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THE CHEMISTRY OF DERIVATIVES OF 2-BENZAL-1-TETRALONE.[1] IV.

ELIMINATION-REARRANGEMENT REACTION OF 2-BROMO-2-BENZYL-1-TETRALONE

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A previous communication in this series reported upon the isolation of 2-benzyl-1-naphthol (III) from the morpholine promoted elimination-rearrangement reaction of 2-bromo-2-benzyl-1-tetralone (I)[2]. It was thought that under relatively mild acid conditions it might be possible to isolate the intermediate 2-benzyl-1-keto-1,4-dihydronaphthalene (II). Reaction for 2 hours at 90.6° of 0.5 g. of I and 1.0 g. of tetraethylammonium bromide in 10 ml. of acetonitrile[3], evaporation to dryness and ether extraction yielded 0.34 g. of material, m.p. 62-72°. The infrared spectrum indicated it to be 2-benzyl-1-naphthol (III) contaminated with a little unreacted I. Recrystallization from methanol gave pure III, m.p. 70-72°, with infrared and ultraviolet spectra superimposable upon those for an authentic sample[2]. In an attempt to avoid any acid catalyzed rearrangement the above experiment was repeated in the presence of 0.18 g. of the sterically hindered base

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[1] For paper III in this series see A. Hassner and N. H. Cromwell, J. Amer. Chem. Soc. 80, 901 (1958).

[2] A. Hassner, N. H. Cromwell and S. J. Davis, J. Amer. Chem. Soc. 79, 230 (1957).

[3] D. N. Kevill and N. H. Cromwell, J. Amer. Chem. Soc. 83, 3812 (1961).

2,6-dimethylpiperidine; obtained was an 81% yield of III identified by its m.p. and infrared spectrum. It appears that the intermediate II readily undergoes aromatization under either acid or basic conditions.

It was found that the velocities of acid production and of bromide ion production were identical, with a first order dependence upon the concentration of I and of bromide ion.

Table 1

Initial second order rate coefficients, k_2, in the reaction of 2-benzyl-2-bromo-1-tetralone with tetraethlammonium bromide in acetonitrile at various temperatures.

t°C	40.5	74.0	91.9
$10^3 k_2$ [a]	0.32	8.6	40.6

[a] Mean values of several determinations; in l mole^{-1} sec^{-1}. $k_2 = Ae^{-E/RT}$; $A=10^{11.4}$ l mole^{-1} sec^{-1}; E=21.3 Kcal/mole

The values for the second order rate coefficients are very close to those previously reported for dehydrobromination under identical conditions, of 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (IV) to give the endocyclic α,β-unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (V)[3], suggesting that endocyclic α,β-unsaturated ketone formation is rate determining in both reactions; aromatization of V involves a methyl shift which is achieved only by rigorous conditions such as treatment with acetic anhydride-sulfuric acid.[4] Although frequency factor considerations favor I, bromotetralone IV reacts faster due to a move favorable activiation energy of 19.7 kcal/mole. In IV there is $CH_3—C_4—C_2—Br$ (pseudo axial-axial) interaction[5], absent in

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[4] A. Hassner and N. H. Cromwell, J. Amer. Chem. Soc. 80, 893 (1958).

[5] N. H. Cromwell, R. P. Ayer and P. W. Foster, J. Amer. Chem. Soc. 82, 130 (1960).

bromotetralone I, which is relieved by elimination of bromide ion.

Bunnett, Davis and Tanida[6] have recently questioned the mechanism of merged substitution and elimination as put forward by Winstein et al;[7] however, their manuscript was written prior to the publication of a communication[8] in which we proposed a new type of merged mechanism in connection with our studies of eliminations with certain α-halogenated ketones. Briefly the mechanism, especially applicable to reactions involving an easily ionizable carbon-halogen bond in RX proposes the formation of an intermediate involving the attacking nucleophile and the R^+ entity with however possible retention of weak binding to the outgoing X^- entity. The intermediate can then either collapse to substitution products or alternatively the nucleophile can abstract a β-proton. This mechanism was subsequently discussed in greater detail[9] and it was suggested that the abnormally large rate for elimination from t-butyl chloride, as promoted by thiophenoxide ions in solvent ethanol[10] was in accord with the reaction following this type of merged mechanism.

Bunnett, Davis and Tanida[6] have similarly found that thioethoxide is more effective than methoxide in promoting elimination from tertiary chlorides. In considering their reactions to be E2 in character they assumed that mercaptide reagents, although weaker bases thermodynamic-

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[6] J. F. Bunnett, G. T. Davis and H. Tanida, J. Amer. Chem. Soc. **84**, 1606 (1962).

[7] S. Winstein, D. Darwish and H. J. Holness, J. Amer. Chem. Soc. **78**, 2915 (1956).

[8] D. N. Kevill and N. H. Cromwell, Proc. Chem. Soc. 252 (1961).

[9] D. N. Kevill and N. H. Cromwell, J. Amer. Chem. Soc. **83**, 3815 (1961).

[10] P. B. D. DeLaMare and C. A. Vernon, J. Chem. Soc. **41** (1956).

ally, are stronger bases in the kinetic sense than alkoxide ions. In attempting to justify this assumption, they suggest that the thermodynamic affinity of the thiophenoxide ion for carbon parallels that for hydrogen. The study upon which this suggestion was based[11] was carried out in a protic solvent and, as Parker pointed out,[12] such results are misleading, since solvation superimposes an hydrogen basicity effect upon the carbon basicity. More recently Miller[13] has shown that in 95% ethanol the carbon basicity of a thiol anion is more than 10^4 times as great as its hydrogen basicity.

The low values, approximately 2.5, obtained[6] for the deuterium isotope effect in bimolecular eliminations from α,α-dimethylphenethyl chloride show that the extent of C-X breaking in the transition state is greater than the extent of C-H breaking. Such a state of affairs is, of course, an integral part of the merged mechanism as we envisage it. The merged mechanism differs from the modified E2 mechanism of Bunnett et al in that they suggest that the nucleophile (base) attacks directly at the β-hydrogens, but through a scheme in which considerable weakening of the carbon-halogen bond has occurred, while we suggest that the developing dipole is favorable for approach of the nucleophile towards the α-carbon such that the nucleophile assists in the development of the dipole, by what is essentially an SN2 process, prior to its attack being diverted towards a β-proton; such diversion is favored by the large degree of steric hindrance present in tertiary structures. The merged mechanism logically explains the rate dependence upon nucleophilicty rather than upon basicity and it incorporates an initial attempt by the nucleophile to approach towards the positively charged carbon of the developing dipole, which for a strong nucleophile seems more probable than a direct attack at a relatively uncharged hydrogen atom.

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[11] J.F. Bunnett, C.F. Hauser and K.V. Nahabedian, Proc. Chem. Soc. 305 (1961).

[12] A. J. Parker, Proc. Chem. Soc. 371 (1961).

[13] B. Miller, Proc. Chem. Soc. 303 (1962).