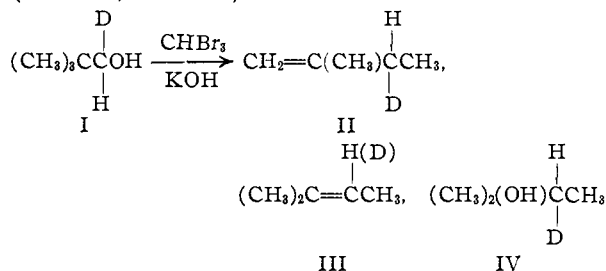
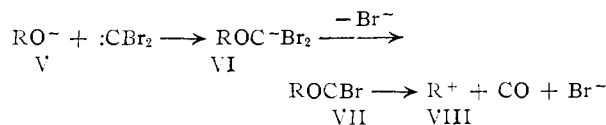


Hine and co-workers⁴ and applied to neopentyl alcohol by Skell, Starer and Krapcho.⁵ From this reaction was isolated a mixture of 2-methyl-1-butene-3-*d* (II, 31% yield), 2-methyl-2-butene-3-*d* (III, 14% yield), 2-methyl-2-butanol-3-*d* (IV, 3% yield) and unreacted neopentyl alcohol-1-*d* (2.2 g., 24% recovery), acid phthalate [α]^{25D} -1.10 ($C = 9$, acetone). The rotation of the rear-



ranged 2-methyl-1-butene-3-*d* (II) was $\alpha^{25D} +1.22 \pm 0.02$ ($l = 2$, neat), after purification by gas chromatography on a 300-cm. Ucon polar column in a Megachrome. Its retention time, infrared spectrum and n.m.r. spectrum were as expected for 2-methyl-1-butene-3-*d*.

Integration of the n.m.r. spectrum of the starting neopentyl alcohol-1-*d* indicated 1.00 ± 0.05 deuterium atoms per molecule in the one position; that of the 2-methyl-1-butene-3-*d* indicated 0.97 ± 0.05 deuterium atoms per molecule in the three position. There can be no doubt that this material owes its optical activity to a stereospecific rearrangement resulting in optically active olefin by virtue of isotopic substitution. The mechanism proposed for this reaction⁶ postulates the formation of an intermediate carbonium ion, VIII, resulting from the decomposition of VII, which in turn is formed by the reaction of the alkoxide ion and dibromocarbene. From our



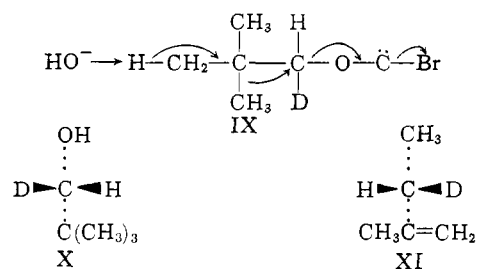
results it is quite apparent that under these basic conditions a carbonium ion, as a free entity, is not formed as the sole intermediate.⁷ Previous evidence^{5,8} has discounted the formation of a protonated cyclopropane intermediate in this rearrangement and the present evidence is also incompatible with such an interpretation. It was suggested⁴ that some of the steps represented by $\text{V} \rightarrow \text{VIII}$ might be concerted and our results support this view. A proposed concerted transition state is represented by IX for the formation of 2-methyl-1-butene-3-*d*. This represents the decomposition of VII; it might be represented just as readily for VI with the simultaneous loss of two bromide ions. This concerted transition state not only would explain the stereospecificity of the

(5) P. S. Skell, I. Starer and A. P. Krapcho, *J. Am. Chem. Soc.*, **82**, 5257 (1960).

(6) P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959).

(7) This does not exclude such an open carbonium ion under neutral or acid conditions. Preliminary experiments indicate that the *t*-amyl alcohol obtained from treatment of optically active neopentyl iodide-1-*d* with aqueous silver nitrate is optically inactive.

(8) G. F. Karabatsos and J. D. Graham, *J. Am. Chem. Soc.*, **82**, 5250 (1960).



reaction but also the isomer ratio of about 2.3:1 in favor of the thermodynamically less stable olefin, 2-methyl-1-butene, as compared to a ratio of about 1:7 in favor of 2-methyl-2-butene in the acid catalyzed dehydration of *t*-amyl alcohol.⁹ Not only are there nine equivalent hydrogens on the *gamma* carbon atoms versus two on the *alpha*, but the approach of the hydroxide ion to the position farthest removed from the leaving bromide ion would be the pathway of lowest energy.

The S absolute configuration,¹⁰ X, has been assigned to the starting neopentyl alcohol-1-*d*. The mechanism represented by IX presumes that inversion occurs on the isotopically substituted carbon atom during the rearrangement. On this basis we predict that the (+)-2-methyl-1-butene-3-*d* will have the absolute S configuration XI. Synthesis of XI by a method which will independently establish its absolute configuration and that of the related *t*-amyl alcohol is in progress.

(9) F. C. Whitmore, C. S. Rowland, S. N. Wrenn and G. W. Kiltner, *ibid.*, **64**, 2970 (1942).

(10) Designation of R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

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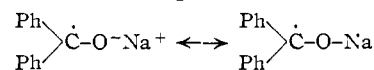
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RECEIVED OCTOBER 2, 1961

THE SOLVENT EFFECT ON SPECIFIC CATION-ANION INTERACTION. SPECTRA OF THE ALKALI KETYLs.

Sir:

We have found that the position of the visible band of the spectrum of sodium benzophenone (ketyl) (I) varies among a series of non-polar sol-



vents in a pronounced fashion. Carter, McClelland, and Warhurst¹ recently have reported the same observation for a single pair of solvents, as well as the observation, which we confirm, that there is also a large effect of the nature of the cation on the position of the same band. The variations are considerably more pronounced than the variations of the $n \rightarrow \pi^*$ transition of cyclohexanone among the same solvents. The table contains the pertinent data. The ketyl band under consideration is a broad, structureless band, centered in the neighborhood of 6500 Å. The shape of the band and the width at half height, 11.1 ± 0.3 kcal./mole, are invariant with solvent.

On the basis of considerations of the shifts due to changes in the metal ion, the effects of substituents,

(1) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455, (1960); see also B. J. McClelland, *ibid.*, **57**, 1458 (1961).

TABLE I
SOLVENT EFFECTS ON ELECTRONIC TRANSITIONS OF KETYL
AND CYCLOHEXANONE

Solvent	E_T ketyl, ^{a,b} kcal./mole	E_T cyclo- hexanone, ^a kcal./mole
<i>n</i> -Butyl ether	45.4	98.7
Diethyl ether	45.1	98.7
1,1-Dimethoxyethane	44.4	99.1
1,4-Dioxane	44.3	99.1
Tetrahydrofuran	42.1	99.1
1,2-Dimethoxyethane	40.7	99.6
Benzene	45.4	99.0
Triethylamine	45.4	...
<i>tert</i> -Butylamine	43.0	99.2
<i>n</i> -Propylamine	41.9	98.0
Pyridine	40.2	...
1,4-Dioxane (Li ⁺) ^c	46.0	
1,4-Dioxane (Na ⁺) ^c	44.3	
1,4-Dioxane (K ⁺) ^c	41.7	

^a Energy of transition at room temperature. The limits of accuracy are estimated at ± 0.2 kcal./mole. ^b Unless otherwise noted, the ketyl in question is that derived from sodium and benzophenone. ^c From reference (1).

the extinction coefficient (*ca.* 7000 at the maximum),² and the orbital energies of benzophenone,³ we concur with Carter, McClelland, and Warhurst in the tentative assignment of the transition as a $\pi \rightarrow \pi^*$ transition of the radical-anion.

The latter authors extrapolated E_T (energy of transition) to infinite cation radius, and found a residual solvent shift of the same order of magnitude as that observed in the actual experiments. This implies that the ketyl solvent shifts are due primarily to interactions of the radical-anion with the solvent. The extrapolations mentioned are long and are based on an assumed form of dependence of E_T on the crystal radius of the metal ion. If the solvent shifts are due primarily to interactions between the radical-anion and the solvent, one reasonable theory for their origin would invoke the Franck-Condon principle and the loss of solvation energy in attaining the excited state, as in the theory of McConnell concerning $n \rightarrow \pi^*$ transitions.⁴ On this basis, the shifts in the ketyl spectrum due to solvent variation ought to parallel the shifts in the $n \rightarrow \pi^*$ transitions of ketones in the same solvents. In the case of cyclohexanone, for which the $n \rightarrow \pi^*$ transition correlates well with Kosower's Z values,⁵ there is little correlation with the ketyl shifts, except that among the ethers the trends are in *opposite* directions, that is, ethers which increase the energy of the $n \rightarrow \pi^*$ transition of cyclohexanone decrease the energy of the ketyl transition under consideration.

As an alternative hypothesis, we propose that the ketyl solvent shifts reflect variations in the detailed structures of the associated ionic species. Ionic association must be pronounced in these solvents,⁶ and the detailed structure of the ionic aggregates

(2) H. E. Bent and A. J. Harrison, *J. Am. Chem. Soc.*, **66**, 969 (1944).

(3) As constructed from the data of D. S. McClure and P. L. Hanst, *J. Chem. Phys.*, **23**, 1772 (1955).

(4) H. McConnell, *ibid.*, **20**, 700 (1952).

(5) E. M. Kosower and G. S. Wu, *J. Am. Chem. Soc.*, **83**, 3142 (1961). See also E. M. Kosower, *ibid.*, **80**, 3253 (1958), and later papers of the series.

ought to be expected to vary with the detailed structure of the solvent, since the molecules of the various solvents must, by virtue of their structural differences (consider 1,1-dimethoxyethane and 1,2-dimethoxyethane), possess varying capacities and varying steric requirements in solvating ions and ionic aggregates. The data are accounted for on the basis of the hypothesis that the energy of the ketyl transition is sensitive to the magnitude of the electric field, due to the cation, which the radical-anion experiences. The strength of the field experienced by the radical-anion depends on the detailed structure of the ionic aggregate (related to the radii and geometric disposition of the ions) and the degree of dispersion of the cationic charge by solvation.⁷ These effects are no doubt intimately related, and probably parallel one another. The direction of the solvent effect on the ketyl spectrum, considered together with the direction of the cation effect, suggests that in 1,2-dimethoxyethane ionic dissociation and/or charge dispersion through solvation is present to a greater degree than in diethyl ether. This is in accord with qualitative observations.⁸

A host of solvent effects on kinetics and products recently have been reported for systems in which ionic aggregation must be important.⁹⁻¹⁴ It appears that the ketyl spectra may provide an index to such behavior for solvents of the type studied here, and possibly a quantitative one, in view of the success of the correlations of Kosower,⁵ which are based on similar spectral effects.

Acknowledgment.—This work was supported by Office of Ordnance Research Contract DA-04-495-ORD-1542 and Army Research Office (DURHAM) Grant DA-ARO(D)-31-124-G118.

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RECEIVED NOVEMBER 3, 1961

(6) Inasmuch as the unpaired electron of alkali benzophenone ketyls in 1,2-dimethoxyethane are split in the ESR spectrum by the metal nucleus, there can be no doubt that at least some intimate association occurs. See F. C. Adam and S. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).

(7) Another manner in which the solvent might affect the detailed structure of the associated ions involves an effect of solvent on the relative contributions of ionic and covalent structures to the structures of **I**. Such effects have been recently discussed by R. W. Taft, Jr., R. E. Glick, I. C. Lewis, I. Fox, and S. Ehrenson, *ibid.*, **82**, 756 (1960), and by others cited therein.

(8) For example, (a) sodium adds to naphthalene readily in 1,2-dimethoxyethane or dimethyl ether, but does not in diethyl ether, N. D. Scott, J. F. Walker, and V. L. Hansley, *ibid.*, **53**, 2442 (1936); (b) disodium tetraphenylethylene is soluble in diethyl ether, but the dipotassium compound is not, H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936); on the other hand, the dipotassium compound is readily soluble in 1,2-dimethoxyethane, R. S. Cole, unpublished observations from this laboratory. The formation of vinyl Grignard reagents in tetrahydrofuran but not in diethyl ether (H. Normandt, *Compt. rend.*, **239**, 1310 (1954)) also correlates with the spectral data.

(9) D. J. Cram, L. L. Mateos, F. Hauck, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959), and earlier papers of the series.

(10) D. J. Cram, C. C. Kingsbury, and B. Rickborn, *ibid.*, **81**, 5335 (1959).

(11) D. J. Cram, B. Rickborn, and G. R. Knox, *ibid.*, **82**, 6412 (1960).

(12) H. D. Zook and T. J. Russo, *ibid.*, **82**, 1258 (1960).

(13) H. E. Zaugg, *ibid.*, **83**, 837 (1961).

(14) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).