. Amer. Chem. Soc., 81, 320 (1959); H. Hart and P. A. Law, ibid., 84, 2462 (1962).

(4) The 10^6 rate enhancement for IV (X = m,m'-(CF$_3$)$_2$) is similar to the value, 5 × 10^5, estimated for a secondary cyclopropylcarbinyl cation.[5] From the relative reactivities of a bis(3,5-trifluoromethyl)phenyl and a hydrogen adjacent to a carbonium ion center,[6] a rate enhancement of about 10^9 would appear to be more appropriate for secondary cyclopropylcarbinyl systems.

(5) J. E. Baldwin and W. D. Foglesong, J. Amer. Chem. Soc., 90, 4303 (1968); also see T. Tsuji, I. Moritani, and S. Nishida, Bull. Chem. Soc. Jap., 40, 2338 (1967).

(6) H. C. Brown, S. Ikegami, and K.-T. Liu, J. Amer. Chem. Soc., 91, 5911 (1969).

The data reveal excellent linear correlations with σ^+ constants. III yields a ρ value of −4.65 (correlation coefficient 0.999), while IV yields one of −2.78 (correlation coefficient 0.999).[7] Thus, the stabilizing effect of the cyclopropyl group is a linear function of the electron demand of the incipient carbonium ion over the range of reactivity examined.

It is of major importance that application of the same tool to the evaluation of participation by the 1,6 carbon–carbon bond in 2-aryl-2-exo-norbornyl p-nitrobenzoates (VI) reveals that the relative rates with respect to the
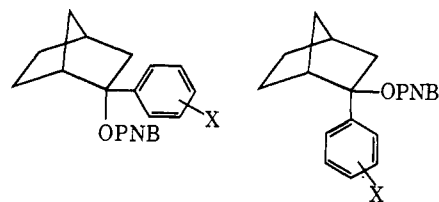
X		
p-CH$_3$O	1.0	284
p-H	1.0	143
p-CF$_3$	1.0	188

corresponding endo isomer (V) remain essentially constant as the electron demand of the cationic center is increased over the same range.[10]

Clearly, application of this tool reveals π participation in the 7-aryl-7-anti-norbornenyl system and stabilization by carbon–carbon bonds in the 1-aryl-1-cyclopropyl-1-ethyl derivatives (IV) but no participation by the 1,6 carbon–carbon bonds in the tertiary aryl norbornyl derivatives (VI).

In conclusion, neighboring group stabilization by carbon–carbon bonds in the 1-aryl-1-cyclopropyl-1-ethyl system (IV) is a linear function of the electron demand of the carbonium ion center. However, significant σ participation in the 2-aryl-2-norbornyl system is absent. Consequently, the high exo:endo rate ratio in the solvolysis of tertiary 2-norbornyl derivatives must be due to some factor other than σ participation. Steric hindrance to ionization has been suggested as an alternative explanation.[10]

(7) The ρ value for IV is lower than the ρ value of −4.2 for the benzhydryl system[8] and is close to the ρ value of −2.5 for the triarylmethyl system.[9] Thus, it appears that the cyclopropyl group in IV stabilizes the cation more than an additional phenyl group would. H. C. Brown and E. N. Peters, J. Amer. Chem. Soc., 95, 2398 (1973).

(8) S. Nishida, J. Org. Chem., 32, 2692 (1967); also see ref 9.

(9) N. C. Deno and W. L. Evans, J. Amer. Chem. Soc., 79, 5804 (1957).

(10) (a) K. Takeuchi and H. C. Brown, ibid., 90, 2693 (1968); (b) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapters 9, 10, and 11.

(11) Graduate research assistant on a grant (GP 31385) supported by the National Science Foundation.

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Solvolysis of the 2-Aryl-2-norbornenyl
p-Nitrobenzoates. Constant Exo:Endo Rate Ratio
with Increasing Electron Demand by the 2-Aryl Group

Sir:

The exo:endo rate ratio in the solvolysis of the 2-aryl-2-norbornenyl p-nitrobenzoates remains essentially constant (~300) as the electron demand of the 2-aryl