DETERMINATION OF MISCIBILITY CHARACTERISTICS OF HIGHLY REACTIVE LIQUIDS

Sir:

A method has been devised in our Laboratory for determining the miscibility characteristics of highly reactive liquids. The need for such information arose when inconsistent results obtained from experiments on the kinetics of the pentaborane–9-hydrazine reaction could only be explained by the fact that these two compounds are immiscible. The rapid rate of reaction between the two suggested that the opposite was true. Since the pentaborane-9 and hydrazine react too rapidly at room temperature for observation by eye, high-speed motion pictures were taken of the phenomena occurring when a drop of hydrazine was added to a bulk quantity of pentaborane-9. By this means it was established definitely that despite rapid reaction at the interface between the two liquids, the bulk liquids are immiscible.

A drawing of the apparatus used for these studies is shown in Fig. 1. The hydrazine was contained in the upper tube (C). The breaker (B) was held in position with an electromagnet (A). When the current to the electromagnet was turned off, the breaker fell and released the hydrazine (D), which then traveled down the tube and flowed dropwise from the drip tip (E) into the pentaborane (F). Earlier experiments had shown that this slower method of addition was required to prevent the splashing and turbulence caused by dropping hydrazine directly from its container into the pentaborane. Since hydrazine is more dense than pentaborane-9 (1.0 g./cc. *vs.* 0.6 g./cc.), the drop penetrated through the bulk liquid after contact.

To facilitate observation, a trace of yellow dye was added to the hydrazine, and the progress of the drop as it descended through the colorless pentaborane was recorded on color film. The apparatus was lighted from the rear by a collimated beam of light. In initial experiments the edges of the pentaborane-9 (F) were opaque, probably due to reflectance of the light by the curved cylindrical glass; consequently the field of view was grossly restricted. To prevent this condition the tube was surrounded in later experiments by a beaker of carbon tetrachloride. The indices of refraction of carbon tetrachloride and Pyrex are essentially the same; thus, no distortion of light occurred at the glass–liquid interface and the column of pentaborane-9 was in clear view.

Photographs were taken at speeds of 1100 to 1500 frames per second. Comparison films were taken of the addition of water to pentaborane (also an immiscible system) and of water to a pentaborane-9–dioxane solution (miscible system by virtue of the common solvent, dioxane). When ether water or hydrazine was added to pentaborane-9, the drops travelled essentially intact to the bottom of the tube, the dye remaining with the descending drop. The only difference between these two chemical systems was in the chemical reactivity, as evidenced by more rapid gas bubble formation (hydrogen) at the droplet liquid interface in the case of hydrazine and pentaborane-9.

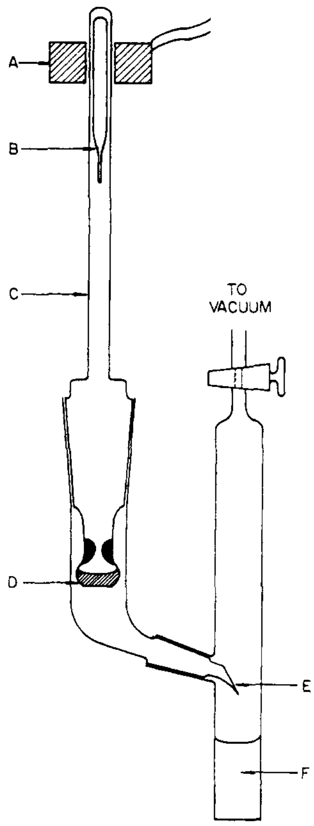

Fig. 1.—Apparatus for miscibility study.

A considerably different situation was observed when water was added to the pentaborane-9–dioxane solution. In this case the drops of water broke up immediately on contact with the pentaborane-9, vapor bubbles emanated from throughout the solution, and the entire system took on the color of the dye.

The authors recommend this technique for the determination of miscibility characteristics in other systems involving highly reactive liquids.

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DEMERCURATION ROUTE TO THE NORBORNYL CATION[1,2]

Sir:

Heterolysis of carbon–metal bonds in the sense of formula I is interesting and important in olefin oxidations by mercury,[3] lead,[4] and thallium[4,5] salts. With 1,2-diphenyl-2-methoxyethylmercuric

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[1] Research sponsored by the U. S. Army Research Office (Durham).

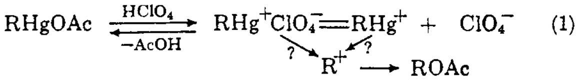
[2] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

[3] *E.g.*, (a) D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **33**, 1002 (1955); (b) A. C. Cope, N. A. Nelson and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954); (c) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 238 (1951).

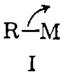
[4] R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

[5] R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).

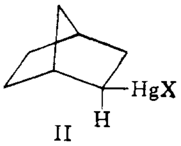
nitrate[3a] and benzyl- and 2-*p*-anisylethylmercuric acetates,[6] Wright and Shearer[3a] and Ichikawa and Ouchi[6] have reported solvolyses which may be interpreted as involving carbon–mercury heterolysis assisted by mercuric salt or perchloric acid. Jensen and Ouellette[7] have pointed out recently that the perchloric acid-catalyzed demercuration of alkylmercuric acetates formulated in equation (1) represents a convenient solvolysis procedure. These authors have recognized the generality of this type of demercuration and have reported an elegant study of a series of alkylmercurials. In these Laboratories we have found demercuration to be an interesting way to generate non-classical cations with a quite different type of leaving group than those in conventional acetolyses. This is illustrated in the present Communication with demercuration of *endo*- and *exo*-norbornylmercuric acetates.



$$RHgOAc \underset{-AcOH}{\overset{HClO_4}{\rightleftarrows}} RHg^+ClO_4^- \rightleftharpoons RHg^+ + ClO_4^- \quad (1)$$
$$\overset{?}{\searrow} R^+ \overset{?}{\swarrow} \longrightarrow ROAc$$



I



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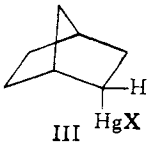
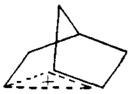


III



IV

An approximately 1:1 mixture of *exo*- and *endo*-norbornylmercuric bromides,[8] m.p. 144-145° (dec.), was obtained from treatment of the Grignard reagent from *exo*-norbornyl chloride with mercuric bromide. By partition column chromatography and subsequent fractional crystallization of the higher melting fractions, pure *exo*-II-Br,[8] m.p. 178-180° (dec.), was obtained. When the above mixture was converted to the mixed norbornylmercuric acetates, m.p. 77-78°. and treated with 0.1 equivalent of perchloric acid in acetic acid solvent, 47% of the mercurial gave rise to metallic mercury very rapidly, while the remainder reacted much more slowly. Recovery of the mercurial after the fast stage led to pure *endo*-III-Br.[8] m.p. 120-121°. The alkylmercuric bromides were converted to II-OAc,[8] m.p. 109°. and III-OAc,[8] m.p. 67-68°.

Partial neutralization of *endo*-III-OAc with perchloric acid in anhydrous acetic acid solvent led to zero order kinetics[7] of formation of mercury and norbornyl acetate, the latter being followed by vapor phase chromatography. The demercuration of the *exo*-II-OAc is so much more rapid that the rate was estimated from several one point determinations at room temperature. In the table are summarized the corresponding first order[7] demercuration rate constants for the norbornylmercuric perchlorates. as well as the cyclohexylmercuric analog measured for comparison.

TABLE I

DEMERCURATION OF 0.01–0.02 *M* ALKYL MERCURIC PERCHLORATES IN ACETIC ACID (0.02 *M* Ac_2O)

RHgOAc	Temp., °C.	$HClO_4$, %	10^6k, sec.$^{-1}$	Rel. rate
III-OAc	25.0	17.0	1.46 ± 0.08	1
Cyclo-C_6H_{11}	25.0	17.3	62.5 ± 0.5	43
II-OAc	21[a]	17.7	5.9 × 10^3	5 × 10^3
II-OAc	23[a]	15.9	4.3 × 10^3	
II-OAc	23	27.2	4.9 × 10^3	

[a] Based on fast portion of *endo-exo* mixture.

Comparing the *endo*-III system with cyclohexyl, it is seen that the blend of angle and eclipsing strains and other effects render *endo*-norbornyl less reactive than cyclohexyl in demercuration by a factor of *ca.* 40, instead of leaving it approximately as reactive as cyclohexyl as in acetolysis of bromobenzenesulfonates.[9] Using the *exo*:*endo* reactivity ratio to estimate anchimeric acceleration of carbon–mercury heterolysis in the *exo*-mercurial, it is seen that this ratio of *ca.* 5000 is similar to, and slightly larger than, the analogous factor of *ca.* 1500 obtained in acetolysis of the bromobenzenesulfonates when allowance is made for ion pair return with the *exo*-epimer.[9] As regards the norbornyl acetate which is produced quantitatively from demercuration of both II-OAc and III-OAc, the *exo*-content, estimated vapor-phase chromatographically, is at least 99.7%, just as with the bromobenzenesulfonates.[9,10] While further stereochemical tests[9] have not yet been carried out, the acetate product is considered to arise entirely from the non-classical cation IV in demercuration of the *exo*-mercurial, and mainly from this cation with the *endo*-epimer III.

One difference in the nature of the products from demercuration, on the one hand, and acetolysis of bromobenzenesulfonates, on the other, is in the proportion of hydrocarbon observed. At 25°, the proportion of nortricyclene is *ca.* 0.6% from demercuration of *exo*-II and 4.4% from acetolysis of *exo*-norbornyl bromobenzenesulfonate.[10] The difference is thought to involve ion pair considerations.

In the case of oxymercurials from oxymercuration of olefins, treatment of the β-oxyalkylmercuric acetates with perchloric acid in acetic acid tends to give deoxymercuration instead of demercuration. However, with some oxymercurials. such as *cis*-2-methoxycyclohexylmercuric acetate[11a] or *exo-cis*-oxymercurials from norbornene.[11b] demercuration can be made to dominate largely over deoxymercuration by use of low concentrations of perchloric acid catalyst.

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[6] K. Ichikawa and H. Ouchi, *J. Am. Chem. Soc.*, **82**, 3876 (1960).

[7] F. R. Jensen and R. J. Ouellette, *ibid.*, **83**, 4477, 4478 (1961).

[8] Correct carbon, hydrogen and mercury analyses were obtained for the indicated new compounds.

[9] (a) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1127 (1952); (b) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1154 (1952); (c) A. Colter and E. Clippinger, unpublished work.

[10] E. Vogelfanger, unpublished work.

[11] (a) C. Anderson, unpublished work; (b) K. C. Pande, unpublished work.