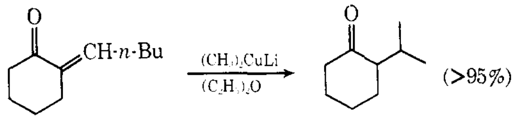

The mechanistic similarity between the reactions of α,β-unsaturated ketones with dissolving metals and dialkylcopper lithium reagents[14] suggested the possibility of effecting a double conjugate addition with the latter. Reaction of dimethylcopper lithium with 2-*n*-butylthiomethylenecyclohexanone in ether at 0° gave, after hydrolytic work-up, a virtually quantitative yield of 2-isopropylcyclohexanone. An attempt to alkylate the enolate intermediate was unsuccessful. This interesting reaction should prove useful for introducing symmetrically branched α substituents, a conversion which proceeds in poor yield by direct alkylation.

A typical procedure for the reduction–alkylation is as follows:[8] a solution of 2-*n*-butylthiomethylenecyclohexanone (1.57 g, 7.93 mmol) and 0.28 g (15.85 mmol) of water in 40 ml of ether is added to a refluxing solution of lithium (0.33 g, 47.6 mg-atoms) in 160 ml of liquid ammonia with stirring over a 30-min period. After an additional 30 min, 80 ml of ether and then a solution of 13.5 g (95.1 mmol) of methyl iodide in 40 ml of ether were added, the latter over a 30-min period. This mixture was allowed to stir for 30 min and the ammonia evaporated. After a standard extractive work-up and removal of the ether by distillation, a yellow liquid was obtained which consisted of methyl *n*-butyl sulfide, 2,2-dimethylcyclohexanone (83%), and 2,2,6-trimethylcyclohexanone (2%), according to glpc analysis using cyclohexanone as internal standard.

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2,2-dimethyl-3-cholestanone in poor yield, for reasons as yet unclear. Further experiments to improve these reactions are intended.

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The Dependence of Solvolytic α-Deuterium Rate Effects on the Nature of the Leaving Group[1]

Sir:

We wish to report experimental observations which confirm and extend earlier theoretical predictions[2] of how the characteristic *maximum* α-deuterium isotope effect on solvolysis rate varies as a function of leaving group. Earlier studies[3,4] on 1-phenylethyl bromide and chloride first indicated that the α-deuterium effect on solvolysis rates was dependent on the nature of the leaving group *even within the same reaction mechanism.* Calculations based on the methyl halides as models[2] indicated that this leaving group dependence was primarily caused by the dependence of *initial state* isotopic zero-point energy differences on the nature of the leaving group. The further conclusion was reached that the isotopic *transition-state* zero-point energy differences in the apparently limiting reactions studied were *not* (within the limits of accuracy involved) dependent on leaving group. The transition states could thus, to a good approximation, be represented as ion pairs R^+X^-, where the force constants of R^+ were independent of the nature of X^-. These calculations allowed the prediction that the maximum isotope effect for a limiting solvolysis of an iodide of $\sim$1.09 would correspond to values of $\sim$1.125 for the bromide and $\sim$1.15 for the chloride if all reactions followed the same mechanism.

During a study of the mechanism of solvolysis of a series of propargyl derivatives it became apparent that 3-pentyne-2-toluenesulfonate, bromide, and iodide would solvolyze in aqueous trifluoroethanol at convenient rates by an apparently limiting mechanism. This series, therefore, provided a convenient way to test the earlier theoretical predictions and, of equal importance, a way to determine the maximum effect for a sulfonate leaving group, a value which could not be predicted accurately from theory.

The solvolysis rates and isotope effects are given in Table I. In the first two horizontal entries it appears from α-*d*, β-d_3, and δ-d_3 effects that the solvolysis of the toluenesulfonate in 60% ethanol may have a slight nucleophilic component. It seems reasonable to conclude, however, that the reaction in 70% trifluoroethanol is very predominantly, if not exclusively, limiting. The α-*d* effect (1.226) is one of the largest observed for the solvolysis of a sulfonate ester and is, within experimental error, the same as that observed for the trifluoroacetolysis of isopropyl-α-*d* toluenesulfonate (1.22 ± 0.02).[5,6] In the fourth entry of Table I it is seen that the bromide has, within very narrow limits, the same β-d_3 and δ-d_3 isotope effects in 70% trifluoroethanol as the toluenesulfonate. The α-*d* effect (1.123) is, however, considerably lower and, strikingly, almost the same as the α-*d* effect (1.122) in the apparently limiting solvolysis of α-phenylethyl bromide in 80% aqueous ethanol.[3] This reinforces the conclusion that the reactions of the three propargyl derivatives in 70% trifluoroethanol are near limiting.

The β-d_3 effect for the iodide in 70% trifluoroethanol (1.283) is very close to that for the bromide (1.280) and toluenesulfonate (1.281) in the same solvent indicating that all three derivatives follow the same mechanism. The α-*d* effect for the iodide in this solvent is 1.089. This compares favorably with the theoretical prediction

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[1] (a) Taken in part from the Thesis of W. Dowd submitted to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree, 1970. (b) Supported in part by a Petroleum Research Fund Fellowship for Graduate Education and Fundamental Research administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. (c) Also supported in part by Grant No. AT(11-1)-1008 from the U.S. Atomic Energy Commission (Document No. COO-1008-13). (d) Electronic computations of rate constants were performed with the facilities of the Indiana University Research Computing Center.

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Table I. Rates and Isotope Effects in Solvolysis of 3-Pentyn-2-yl Compounds

Leaving group	Solvent^a	k_H, sec^{-1} ^{b}	$k_H/k_{\alpha\text{-}d}$^{c}	$k_H/k_{\beta\text{-}d_3}$^{c}	$k_H/k_{\gamma\text{-}d_3}$^{c}
OTs^d	60 E	3.613×10^{-3}	1.213	1.241	1.104
OTs	70 T	8.755×10^{-3}	1.226	1.281	1.109
Br	50 E	1.203×10^{-5}	1.101	1.200	1.081
Br	70 T	8.823×10^{-6}	1.123	1.280	1.108
I	50 E	4.150×10^{-6}	1.087	1.278	
I	70 T	4.666×10^{-6}	1.089	1.283	

^{a} 60 E is 60 vol % ethanol–40 vol % water; 70 T is 70% trifluoroethanol–30% water, etc. ^{b} Errors are of the order of 0.1–0.2%. ^{c} Errors are in the range of 0.2–0.4%. ^{d} *p*-Toluenesulfonate.

of ~1.09 made earlier.[2] The reaction of the iodide in 50% ethanol also seems to be limiting since both *α-d* and *β-d_3* effects are very similar to those in 70% trifluoroethanol. The lower *β-d_3* effects for the bromide (1.200) and toluenesulfonate (1.241) indicate that the reactions for these compounds in the ethanolic solvents are partly nucleophilic.

The products for the solvolysis of these compounds in 70% trifluoroethanol and 50% ethanol are given in Table II. While the amounts of alcohol and ether formed with tosylate and iodide as leaving groups are nearly the same in 70% trifluoroethanol, the products formed with bromide as a leaving group in this solvent are clearly different. Since the tosylate solvolysis is nearly limiting in 60% ethanol, it is possible to compare its solvolysis products in 50% ethanol with those of the limiting reaction with iodide leaving group in this solvent. Again, the amounts of alcohol and ether formed are different with different leaving groups. Since the leaving group should have no influence on products formed from the free carbonium ion,[7–9] it is apparent that the free ion is not an intermediate in all three reactions. Since the large isotope effects indicate little or no covalent attachment in the rate-determining step[2–4,6] the simplest interpretation of these findings is that the rate-determining step is the interconversion of two ion pairs and that the product-forming step is nucleophilic attack on the second-formed ion pair.

Table II. Products of Solvolysis of $CH_3C{\equiv}C{-}CH(X)CH_3$^{a}

X	Solvent^b	% ether	% alcohol
OTs	70 T^c	20.6 ± 2	79.4 ± 3
Br	70 T^c	25.4 ± 2	74.6 ± 3
I	70 T^c	19.2 ± 2	80.8 ± 3
OTs	50 E^d	22.7 ± 2	77.3 ± 3
Br	50 E^d	25.8 ± 2	74.2 ± 2
I	50 E^d	33.2 ± 3	66.8 ± 3

^{a} Analyzed by pmr at 100 MHz. ^{b} 50 E is 50 vol % ethanol–50 vol % water, 70 T is 70% trifluoroethanol–30% water. ^{c} Trifluoroethyl ether, pmr (70 T) δ 1.42 (d, 3, J = 7 Hz, CH_3CH–), 1.83 (d, 3, J = 2.5 Hz, $CH_3C{\equiv}$); alcohol, pmr (70 T) δ 1.39 (d, 3, J = 7 Hz, CH_3CH), 1.80 (d, 3, J = 2.5 Hz, $CH_3C{\equiv}$). ^{d} Ethyl ether, pmr (50 E, $CD_3CH_2ODD_2O$) δ 1.37 (d, 3, J = 7 Hz, CH_3CH–), 1.83 (d, 3, J = 2.5 Hz, $CH_3C{\equiv}C$); alcohol, pmr (50 E, $CD_3CH_2ODD_2O$) within 1 Hz of that given in *c*.

It is also interesting to note that the OTs/Br rate ratio observed for the 3-pentyne-2 compounds (994 in 70 T) is in the range of those found for limiting solvolyses[10,11] (466–5126) of such alkyl groups as *tert*-butyl and α-phenylethyl even though it is now understood that this ratio bears no simple direct relationship to mechanism.[12,13] The fact that the bromide solvolyzed faster than the iodide (Br/I, 2.89 in 50 E and 1.89 in 70 T) is at first sight surprising but the same relationship has been observed by Robertson for other alkyl groups.[14]

It is especially important to recognize the dependence of α-deuterium rate effect on leaving group because it allows one to properly compare *α-d* effects of reactions which involve different leaving groups and to identify subtle shifts in mechanism. In practical terms the comparison between chlorides or bromides and arenesulfonates is of particular importance because many solvolyses of secondary arenesulfonates show *α-d* effects of ~1.15. If these values are incorrectly compared with those from the halides the reactions appear to be limiting. However, comparison with the value of 1.23 indicates that these common secondary sulfonate solvolyses involve some nucleophilic attachment to carbon in the transition state. As indicated before[15] in some of these examples the rate-determining step is the formation of the tight ion pair and in others nucleophilic attack on the tight ion pair. SN2 transition states have such strong nucleophilic attachment to carbon that their *α-d* rate effects are near unity.[16]

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Nuclear Quadrupole Resonance Spectra of Some Alkylaluminum Derivatives[1]

Sir:

In a recent communication[2] we reported a study of the nqr spectrum of $Al_2(CH_3)_6$ which confirmed the bridged structure **1** first suggested by Longuet-Higgins,[3]

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