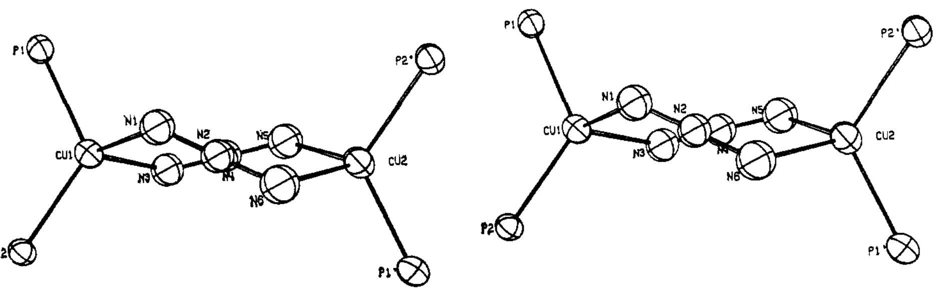


Figure 1. A stereoscopic view of the coordination geometry of the dimeric molecule $[((C_6H_5)_3P)_2CuN_3]_2$.

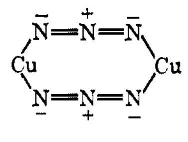
positional, thermal, and scale parameters converged to a final R factor of 6.5% and a weighted R factor of 7.2% for 2628 reflections above σ. The hydrogen atom contributions to the calculated structure factors were included as fixed contributions in the final cycles of refinement.

The structure consists of well-separated dimers, in which the two copper atoms are bridged by the two azide groups through the end nitrogen atoms to form an eight-membered ring. Each copper atom thus possesses a four-coordinate geometry. A stereoscopic view of the coordination geometry of the dimer is presented in Figure 1; selected bond distances and angles are in Table I. The tetrahedral geometry about the Cu atoms exhibits significant distortions as manifested in the large P–Cu–P bond angles.[8]

Table I. Selected Intramolecular Distances and Angles

Distances, Å		Angles, deg	
Cu_1–N_1	2.102 (10)	N_1–Cu_1–N_3	98.0 (4)
Cu_1–N_3	2.085 (10)	N–Cu_2–N	99.7 (4)
Cu_2–N_5	2.109 (11)	P_1–Cu_1–P_2	122.3 (1)
Cu_2–N_6	2.116 (10)	P_1'–Cu_2–P_2'	120.8 (1)
Cu_1–P_1	2.271 (4)	N_1–N_2–N_6	177.0 (1.0)
Cu_1–P_2	2.250 (3)	N_3–N_4–N_5	178.6 (1.1)
Cu_2–P_1'	2.269 (4)		
Cu_2–P_2'	2.266 (3)		
N_1–N_2	1.169 (11)		
N_2–N_6	1.193 (12)		
N_3–N_4	1.179 (13)		
N_4–N_5	1.194 (12)		

The inner coordination of the dimer possesses essentially D_2 symmetry although no crystallographic symmetry conditions are imposed on the structure. As can be seen from the table, all of the N–N distances in the bridging azide groups are equal within experimental error, averaging 1.178 (12) Å, and both N_3^- ions possess an essentially linear structure. The four independent Cu–N bond distances also exhibit structural equivalency and average 2.102 (10) Å. It should be noted that the N–N distances are approximately the same as the corresponding values observed in ionic azides.[2] Hence, we believe that the predominant canonical form describing the ground state structure of the dimer is



As illustrated in the structure, the eight-membered ring formed by the two copper atoms and the two azide groups is not planar. The two azide ions are tilted by 38° with respect to each other and each of the Cu–N_3–Cu bridges deviates quite significantly from planarity. Two factors which may contribute to this unusual geometry are first, packing effects which optimize the efficiency of the packing and minimize the nonbonded repulsions between the phenyl rings, and second, the allenic nature of the middle nitrogen atom which opposes the planarity of the Cu–N_3–Cu bridge.

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[8] For a compilation of the P–Cu–P angle in phosphine complexes of Cu(I) see S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 8, 2755 (1969).

[9] Temple University Fellow, 1969–1970.

Chlorine Kinetic Isotope Effects in Nucleophilic Displacements at a Saturated Carbon

Sir:

We have studied the reactions of various aliphatic and aromatic chlorides with both aromatic and aliphatic oxides and thiooxides in methanol. Product analysis by nmr shows that these second-order nucleophilic displacement reactions result in near-quantitative production of ethers or thioethers along with chloride anion. These reactions have been thought to proceed by way of a concerted transition state[1] symbolized as

$$N: + RCl \longrightarrow [N\sim R\sim Cl] \longrightarrow NR + :Cl$$

We chose to make changes in electron density at N and R (when R = benzyl) in order to determine if the chlorine leaving group kinetic isotope effects offered a valid probe for studying subtle changes in transition-state geometry. We believe that these effects may provide a highly informative test of our concepts of transition-state structure and may also suggest the relative importance of the factors thought to be involved in determining the nucleophilic power of the attacking group.

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 310.

Table I. Rates and Chlorine Kinetic Isotope Effects for Reactions of *para*-Substituted Benzyl Chlorides (0.025 *M*) with Thiophenoxide (0.025 *M*) and Methoxide[a]

		Substituents		
	Nucleophiles	OMe	H	NO_2[b]
k^c	$C_6H_5S^-$	8.2×10^{-2}	1.3×10^{-2}	7.6×10^{-2}
k_{35}/k_{37}		1.0098	1.0095	1.0092
k^c	CH_3O^-	First order[d]	1.2×10^{-5} [e]	2.0×10^{-5} [e]
k_{35}/k_{37}		1.0088	1.0080	1.0076

[a] In methanol at 20° with added 0.25 *M* $LiOCH_3$. [b] Less than 4% stilbene is formed in the methoxide reaction and none in reaction with the thiophenol anion. [c] M^{-1} sec^{-1}. [d] The rate was 1.7×10^{-4} sec^{-1}. [e] The competitive first-order solvolysis was negligible.

Table II. Rates and Chlorine Kinetic Isotope Effects for the Reactions of *p*-Nitrobenzyl Chloride (0.025 *M*) and *n*-Butyl Chloride (0.025 *M*) with Thiophenoxide (0.025 *M*) and *n*-Butylthiol Anion (0.025 *M*)[a]

		Nucleophiles	
	Substrates	$C_6H_5S^-$	n-$C_4H_9S^-$
k^b	$O_2NC_6H_4CH_2Cl$[c]	7.6×10^{-2}	10.0×10^{-2}
k_{35}/k_{37}	(at 20°)	1.0092	1.0087
k^b	C_4H_9Cl	2.3×10^{-4}	3.1×10^{-4}
k_{35}/k_{37}	(at 40°)	1.0084	1.0081

[a] In methanol (0.25 *M* in $LiOCH_3$). [b] M^{-1} sec^{-1}. [c] No substituted stilbenes were formed.

with the alteration of the relative importance of bond breaking and bond making in the transition state as the *para* substituent is changed from more electron donating to more electron withdrawing.[7] The isotope effect data shown for each reaction are consistent with this explanation since a greater chlorine isotope effect should be observed where bond breaking is more complete in the transition state and are consistent with Thornton's[3] prediction that increasing the electron density on the central carbon atom will result in a weaker carbon–chlorine transition-state bond.

If we alter the nucleophile but leave the attacking atom of the nucleophiles unchanged we obtain the data of Table II. In this case the basicity of the nucleophiles can be used as a rough measure of their relative nucleophilic power. Because the aliphatic thiooxide is more basic, it should be the stronger nucleophile and lead to larger relative rate constants. The smaller observed chlorine isotope effects for both reactions indicate that the stronger nucleophile does yield a transition state where carbon–chlorine bond breaking has not proceeded as far as with a weaker nucleophile. This observation is consistent with the predictions of Thornton[3] and also with those derived from the Hammond postulate where a stronger nucleophile is predicted to produce a more reactant-like transition state.

Table III. Rates and Chlorine Kinetic Isotope Effects for Reactions of *p*-Nitrobenzyl Chloride (0.025 *M*) and *n*-Butyl Chloride (0.025 *M*) with Various Oxides and Thiooxides[a]

		Nucleophiles			
	Substrates	CH_3O^-	n-$C_4H_9S^-$	$C_6H_5O^-$	$C_6H_5S^-$
k^b	$O_2NC_6H_4CH_2Cl$	2.0×10^{-5}	1.0×10^{-1}	8.0×10^{-6}	7.6×10^{-2}
k_{35}/k_{37}	(at 20°)	1.0076	1.0087	1.0079[c]	1.0092
k^b	C_4H_9Cl	9.6×10^{-7}	3.1×10^{-4}		
k_{35}/k_{37}	(at 40°)	1.0074	1.0081		

[a] In methanol (0.25 *M* $LiOCH_3$). [b] M^{-1} sec^{-1}. [c] The kinetic isotope effect here is complicated by a 20% reaction with $^-OCH_3$, and the value before correction for this complication was 1.00785.

As Hill and Fry[2] observed from their studies of SN1 and SN2 reactions, the chlorine kinetic isotope effect is larger for reactions involving greater carbon–chlorine bond breaking in the transition state. The more subtle changes in reactant and nucleophile and their effects on the transition-state geometry have been predicted by Thornton.[3] These predictions served as an initial test of the leaving group isotope effect.

The chlorine kinetic isotope effects of these reactions were determined by the competitive reaction rate technique.[4] The chlorine isotope abundance ratios were measured with a Nuclide (Model RMS-6-60) isotope ratio mass spectrometer as described by Taylor and Grimsrud[5] with minor modifications. A precision of one part per 10,000 was routinely obtained for the isotope effect measurement, allowing small differences to be detected. Rate constants were determined by both polarography and titration of aliquots with Ag^+ using a silver wire electrode.

Some rate constants and chlorine kinetic isotope effects (k_{35}/k_{37}) are given in Table I. These data show a rate minima for the unsubstituted benzyl chloride similar to that observed by others.[6] This is in accord

Because the leaving group isotope effects did give agreement with the predictions and conclusions of others, it was of interest to see if the relative isotope effects might also be used as a criterion for determining the relative nucleophilicities of more diverse types of attacking species. Some of these data are shown in Table III.

The rate constants for the reactions of both substrates indicate that the thiooxides are much more reactive than the oxides and, on this basis, thiooxides would have to be considered better nucleophiles than oxides. The oxide nucleophiles, however, result in consistently lower chlorine kinetic isotope effects than do the thiooxides, and this would seem to imply that the oxides are the stronger nucleophiles. To examine this apparent contradiction, we must consider the factors which control the reaction rate of the nucleophile.

Basicity, polarizability, and solvation effects on the nucleophile[8] are thought to be the factors influencing the relative reaction rates for the type of nucleophiles we have used here. The first two factors, basicity and polarizability, should also affect the structure of the transition state (and, therefore, the chlorine kinetic

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(2) J. W. Hill and A. Fry, *J. Am. Chem. Soc.*, **84**, 2763 (1962).

(3) E. R. Thornton, *ibid.*, **89**, 2915 (1967).

(4) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 36 (1958).

(5) J. W. Taylor and E. P. Grimsrud, *Anal. Chem.*, **41**, 805 (1969).

(6) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962).

(7) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73**, 2813 (1951).

(8) C. A. Bunton, "Nucleophilic Substitutions at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 75.

isotope effect). The third factor, the solvation of the nucleophile, would, however, affect mainly the reaction rate and not the transition-state structure because the desolvation would be expected to occur prior to the transition state. This desolvation energy would be expected to be much greater for the oxygen nucleophiles than for the sulfur nucleophiles since stronger hydrogen bonds to oxygen are well known, apparently due to oxygen's small size and greater electron density. Therefore, this "deshielding" of an unshared pair of electrons on the nucleophile might be expected to retard the reactivity of the oxides much more than that of the thiooxides. This conclusion is supported by the data of others[9, 10] where the solvent was varied and may explain why the relative reaction rates of oxygen- and sulfur-containing nucleophiles do not parallel the isotope effect data. The polarizability of the nucleophile would lead to a conclusion which does not fit the observed kinetic isotope effects, and this suggests that polarizability may not be a dominant factor in these reactions. Because the oxides are more basic than the corresponding thiooxides, however, we would predict that the oxides would be more nucleophilic, once desolvation has occurred. This explanation does fit the observed isotope effects. Our initial results, therefore, suggest that the great speed of many displacement reactions involving large atom nucleophiles in protic solvents may not be due so much to their polarizability as to their ease of desolvation, and that the leaving group isotope effects provide a probe for distinguishing between the two. These results are also consistent with the operation of a concerted transition state as opposed to an intermediate ion-pair mechanism such as proposed by Sneen and Larsen[11, 12] for other reactants and solvents.

If these initial conclusions are substantiated by further experiments and are not found to be unduly complicated by the intervention of specific solvation of substituents,[13] specific solvation of the leaving group, or mass effects upon changing the nucleophile, the kinetic isotope effects of leaving groups may result in one of our more powerful yet subtle probes for transition-state geometry. We propose to explore these possible complications further.

Acknowledgment. This research was supported in part by National Science Foundation Grant GP-8369 and the Wisconsin Alumni Research Foundation.

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(9) S. Winstein, L. G. Savedoff, S. Smith, I. P. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, No. 9, 24 (1960).

(10) R. F. Rodewald, K. Mahendran, J. L. Bear, and R. Fuchs, *J. Am. Chem. Soc.*, 90, 6698 (1968).

(11) R. A. Sneen and J. W. Larsen, *ibid.*, 91, 362 (1969).

(12) R. A. Sneen and J. W. Larsen, *ibid.*, 91, 6031 (1969).

(13) R. Alexander, E. C. F. Ko, A. J. Porker, and T. J. Broxton, *ibid.*, 90, 5049 (1968).

(14) Graduate School Fellow, Summer, 1968; NDEA Fellow, 1968–1970.

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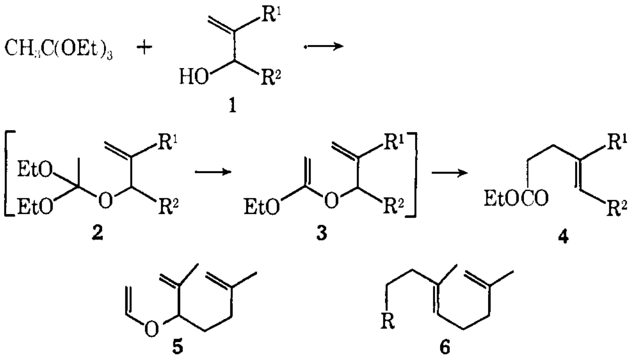
A Simple Stereoselective Version of the Claisen Rearrangement Leading to *trans*-Trisubstituted Olefinic Bonds. Synthesis of Squalene

Sir:

We wish to disclose a version of the Claisen rearrangement which is highly stereoselective and can be applied to the synthesis of *trans*-trisubstituted olefinic bonds. The method simply involves heating an allylic alcohol, **1**, with excess ethyl orthoacetate in the presence of a trace of weak (*e.g.*, propionic) acid. Evidently a mixed orthoester, **2**, is first formed and loses ethanol to form the ketene acetal **3** which rearranges to the olefinic ester **4**.[1]

As compared with the classical pyrolysis of simple vinyl ethers (**3** with H in place of EtO), this orthoester process is simpler to perform (one instead of two operations), and the overall yield as well as stereoselectivity is higher. The high stereoselectivity is probably attributable to nonbonded interactions between the ethoxy and R^2 groups (**3**) that develop only in the transition state leading to *cis* product.[2]



Thus the alcohol **1** (R^1 = Me, R^2 = $CH_2CH_2C(Me){=}CH_2$), on heating with 7 equiv of ethyl orthoacetate and 0.06 equiv of propionic acid at 138° for 1 hr under conditions for distillative removal of ethanol, was converted into the diene ester **4** (R^1 = Me; R^2 = $CH_2CH_2C(Me){=}CH_2$) in 92% yield (distilled[3] at <5 mm). Analysis by vpc indicated that this product consisted of >98% *trans* and <2% *cis* isomer. This result is to be compared with the vinyl ether approach: the alcohol **1** (R^1 = Me; R^2 = $CH_2CH_2C(Me){=}CH_2$) was converted by reaction with ethyl vinyl ether and mercuric acetate[4] into the vinyl ether **5** (60% yield after distillation[3] from sodium at 20 mm) which was heated at 83–98° for 61 hr, giving the aldehyde **6** (R = CHO) in 98% yield. Analysis by vpc indicated that this product contained 86% *trans* and 14% *cis* isomer. The essentially pure *trans* aldehyde **6** (R = CHO), on the other hand, can be obtained readily in 80% (distilled[3] at <0.5 mm) yield by reduction of the aforementioned diene ester with excess lithium aluminum hydride in ether at 0° (giving **6**, R = CH_2OH) followed by oxidation with 4 equiv of filtered Collins solution[5] in the presence of Drierite.

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(1) We have found also that an analogous stereospecific reaction occurs on heating 1-dimethylamino-1,1-dimethoxyethane [A. E. Wick, D. Felix, K. Steen, and A. Eschenmoser, *Helv. Chim. Acta*, 47, 2425 (1964)] with an allylic alcohol giving the pure *trans* olefinic amide in practically quantitative yield, *e.g.*, 1 (R^1 = Me; R^2 = $CH_2CH_2C(Me){=}CH_2$) → 6 (R = $CONMe_2$). The amino acetal is a precursor of and is easier to prepare than 1-dimethylamino-1-methoxyethylene which has formerly been used for Claisen rearrangements [D. Felix, K. Gschwend-Steen, A. E. Wick, and A. Eschenmoser, *Helv. Chim. Acta*, 52, 1030 (1969)].

(2) *Cf.* C. L. Perrin and D. J. Faulkner, *Tetrahedron Letters*, 2783 (1969), and ref 3b,d,e, 4, and 5 cited therein.

(3) Evaporative bulb-to-bulb distillation using a Büchi kugelrohrofen.

(4) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, 79, 2828 (1957).

(5) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Letters*, 3363 (1968).