Therefore, it would appear that acetate formation is determined when acetic anhydride becomes covalently bound to the carbonium ion to yield a species like V, the latter reacting inevitably with, e.g., AcOH or OBs⁻ to yield I-OAc along with Ac₂O or AcOBs. The latter substance titrates as HOBs in the titrimetric procedure.

Products from I-OBs have been determined by vapor phase chromatographic analysis much more accurately than was possible in the former work[2e] in acetic acid. We find that acetate I-OAc is produced nearly exclusively both in AcOH (99.7%) and pure Ac₂O (99.4%). The I-OAc obtained is completely dl-threo (>99.9%), no erythro contaminant being visible, whereas 0.1% is easily detectable. Traces of olefin accompany the I-OAc in the solvolysis product, 0.3% being observed in AcOH and 0.6% in Ac₂O. Analysis of the olefin from Ac₂O at 50° with or without added potassium acetate showed it to be nearly entirely the terminal olefin VI (>97%). The nature of the products, as well as the high rate of solvolysis[2] compared to the 3-phenyl-2-butyl system, points to a very high ratio of anchimerically assisted ionization of I-OBs to a bridged ion (k_Δ) over anchimerically unassisted ionization to a classical ion (k_s). This ratio is understandably greater than in the case of the 3-phenyl-2-butyl system.[4] On the basis of classical carbonium ions, one cannot account for the high rate and the unique stereochemical result. Also, one could not understand the very small proportion of olefin and the tendency for the latter to be terminal rather than internal. General experience with carbonium ions suggests that a classical 3-anisyl-2-butyl cation would give considerable elimination, preferably leading to internal olefin. The bridged ion accounts not only for the high rate and stereospecificity, but also the difficulty in producing internal olefin and the preference for the terminal one. Elimination of a proton from the bridged ion to yield internal olefin can be expected to be stereoelectronically unfavorable because of the geometric position of the hydrogen atoms on C_b and C_c, but no such difficulty opposes removal of a proton from C_a or C_d to form terminal olefin.

One wonders whether H. C. Brown[5] would explain

(4) D. J. Cram, J. Am. Chem. Soc., **71**, 3863 (1949); **74**, 2129 (1952).
(5) H. C. Brown, paper at Transition State Symposium, Sheffield, Eng.. April 3–4, 1962; Special Publication No. 16, The Chemical Society, London, 1962, pp. 140–157, 176–178. In our opinion this paper gives a poor perspective on the role of anchimerically assisted ionization and bridged or nonclassical ions in various solvolyses. Also, the paper suffers from important misquotations and omissions.

the present facts without recourse to a bridged carbonium ion.

Dissociated Ions and Ion Pairs in Acetolysis of threo-3-Anisyl-2-butyl p-Bromobenzenesulfonate[1]

Sir:

Recent results of our further kinetic study of the acetolysis of threo-3-anisyl-2-butyl p-bromobenzenesulfonate[2] (I-OBs) are helpful in understanding the competition between ion pairs and dissociated carbonium ions[2a,d] in solvolysis.

Kinetic data for acetolysis of I-OBs in a series of acetic acid–acetic anhydride mixtures of decreasing ionization power and increasing dissociating ability[3] are illustrated in Table I for AcOH, 50% AcOH–Ac₂O,

TABLE I
KINETIC DATA FOR ACETOLYSIS OF I-OBs

	AcOH (25.0°)	50% AcOH–Ac₂O (25.0°)	Ac₂O (50.0°)
$10^7 k_\alpha^0$, sec.⁻¹ (polarimetric)	798	578	442
$10^7 k_t^0$, sec.⁻¹ (titrimetric)	196	318	107
k_α^0/k_t^0	4.1	1.8	4.1
k_{ext}^0/k_t^0	2.58	1.56	1.47
k_t^0/k_t^d	1.00	2.39	12.7
$10^4 (Bu_4NOBs)_{0.5}$, M	...	3	0.8
k_3/k_s^{III}	ca. 0	3.87	35.7
% ROAc from III	ca. 100	21	3
% ROAc from IV	ca. 0	79	97

and pure Ac₂O. As acetic anhydride is added, to acetic acid solvent, the titrimetric rate constant, k_t^0, rises at first and passes through a maximum before dropping steeply as pure acetic anhydride is approached. On the other hand, the ionization rate constant, k_i^0, equal to the polarimetric value, k_α^0, drops as acetic anhydride is added. The maximum in k_t^0 is associated with a minimum in the over-all importance of ion-pair return as gauged by the ratio (k_α^0/k_t^0). The size of the special salt effect of added lithium perchlorate, a
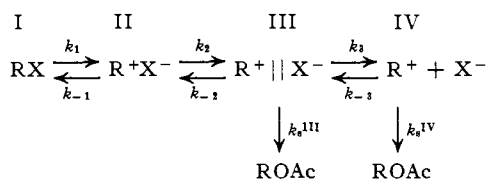
(1) Research sponsored by the National Science Foundation.
(2) S. Winstein, et al.: (a) Chem. Ind. (London), 66·' (1954); (b) J. Am. Chem. Soc., **74**, 1140 (1952); (c) ibid., **76**, 2597 (1954); (d) ibid., **78**, 328 (1956); (e) ibid., **80**, 169 (1958); **83**, 885, 4986 (1961).
(3) S. Smith, A. H. Fainberg, and S. Winstein, ibid., **83**, 618 (1961).

partial measure of ion pair return, is indicated in Table I by the ratio (k_{ext}^0/k_t^0).

The large effect of solvent change on the relative importance of ion pairs and dissociated carbonium ions is disclosed by common-ion rate depression studies. In acetic acid solvent, no common-ion rate depression due to developing HOBs[2d] or added LiOBs[2d] or Bu₄NOBs can be detected. Using the symbolism of the solvolysis scheme with two varieties of ion pairs,[2,4] II and III, and dissociated carbonium ion, IV, the absence of common-ion rate depression in AcOH was shown[2a,d] to indicate that dissociation of the product-forming ion pair III (k_3) does not compete with its solvolysis (k_s^{III}). As acetic anhydride is added to the acetic acid solvent, common-ion rate depression becomes more and more important. As Bu₄NOBs is added in each binary solvent mixture, there is an upper limit to the amount of depression it is possible to achieve before the very shallow normal rate acceleration sets in. Such a limit is exactly what is expected from a solvolysis scheme where I-OAc may arise from ion pairs as well as dissociated carbonium ions. The amount of depression possible is indicated in Table I by the ratio, k_t^0/k_t^d, between undepressed and fully depressed rate constants. Thus, the fully depressed rate constant, k_t^d, is 42% of k_t^0 in 50% AcOH–Ac₂O, and only 8% of k_t^0 in Ac₂O. The depression of rate by common-ion Bu₄NOBs salt is very efficient and this is indicated by the low salt concentrations required to introduce half of the achievable depression, symbolized by (Bu₄NOBs)₀.₅.

$$\text{I}\qquad\text{II}\qquad\text{III}\qquad\text{IV}$$
$$\text{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^+\text{X}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{R}^+||\text{X}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{R}^+ + \text{X}^-$$
$$\qquad\qquad\qquad\downarrow k_s^{III}\qquad\quad\downarrow k_s^{IV}$$
$$\qquad\qquad\qquad\text{ROAc}\qquad\quad\text{ROAc}$$

The increasing importance of common-ion rate depression as the solvent varies corresponds to increasing ratios of dissociation to solvolysis rate constants of ion pair III, (k_3/k_s^{III}). From a kinetic analysis of the solvolysis scheme, eq. 1 may be derived for evaluating the (k_3/k_s^{III}) ratios, and these are listed in Table I. These ratios permit one to calculate the percentage of I-OAc product arising from ion pair and that from dissociated carbonium ion when the solvolysis is undepressed (see Table).

$$(k_3/k_s^{III}) = (k_{ext}^0/k_t^d)[(k_t^0 - k_t^d)/(k_{ext}^0 - k_t^0)] \quad (1)$$

$$k_{-3} = 1.13 \times 10^{10}\Lambda_0/D \quad (2)$$

The increasing (k_3/k_s^{III}) values and growing importance of dissociated carbonium ions as the solvent varies may be discussed in terms of the separate k_3 and k_s^{III} values. The order of magnitude of k_3 can be estimated, since it is equal to $k_{-3}K$, where K represents the ion-pair dissociation constant of ion pair III. For a rough calculation, one can employ the K^5 for Bu₄NOTs and a k_{-3} estimated from Debye's expression[6] for the rate constant for diffusion-controlled

(4) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).

(5) P. Klinedinst, S. Smith, and L. Savedoff, unpublished work.

(6) (a) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); H. Eyring and E. M. Eyring, "Modern Chemical Kinetics," Reinhold Publishing Corp., New York, N. Y., 1963, Chapter 6.

association of two oppositely charged univalent ions. As was first pointed out to us by Dr. Ernest Grunwald some years ago, Debye's expression at 25.0° may be put in the form of eq. 2, where D and Λ_0 are dielectric constant and limiting equivalent conductance, respectively. On this basis in AcOH $(D = 6)$, K,[5] k_{-3}, and k_3 are 10^{-6}, 6.3×10^{10} l. mole^{-1} sec.$^{1-}$, and 6×10^4 sec.$^{-1}$, respectively. Since k_3 does not compete with k_s^{III}, the latter must exceed 10^6 sec.$^{-1}$. In Ac₂O $(D = 20.7)$, K for Bu₄NOTs is not available, but we might use the K and Λ_0 values in acetone[5] $(D = 20.7)$ for this purpose. On this basis, K, k_{-3}, and k_3 turn out to be 2.5×10^{-3}, 8.5×10^{10} l. mole^{-1} sec.$^{1-}$, and 2.1×10^8 sec.$^{-1}$, respectively. From the (k_3/k_s^{III}) value in Ac₂O, k_s^{III} is thus estimated at 6×10^6 sec.$^{-1}$.

We see from the above estimates of rate constants that the large increase in the importance of dissociated carbonium ions as the solvent varies in acetolysis of I-OBs is associated with a *ca.* 3500-fold increase in k_3, an ion-pair dissociation rate constant. The present results and general treatment furnish considerable added insight into the effect of solvent on the roles of ion pairs and dissociated ions in solvolysis and related reactions.

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The Photochemical Isomerization of B-Nor-1-dehydrotestosterone Acetate in Dioxane Solution[1]

Sir:

Dehydrogenation of the known B-nortestosterone acetate[2] with dichlorodicyano-*p*-benzoquinone in boiling dioxane gave the 1-dehydro derivative 1, m.p. 142°, $[\alpha]_D$ −43° $(c$ 0.55, CHCl₃); λ_{max}^{EtOH} 245 mμ $(\epsilon$ 16,800); $\nu_{max}^{CHCl_3}$ 1722, 1657, 1625, 1592, and 1250 cm.$^{-1}$.[3] This dienone (1) was converted to a single isomer 2 (Scheme I), m.p. 196–198°, $[\alpha]_D$ +20° $(c$ 0.57, CHCl₃); λ_{max}^{EtOH} 299 mμ $(\epsilon$ 14,500); $\nu_{max}^{CHCl_3}$ 1720, 1700, 1674, 1583, and 1260 cm.$^{-1}$, on irradiation of a 0.032 M dioxane solution at room temperature, using a low-pressure mercury lamp.[4] A *ca.* 68% conversion of 1 to 2 was observed after a 2-hr. irradiation period.[5] Partial hydrogenation of 2 over Raney nickel in ethanol gave rise to the dihydro derivative 4, m.p. 187–189°, $[\alpha]_D$ +114° $(c$ 0.25, CHCl₃); λ_{max}^{EtOH} 236 mμ $(\epsilon$ 16,500); ν_{max}^{KBr} 1730, 1704, 1670, 1620, and 1250 cm.$^{-1}$. Complete saturation either of the photoketone, 2, or of the dihydro derivative, 4, furnished the tetrahydro acetoxy ketone, 5 (17-OAc), m.p. 113°, $[\alpha]_D$ +98° $(c$ 0.25, CHCl₃); $\nu_{max}^{CHCl_3}$ 1727 (broad), 1255 cm.$^{-1}$. Hydrolysis of 5 with ethanolic potassium carbonate at room temperature gave the corresponding hydroxy ketone 5 (17-OH), m.p. 125°, $[\alpha]_D$ +113° $(c$ 0.17, CHCl₃). In the latter the presence of a cyclopentanone

(1) Photochemical Reactions, Part 27; Part 26: *Helv. Chim. Acta*, **47**, 637 (1964).

(2) J. Joska, J. Fajkoš, and F. Sorm, *Collection Czech. Chem. Commun.*, **25**, 1086 (1960).

(3) Satisfactory mass spectra of the new compounds have been obtained.

(4) NK 6/20, Quarzlampen GmbH, Hanau (*ca.* 90% emission at 2537 Å.).

(5) Estimated from the ultraviolet absorption of the crude reaction mixture composed of isomers 1 and 2.