Table I records values of k_r for the release of *p*-nitrophenol from a number of *p*-nitrophenyl carboxylates. With one exception (discussed below) a linear dependence on ester concentration was observed in reactions with compound I. Menger and Portnoy[9] have shown that the rate of alkaline hydrolysis of *p*-nitrophenyl dodecanoate decreases as the ester concentration is increased and have attributed this phenomenon to complexation. As indicated by the ratio of k_{II} for the acetate to k_{II} for the dodecanoate which is consistent with similar data in analogous studies,[1a,k] and by the fact that semilogarithmic plots were linear to greater than 2 half-lives for the reaction of I with the dodecanoate ([I] > [ester]), aggregation phenomenon is probably unimportant in this study because of the low ester and high organic solvent concentrations employed; the small k_{II} value is probably an intramolecular steric effect.[1a,k,10]

It is difficult to account for the irregular increase in k_r with acyl chain length by other than stereospecific productive binding on the path to products. If hydrophobic association between substrate and I does exist, as Table I implies, it should be possible to observe Michaelis–Menten kinetics. In fact saturation of I by *p*-nitrophenyl butyrate (*p*NPB) does indeed occur.

Considering the high methanol–acetonitrile concentration present, binding between I and *p*-NPB is very strong ($K_s = 9.9 \pm 0.2 \times 10^{-4}$ *M*). For example, an increase in acetonitrile concentration from 0.5 to 10% causes a tenfold increase in K_s for cyclodextrin substrates.[11] The aliphatic portion of *p*-NPB must be primarily responsible for binding, since fourfold higher concentrations of *p*-NPA were linear in ester concentration.

The evidence for a discrete binding site is further substantiated by the effect of potassium iodide on the kinetics of phenol release from *p*-nitrophenyl hexanoate. With II present addition of KI causes a small rate enhancement. In contrast, though hydrophobic binding normally increases with increasing ionic strength,[12] KI inhibits the I-accelerated reaction in excellent accord with $v/v_i = 1 + i/K_i$.[12] Simmons and Park[14] have reported evidence consistent with encapsulation of iodide within the cavity of an *in,in*-[10.10.10]diazabicycloalkane with an association constant greater than 10, comparable to the K_i of 7×10^{-2} *M* measured for this system. The qualitative agreement of this inhibition data with Simmons' findings, the X-ray structural determinations of Dunitz[15] on cyclic amines, the conformational predictions of Dale[16] based on space-filling molecular models and physical constants of cyclic alkanes, and the observation that 1,8,15,22-tetraazacyclooctacosane crystallizes from aqueous solution with a molecule of water included in its cavity[17] all support the hypothesis that the productive binding site for I is a cavity approximately 5.6 Å in diameter formed by the aliphatic chains of I. The possibility that binding outside the cavity of I leads to rate acceleration cannot, however, be discounted.[1a]

Table II. Effect of Cupric Chloride on *p*-Nitrophenol Release from *p*-Nitrophenyl Carboxylates in the Presence of I and II[a]

Ester	Ester concn $\times 10^4$, *M*	$CuCl_2$ concn $\times 10^5$, *M*	$k_{obsd} \times 10^4$, sec^{-1} [b]
	[I] = 9.5×10^{-6} *M*		
Propionate	2.77	0	3.8
Propionate	2.77	1.08	32
Hexanoate	0.755	0	4.8
Hexanoate	0.755	1.08	59
	[II] = 1.35×10^{-3} *M*		
Hexanoate	0.755	0	29
Hexanoate	0.755	13.5[c]	32

[a] 25°, in aqueous phosphate buffer, $\mu = 0.088$, containing 10.55% methanol–1.75% acetonitrile. [b] Observed pseudo-first-order rate constant. [c] Limited by buffer precipitation at higher $CuCl_2$ concentration.

Finally, the preliminary data collected in Table II indicate that an equivalent of $CuCl_2$ accelerates the reaction of I with *p*-nitrophenyl carboxylates about tenfold, but has no effect of the reactivity of II.[18] Consequently, k_r for *p*-nitrophenyl hexanoate is about 150 while that for the dodecanoate is approximately 60,000 with $CuCl_2$ present.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

(18) The reaction of *N*-methylacetohydroxamic acid with *p*-nitrophenyl acetate is not affected by the presence of cupric ion.[4]

(19) NIH Predoctoral Fellow, 1966–1969.

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Remote Secondary Deuterium Isotope Effects. III.[1] β-Arylalkyl Systems

Sir:

Based on an analysis of curved Hammett plots, it has been proposed[2] that the acetolysis of secondary β-arylalkyl derivatives involves rate-determining competition between two discrete strongly assisted pathways: k_S (solvent assisted) and k_Δ (aryl assisted).[5] In this analy-

(1) Part II: R. H. Griffin and J. G. Jewett, *J. Amer. Chem. Soc.*, **92**, 1104 (1970).

(2) (a) P. v. R. Schleyer, *et al.*, *ibid.*, **91**, 4291, 4294, 4296, 4297 (1969). This proposal has been advanced to explain the apparent "rate-product dichotomy"[3] inherent in the phenonium ion interpretation[4] of the solvolysis behavior of β-arylalkyl derivatives; (b) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); (c) C. J. Kim and H. C. Brown, *ibid.*, 91, 4286, 4287, 4289 (1969).

(3) (a) H. C. Brown, *Chem. Soc., Spec. Publ.*, No. 16, 140 (1962); (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, 87, 2137 (1965).

(4) (a) D. J. Cram, *ibid.*, 71, 3863, 3875 (1949); (b) *ibid.*, 86, 3767 (1964).

(5) The k_S, k_Δ scheme was first proposed by Winstein to explain the solvolytic behavior of primary β-arylalkyl derivatives.[6] For such primary systems, the k_S pathway is considered to involve direct SN2 displacement by solvent on covalent substrate.[6c,d,g] For secondary systems, the role of the solvent has been less precisely defined.

(6) (a) S. Winstein, *Bull. Soc. Chim. Fr.*, 18, C55 (1951); (b) A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968), and intervening papers; (c) J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *ibid.*, 91, 1154 (1969); (d) M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969); (e) R. J. Jablonski and E. I. Snyder, *ibid.*, **91**

(9) F. M. Menger and C. E. Portnoy, *J. Amer. Chem. Soc.*, **90**, 1875 (1968).

(10) G. Nemethy and H. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

(11) M. L. Bender, R. L. Van Etten, G. A. Clowes, and J. F. Sebastian, *J. Amer. Chem. Soc.*, **89**, 3242, 3253 (1967).

(12) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, Chapter 8.

(13) S. Bernhard, "The Structure and Function of Enzymes," W. A. Benjamin, New York, N. Y., 1968, pp 80–85.

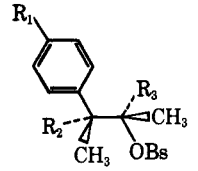
(14) C. H. Park and H. E. Simmons, *J. Amer. Chem. Soc.*, **90**, 2431 (1968).

(15) J. D. Dunitz and E. F. Meyer, Jr., *Helv. Chim. Acta*, 48, 1441 (1965).

(16) J. Dale, *J. Chem. Soc.*, 93 (1963).

(17) H. Zahn and H. Spoor, *Chem. Ber.*, **92**, 1375 (1959).

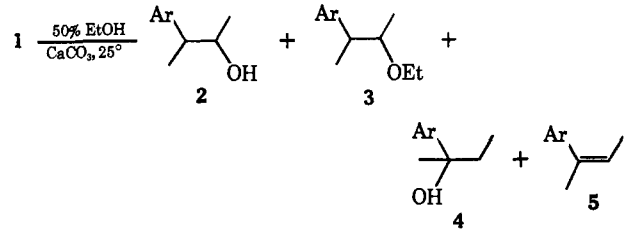
sis of secondary β-arylalkyl solvolysis, it has been postulated that the solvent participates nucleophilically in the k_S pathway to afford inverted substitution and elimination products *via* "transition states and intermediates that are strongly bound at the rear to solvent, rather than open ions or ion pairs."[2a,7] One possible mechanism for the k_S pathway suggested by this postulate involves nucleophilic solvent participation at the stage of the covalent substrate.[8] According to this mechanism, the specific rate of the k_S pathway should depend on solvent nucleophilicity (or a blend of nucleophilicity and ionizing power), while that of the k_Δ pathway should depend only on ionizing power.[6,7] We have found that a dual path mechanism is operative for solvolysis of *threo*-3-phenyl-2-butyl brosylate (**1**) in



1, $R_1 = R_2 = R_3 = H$
1-α-*d*, $R_1 = R_2 = H$; $R_3 = D$
1-β-*d*, $R_1 = R_3 = H$; $R_2 = D$
1-*p*-*d*, $R_2 = R_3 = H$; $R_1 = D$

aqueous ethanol as well as acetic acid. However, our investigation provides evidence that rate-determining nucleophilic solvent attack on covalent substrate is *not* involved in the aryl unassisted pathway and we here present some initial results.

Solvolysis of **1** in 50% ethanol afforded the substitution products **2**, **3**, and **4**, and a *single* elimination product **5**. The product data for **1** and its α- and β-deuter-



ated analogs are summarized in Table I. Two striking features emerge from these results: (1) *in spite of the high nucleophilicity of the solvent*,[11] virtually all of the secondary substitution product is formed from a phenonium ion or its stereochemical equivalent; (2) elimination occurs from a species, most likely an open threo intimate ion pair,[13] subject to the stereoelectronic constraints of an E2 process. That such elimination and phenonium ion formation (or destruction) share in the rate-determining process for this solvolysis is established by the remote and proximate kinetic isotope effects presented in Table II.

Table I. Products of Solvolysis of **1**, **1-α-*d***, and **1-β-*d*** (50E,[a] 25°)

Compd	Product, %[b] 2	3	4	5	Configuration[c] of 2, 3	Scrambling of C_α, C_β in 2, %[d]
1	60.8	17.4	5.0	16.8	>98% threo	
1-α-*d*	63.2	17.4	4.7	14.7		100
1-β-*d*	67.9	19.2	3.5	9.4		

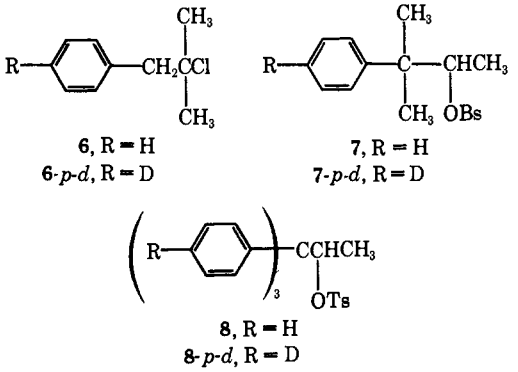
[a] 50E refers to 50% ethanol, v/v, before mixing. [b] The values represent mole per cent, derived from glpc data using an internal standard analysis. [c] Determined by nmr analysis, directly for **3** and on the derived acetates[7a] for **2**. [d] Analysis by nmr on the product from solvolysis of **1-α-*d***.

Table II. Isotope Effects on Rates of Solvolysis of β-Arylalkyl Derivatives (25°)

Compd	Solvent[a]	$k \times 10^5$, sec^{-1}[b]	k_H/k_D
1	50E	3.512 ± 0.001	
1-α-*d*	50E	3.094 ± 0.001	1.135
1-β-*d*	50E	3.070 ± 0.001	1.144
1-*p*-*d*	50E	3.562 ± 0.001	0.986
6	40E	10.405 ± 0.002	
6-*p*-*d*	40E	10.441 ± 0.003	0.997
7	80E	9.732 ± 0.001	
7-*p*-*d*	80E	9.862 ± 0.001	0.987
8	80E	8.886 ± 0.003	
8-*p*-*d*	80E	9.097 ± 0.002	0.977

[a] See footnote *a*, Table I. [b] Rates determined conductometrically; duplicate runs except for **6** and **6-*p*-*d*** which were run in triplicate.

The "para-d" effect for solvolysis of **6**,[15] which is structurally disposed against phenyl participation and



migration,[2a,16] is essentially *nil*. On the other hand, there is a large[17] inverse para-d effect for solvolysis of

4445 (1969); (f) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968); (g) J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969).

(7) A concurring view for secondary systems has been put forth by the UCLA groups: (a) J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969); (b) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

(8) Such solvent attack could take the form of assistance to ion-pair formation or a direct SN2–E2 reaction. A current controversy[9,10] concerning the mechanism of solvolysis of simple secondary derivatives also hinges on questions related to the timing and nature of solvent involvement.

(9) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4821 (1971), and references therein.

(10) V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2553 (1971), and references therein.

(11) A referee has pointed out that the balance between the k_S and k_Δ pathways might remain nearly the same in 50% ethanol as in acetic acid since the former solvent is both more nucleophilic and more ionizing than the latter. While it is possible that k_S and k_Δ are increased to the same extent by the solvent change, we consider this to be unlikely. Furthermore, we have found that solvolysis of **1** in 97.5% ethanol affords 52% of *threo*-**3**, 37% of **5**, and 9% of *erythro*-**3**. Thus, increased solvent nucleophilicity, even at constant ionizing power,[12] does not substantially alter the balance[2b] between the two pathways.

(12) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 78, 2770 (1956).

(13) The β-isotope effect on the yield of **5** is 1.95 which is reasonable for elimination from an ion pair, but unusually small if elimination were occurring from covalent substrate.[14]

(14) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953).

(15) A. Landis and C. A. VanderWerf, *ibid.*, **80**, 5277 (1958).

(16) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968).

(17) The para-d effects for **1**, **7**, and **8** are larger than that for benzhydryl chloride solvolysis.[18]

(18) A. Streitwieser, Jr., and H. S. Klein, *ibid.*, **86**, 5170 (1964).

the other extreme model systems **7** and **8** for which the rate-determining activated complex resembles a phenonium ion.[19] Such inverse isotope effects are observed when electron deficiency develops at nonhyperconjugating isotopically substituted sites in the activated complex.[1,18] Since the para-d effect for solvolysis of **1** is also large and inverse, we conclude that the rate-determining activated complex (for substitution with retention) closely resembles a phenonium ion.

The secondary kinetic β-isotope effect on the (major) aryl assisted pathway for **1** is expected to be very small.[20] Therefore, we conclude that the observed kinetic β effect on the solvolysis of **1** is largely due to competing rate-determining elimination of the β hydrogen atom in the (minor) aryl unassisted pathway. The magnitude of the kinetic β effect is congruent with this proposal that the rate-determining and product-determining steps are the same for the aryl unassisted pathway. The magnitude of the kinetic α-isotope effect is also consistent with the proposed dual path mechanism, since participation by neighboring carbon does not substantially lower the α effect below that expected for rate-determining ion-pair formation.[21,22]

Thus, the present results provide direct evidence that solvolysis of **1** involves rate-determining formation (or destruction) of a phenyl bridged species in the aryl assisted pathway and rate-determining elimination, probably from an open threo ion pair, in the aryl unassisted pathway. Crossover between the two pathways, in the usual sense of the term,[2] is unimportant because hindered secondary intimate ion pairs are remarkably resistant to nucleophilic attack at carbon and may maintain their stereochemical integrity.[23,24] The rate–product data for acetolysis of *threo*-3-aryl-2-butyl brosylates can be accounted for in a similar fashion as well. The observation of curved Hammett plots may be viewed as resulting from *substitutent induced* changes in the relative rate constants for ionization, phenyl bridging, and elimination.[25] For deactivated derivatives of **1**, ionization to the intimate ion pair is probably rate determining; increased elimination fractions are expected and indeed found.[2b]

Acknowledgments. Support of this work by the National Science Foundation (Grant GP 21307) is gratefully acknowledged. We thank Professors V. J. Shiner, Jr., and P. v. R. Schleyer for stimulating discussions of the present work.

(19) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Amer. Chem. Soc.*, 87, 1280 (1965).

(20) (a) W. H. Saunders, *et al.*, *ibid.*, 80, 2421 (1958); 82, 3586 (1960); (b) S. L. Loukas, M. R. Velkou, and G. Gregoriou, *Chem. Commun.*, 251 (1970).

(21) B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, 92, 3462 (1970).

(22) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, 91, 7748 (1969).

(23) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc. Spec. Publ.*, No. 19, 109 (1965).

(24) (a) H. L. Goering, R. G. Briody, and G. Sandrock, *J. Amer. Chem. Soc.*, 92, 7401 (1970); (b) H. L. Goering and J. F. Levy, *ibid.*, 86, 120 (1964); (c) H. L. Goering and R. W. Thies, *ibid.*, 90, 2967, 2968 (1968).

(25) There is a delicate balance among various rate constants for complex solvolysis schemes.[23,24] Substituent induced changes in rate-determining steps should be anticipated.[26]

(26) V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, 93, 2553 (1971).

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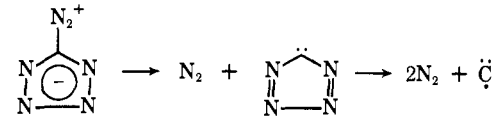
Formation of Atomic Carbon in the Decomposition of 5-Tetrazolyldiazonium Chloride

Sir:

The formation and reactions of atomic carbon have been studied by a variety of methods including the production of energetic carbon atoms by nuclear transformation[1] and the preparation of lower energy carbon species in carbon arcs.[2] We have previously observed the formation of carbon atoms in the decomposition of quadricyclanone *p*-tosylhydrazone.[3]

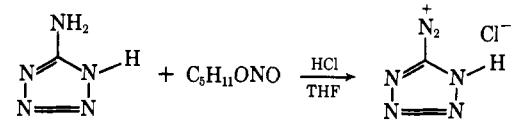
In an attempt to devise a readily available chemical system for preparing and reacting carbon atoms, the decomposition of species related to 5-diazotetrazole (**1**)[4] has been studied. It was anticipated that **1** would



1

decompose to three molecules of nitrogen and a carbon atom. Attempts to prepare **1** in a suitable nonaqueous solvent or in the gas phase have been unsuccessful due to extreme lability of the compound.

However, the corresponding diazonium chloride, 5-tetrazolyldiazonium chloride (**2**), can be isolated. We have prepared **2** by dropwise addition of isoamyl nitrite (10 mmol) to a solution of 5-amino-1*H*-tetrazole (**3**) (9.8 mmol) in 20 ml of THF–5 ml of HCl at 0°.



3 **2**

The diazonium chloride may be extracted into ether and the ether removed at reduced pressure to yield crystalline **2**. The infrared spectra (NaCl plate) of the extremely explosive salt[5] shows ν_{max} 2275 cm^{-1}.

The decomposition of **2** has been studied by coating the salt on the walls of a 500-ml flask and evacuating and immersing the flask in a water bath at 80°. Thermal decomposition of **2** in the presence of two substrates, ethylene and ethylene oxide, has been examined.

When **2** (0.75 mmol) was allowed to decompose at 80° in a system containing 550 mm (17.1 mmol) of ethylene, the products were: nitrogen (0.9 mmol), methane (2.3×10^{-3} mmol), allene (1.9×10^{-3} mmol), propyne (1.2×10^{-3} mmol), and hydrogen cyanide (1.6×10^{-2} mmol).[6] It is proposed that carbon atoms

$$2 + H_2C{=}CH_2 \xrightarrow{\Delta} N_2 + CH_4 + H_2C{=}C{=}CH_2 + CH_3C{\equiv}CH + HCN$$

(1) A. P. Wolf, *Advan. Phys. Org. Chem.*, 2, 201 (1964).

(2) P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, 87, 1135 (1965); P. S. Skell and R. R. Engel, *ibid.*, 88, 3749 (1966); P. S. Skell and R. R. Engel, *ibid.*, 88, 4883 (1966); P. S. Skell and R. R. Engel, *ibid.*, 89, 2912 (1967).

(3) P. B. Shevlin and A. P. Wolf, *Tetrahedron Lett.*, 3987 (1970).

(4) J. Thiele, *Justus Liebigs Ann. Chem.*, 270, 59 (1891).

(5) It should be emphasized that **2** is extremely explosive and should be handled with great care. We recommend that no more than 0.75 mmol of **2** be isolated at one time. Ethereal solutions of **2** are somewhat more stable but explosions have occurred after standing at −70° for 1 hr.

(6) In all reactions the products were separated by gas chromatography and characterized by their ir spectra.