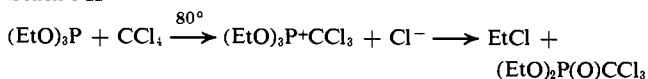


and free radical initiators, the reaction proceeds *via* the heterolytic mechanism shown in Scheme II. In the

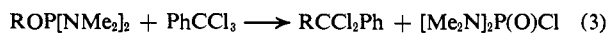
Scheme II



phosphorodiamidite system we favor a nucleophilic attack of phosphorus on halogen rather than on the central carbon.⁶ In addition to the preponderance of product presumably derived from the trichloromethyl anion (which was not observed in the phosphite reaction) the following observations support this contention. No detectable reaction occurs when I is mixed with chloroform or methylene chloride even after several hours at 40°. These compounds should be more susceptible to nucleophilic attack at carbon by the phosphorus since the steric demands are reduced. These observations are, however, in accord with attack at halogen since increasing the number of halogens should stabilize the resulting carbanion by an inductive effect.

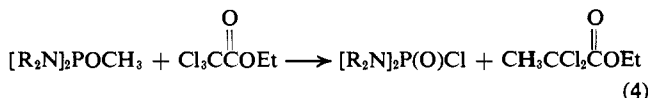
Although a radical pathway may not be rigorously excluded, we detect no products, such as hexachloroethane, which would be expected if a radical process were operative. In addition, no CIDNP signals were observed when the reaction was carried out in the probe of a nmr spectrometer.

In order to investigate the generality of the reaction we have utilized some other polyhaloalkanes. Trichloroethane fails to react, but 1,1,1-trichlorotoluene reacts slowly with I (R = CH₃) to give excellent yields (>80% isolated) of 1,1-dichloro-1-phenylethane (eq 3).



Approximately 2 hr is required for the reaction to go to completion when run at room temperature. This compound was identified by comparison with an authentic sample synthesized by treatment of acetophenone with phosphorus pentachloride. A similar reaction with I (R = PhCH₂) yielded 83% of 1,1-dichloro-1,2-diphenylethane and ~5% of benzyl chloride. The possibility of resonance stabilization of the α,α -dichlorobenzyl anion apparently enhances the reactivity of the trichlorotoluene as compared to that of the trichloroalkanes. Since 1,1-dichloro-1-phenyl alkanes should be readily hydrolyzed to the corresponding ketones, this reaction may prove to be of considerable synthetic utility. It is also interesting to note that the dichlorodiphenylethane is a possible precursor of diphenylacetylene, which is not conveniently synthesized by other means.⁸ This method may allow a novel and convenient synthesis which, depending upon the availability of the appropriate benzyl alcohol, would yield substituted diphenylacetylenes.

A reaction of I (R = CH₃) with ethyl trichloroacetate yields 89% of ethyl 2,2-dichloropropanoate (eq 4). A



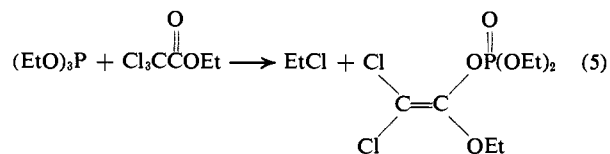
95% yield of ethyl 2,2-dichloro-3-phenylpropanoate was observed upon reaction of I (R = PhCH₂) with ethyl

(6) This proposal has previously been suggested by Miller⁷ to rationalize the reactions of trialkyl phosphites with carbon tetrachloride.

(7) B. Miller, *Top. Phosphorus Chem.*, **2**, 167 (1965).

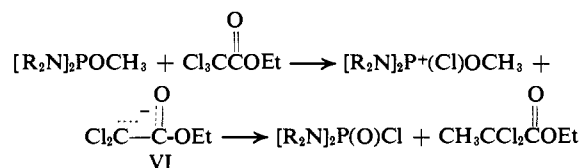
(8) R. H. Mitchell, *J. Chem. Soc., Chem. Commun.*, 955 (1974).

trichloroacetate. Only trace amounts of the alkyl halide (methyl chloride and benzyl chloride, respectively) are observed in these experiments. Surprisingly, we see no evidence for the vinyl phosphate analog normally observed in reactions between trivalent phosphorous compounds and α -halocarbonyl compounds (Perkow reaction)⁹ (eq 5). The reaction observed is best ra-



tionalized by involving a nucleophilic attack of phosphorus on one of the α -halogens of ethyl trichloroacetate generating a phosphonium ion and the resonance stabilized anion, VI, followed by alkylation of the anion and formation of the phosphoryl bond (Scheme III).

Scheme III



We are currently extending our investigation to include a wide variety of phosphorodiamidites and also other polyhalogen compounds. The results of these studies will be published in a subsequent paper.

(9) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

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Do SN2 Reactions Go through Ion Pairs? The Isotope Effect Criterion¹

Sir:

It has been suggested^{2f} that SN2 reactions³ go through ion pairs² and that in borderline³ solvolyses the competing SN1 and SN2 processes occur through common intermediates. This suggestion has been criticized recently.⁴⁻⁸

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) (a) A. Weiner and R. A. Snee, *J. Amer. Chem. Soc.*, **87**, 287, 292 (1965); (b) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965); (c) A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, **87**, 3686 (1965); (d) R. A. Snee and J. W. Larsen, *ibid.*, **88**, 2593 (1966); (e) R. A. Snee, J. V. Carter, and P. S. Kay, *ibid.*, **88**, 2594 (1966); (f) R. A. Snee and J. W. Larsen, *ibid.*, **91**, 362, 6031 (1969); (g) J. A. Cramer and J. G. Jewett, *ibid.*, **94**, 1377 (1972); R. A. Snee, *Accounts Chem. Res.*, **6**, 52 (1973).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 315, 353, 360.

(4) D. J. Raber, I. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4821 (1971); D. J. Raber, J. M. Harris, and P. v. R. Schleyer, *ibid.*, **93**, 4829 (1971).

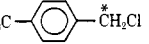
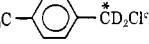


(5) B. J. Gregory, G. Kohnstam, A. Queen, and D. J. Reid, *Chem. Commun.*, 797 (1971).

(6) A. R. Stein, *J. Org. Chem.*, **33**, 4022 (1973).

(7) M. H. Abraham, *J. Chem. Soc., Chem. Commun.*, 51 (1973).

(8) G. A. Gregoriou, *Tetrahedron Lett.*, 233 (1974).

Table I. Carbon-14 and α -Deuterium Isotope Effects in the Formation of Carbinol and Azide during Hydrolyses in Bicarbonate-Buffered, Aqueous Acetone at 60°

Expt	Reactant	Product	k^{12}/k^{14}	k_H/k_D^e
1.	PhCH_2Cl	Benzyl alcohol Benzyl azide	1.085 ± 0.007^e 1.130 ± 0.007	
2.	PhCD_2Cl^b	Benzyl alcohol Benzyl azide		1.003 ± 0.007^e 1.033 ± 0.007
3.		<i>p</i> -Methylbenzyl alcohol <i>p</i> -Methylbenzyl azide	1.061 ± 0.007 1.096 ± 0.007	
4.		<i>p</i> -Methylbenzyl alcohol <i>p</i> -Methylbenzyl azide		0.996 ± 0.007 1.004 ± 0.007
5.		2-Octanol 2-Octyl azide	1.063 ± 0.007 1.105 ± 0.007	
6.		2-Octanol 2-Octyl azide		1.097 ± 0.007 1.106 ± 0.007

^a k_H/k_D per atom of deuterium. ^b Carbon-14 label; indiscriminate in ring. ^c k_H/k_D corrected for k^{12}/k^{14} . ^d Carbon-14 in methyl group. Secondary carbon-14 isotope effect assumed to be within experimental error. ^e Maximum deviation for any experiment.

We applied the isotope effect criterion⁹ to the hydrolyses, in the presence of sodium azide of carbon-14 labeled benzyl chloride, *p*-methylbenzyl chloride, and 2-octyl brosylate. In addition, using our method^{10,11} in which carbon-14 is a tracer for deuterium,¹² we determined the α -deuterium isotope effects.¹³ Both k^{12}/k^{14} and k_H/k_D ratios were observed during formation of both carbinol and azide. The results are displayed in Table I, from which we conclude that the high k^{12}/k^{14} and low k_H/k_D values for benzyl and *p*-methylbenzyl chlorides signify classic SN2 transition states. The extremely high k^{12}/k^{14} ratios require that carbon atom motion is a strong feature of the reaction coordinate, and mean that the transition states must be nearly symmetrical.^{14,15} Neither of these features is compatible with a mechanism in which nucleophilic attack on an ion pair occurs.¹⁶ The higher k^{12}/k^{14} values for

azide *vs.* carbinol formation are understandable in terms of the calculations of Sims, *et al.*,¹⁵ and the changes in the bond orders for the two competing, classical SN2 transition states. The extremely low α -D isotope effects strongly support¹⁵ the above picture of a classic SN2 reaction,^{3,17} require strong bonding in the transition state, and refute the Sneen^{2f} mechanism¹⁸ for the SN2 reactions of benzyl and *p*-methylbenzyl chlorides under the conditions we employed.

Experiments 5 and 6, for the 2-octyl brosylates, are consistent with competing, classical SN1 and SN2 processes. The k_H/k_D values (experiment 6) are considerably larger than the others in the table but still far below the SN1 maximum.^{19,20} The k^{12}/k^{14} ratios are considerable and indicate a strong, competing classic SN2 component in the reaction, but are unintelligible on the basis of an ion-pair^{3f} mechanism; the calculations of Sims and Fry¹⁵ and of Bron¹⁵ as well as the Bigeleisen-Mayer relation¹⁶ require that a highly unsymmetrical transition state, or one stabilized by carbocation resonance, should exhibit k^{12}/k^{14} values much closer to unity.

The recent²¹ finding of Graczyk and Taylor that k^{35}/k^{37} for hydrolysis of *p*-methoxybenzyl chloride increases with increasing azide concentration was interpreted as evidence for the Sneen ion-pair mecha-

(9) Primary heavy atom isotope effects (¹³C and ¹⁴C) should be large in SN2 reactions and small in SN1, whereas α -deuterium isotope effects should be small in SN2 and large in SN1 reactions; A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 172-174. The experimental and theoretical bases for the criterion are to be found in, (a) V. J. Shiner, Jr., "Isotope Effects in Chemical Reactions," ACS Monograph 166, C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N. Y., 1971, Chapter 2, pp 104-135; (b) A. Fry, Chapter 6, pp 377-386.

(10) V. F. Raaen, T. K. Dunham, D. D. Thompson, and C. J. Collins, *J. Amer. Chem. Soc.*, **85**, 3497 (1963).

(11) V. F. Raaen and C. J. Collins, *J. Int. Union Purz Appl. Chem.*, **8**, 347 (1964).

(12) V. F. Raaen, G. A. Ropp, and H. P. Raaen, "Carbon-14," McGraw-Hill, New York, N. Y., 1968, p 56, describe the "low conversion approximation."

(13) The labeled chlorides were prepared by standard methods, A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes," Part I, Interscience, New York, N. Y., 1958, pp 75, 94. Carbon-14 labeled 2-octanols were synthesized using *n*-hexylmagnesium bromide and acetyl-¹⁴C or acetyl-¹³C chloride, followed by reduction of the ketones so obtained with lithium aluminum hydride or deuteride. The azides were reduced to the amines with lithium aluminum hydride and assayed as the crystalline benzoates. All carbon-14 assays were performed by the Tolbert method.¹²

(14) A. Fry, *Pure Appl. Chem.*, **8**, 409 (1964).

(15) L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Repond, and S. W. Cook, *J. Amer. Chem. Soc.*, **94**, 1364 (1972). See also J. Bron, *Can. J. Chem.*, **52**, 903 (1974).

(16) A. J. Kresge, N. N. Lichtin, and K. N. Rao, *J. Amer. Chem. Soc.*, **85**, 1210 (1963), and A. J. Kresge, N. N. Lichtin, K. N. Rao, and R. E. Weston, Jr., *ibid.*, **87**, 437 (1965), found $k/k^* < 1$ for the ionization of trityl chloride. According to the Bigeleisen-Mayer expression [J. Bigeleisen and M. Goepfert-Mayer, *J. Chem. Phys.*, **15**, 261 (1947)], additional bonding in the transition state caused by the strong resonance stabilization of the incipient triphenylmethyl cation shows up as a subtractive $G(u \neq) \Delta u \neq$ term, thus reducing k^{12}/k^{13} below unity.

(17) The data in the table are consistent with the α -D isotope effects and the kinetic data of A. V. Willi, Chih-Kuo Ho, and A. Ghanbarpour, *J. Org. Chem.*, **37**, 1185 (1972), for the hydrolyses of benzyl and *p*-methylbenzyl chlorides in 55% (by volume) aqueous methyl cellosolve. See also K. M. Koshy, R. E. Robertson, and W. M. J. Strachan, *Can. J. Chem.*, **51**, 2958 (1973).

(18) Because it was necessary¹⁰⁻¹² to isolate reasonable quantities of carbinol and azide during the first few per cent of reaction, all of our solvolyses were carried out with solutions considerably more concentrated than those used by others.² In a typical run at 60° 0.25 M *p*-methylbenzyl chloride was hydrolyzed in aqueous acetone (70 mol %) which was 0.0125 M in sodium azide. The brosylates were hydrolyzed in 80% aqueous acetone (by volume). Sufficient sodium bicarbonate was always present to react with the HCl liberated during the reactions. Owing to the generality of Sneen's claim,^{2f} we do not consider our use of such concentrated solutions to affect our arguments seriously.

(19) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 2251 (1971); V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2254 (1971).

(20) It must be remembered that the magnitude of k_H/k_D for an α -deuterium label depends upon the nature of the leaving group, V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, **93**, 1029 (1971); see also V. J. Shiner, Jr., ref 9a.

(21) D. G. Graczyk and J. W. Taylor, *J. Amer. Chem. Soc.*, **96**, 3255 (1974).

nism, and against the operation of competing SN1 and SN2 processes of the classic Ingold types.³ We do not deny the possibility that the Snee mechanism may operate in certain special cases. The results,²¹ however, seem to us to be capable of an alternate explanation. The calculations of Sims and coworkers¹⁵ indicate that "the chlorine isotope effect... increases continuously as ones goes from a reactant-like to a product-like transition state..." in classical SN2 processes. This is just the situation expected for the SN2 component of borderline solvolyses with increasing concentrations of sodium azide.

Acknowledgment. One of us (C. J. C.) wishes to thank Professor V. J. Shiner for helpful comments.

(22) Participant in the Great Lakes Colleges Association Fall Semester Program 1972.

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t-BuOCu·CO and *t*-BuOCu·CN-*t*-Bu. New and Sublimable Copper-Carbonyl and -Isocyanide Complexes

Sir:

We wish to report the preparations, characterizations, and reactions of new and sublimable copper-carbonyl and -isocyanide complexes, *t*-BuOCu·CO (**1**) and *t*-BuOCu·CN-*t*-Bu (**2**). These complexes demonstrate an interesting property of *t*-BuOCu,¹ *i.e.*, a strong affinity toward a π -accepting ligand which has not been observed in common cuprous salts. This feature of *t*-BuOCu may be ascribed to the high σ -donating character of the *tert*-butoxy ligand which enhances the back-donation from the copper to the π -accepting ligand. **1** and **2** offer a convenient method of preparing *h*⁵-cyclopentadienyl-copper complexes *via* metalation of cyclopentadiene.

The following operations were carried out under nitrogen. On passing a stream of carbon monoxide through a suspension of *t*-BuOCu¹ in benzene at room temperature, *t*-BuOCu was dissolved to produce a yellow-brown solution. After filtration of a small amount of precipitate, evaporation of benzene *in vacuo* from the filtrate gave a pale yellow solid which was identified as **1** by the following analyses: Cu content by iodometry 37.9% (calcd for **1**, 38.6%); ir (Nujol) 2062 cm⁻¹ (ν (C≡O)). When an excess of phenylacetylene was added to **1**, stoichiometric amounts of cuprous phenylacetylide (97%), *t*-BuOH (98%), and carbon monoxide (97%) were generated.

When **1** was once isolated, it became insoluble in common organic solvents. However, the Cu/*t*-BuO/CO ratio did not change during the evaporation of benzene. Addition of phenylacetylene to the benzene solution of **1** prepared by the above-mentioned procedure produced cuprous phenylacetylide, *t*-BuOH, and carbon monoxide in a ratio of 1:0.97:0.92. Insolubilization of **1** may probably be due to the association of **1** by the removal of solvated benzene. The nmr spectrum of

(1) T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Amer. Chem. Soc.*, **94**, 658 (1972).

benzene solution of **1** showed one sharp singlet at τ 8.59. **1** is sensitive to oxygen and moisture, but it is stable to heat. On heating to 150° under nitrogen, a partial decarbonylation of **1** took place with a simultaneous formation of *t*-BuOCu. At 60° (1 mm), **1** was isolated by sublimation. **1** is the first example of sublimable copper carbonyl complex. The isolation of **1** by sublimation is especially noteworthy, because most of the carbonyl complexes of copper salts have been known to be unstable. For example, ClCu·CO² can exist only under carbon monoxide atmosphere. CF₃COOCu·CO³ loses carbon monoxide at room temperature *in vacuo*. *h*⁵-C₅H₅Cu·CO⁴ decomposes rapidly at room temperature. Recently, an air- and heat-stable copper carbonyl complex of [HB(pz)₃]Cu·CO⁵ (pz = pyrazolyl) has been prepared using a tridentate ligand of hydrotris(1-pyrazolyl)borate having a strong σ -donor character.

The thermal stability of **1** is due to strengthening of the copper-carbonyl bond. Compared with ν (C≡O) of free carbon monoxide (2143 cm⁻¹), the remarkable reduction of ν (C≡O) of **1** (2062 cm⁻¹) suggests that the increased back-donation of copper 3d electrons to CO π^* orbital is responsible for the strengthening of copper-carbonyl bond. This increased back-donating ability of the copper atom probably results from the strong σ -donor character of the *tert*-butoxy ligand. On the basis of ν (C≡O) of copper carbonyl complex, the σ -donating ability of the *tert*-butoxy ligand may be higher than that of the hydrotris(1-pyrazolyl)borate ligand (ν (C=O) 2083 cm⁻¹) and may be comparable to that of hydrotris(3,5-dimethylpyrazolyl)borate ligand (ν (C=O) 2066 cm⁻¹).⁵ These findings indicate the peculiarity of *tert*-butoxy ligand in copper-complex chemistry.

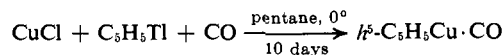
The addition of an equimolar amount of *n*-Bu₃P, (MeO)₃P, or *t*-BuNC to a suspension of **1** in benzene resulted in an immediate and quantitative liberation of carbon monoxide with a formation of the corresponding phosphine or isocyanide complex of *t*-BuOCu. However, no decarbonylation was observed by the additions of nitrogen-containing ligands (pyridine, α,α' -bipyridyl, and tetramethylethylenediamine) and unsaturated hydrocarbons (1,5-cyclooctadiene, styrene, and 3-hexyne).

2 was isolated as a yellow crystalline solid by sublimation at 90° (1 mm) from an equimolar mixture of *t*-BuOCu and *t*-BuNC in benzene: Cu content by iodometry 28.7% (calcd for **2** 29.0%); *tert*-butoxy group content by benzyl alcoholysis 98%; ir (Nujol) 2102 cm⁻¹ (ν (C≡N)); nmr (C₆D₆) τ 8.10 (S, *t*-BuO) and 9.01 (S, *t*-BuNC). An isocyanide ligand is known to behave as either σ -donor or π -acceptor depending

(2) "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie GmbH, Weinheim/Bergstr., Kupfer, Teil B, Lieferung 1, 1958, p. 240.

(3) A. F. Scott, L. L. Wilkening, and B. Rubin, *Inorg. Chem.*, **8**, 2533 (1969).

(4) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 5114 (1970); the *h*⁵-C₅H₅Cu·CO was prepared as an unstable compound according to the following reaction catalyzed by *n*-Bu₃P



(5) M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1124 (1972). For the polypyrazolylborate ligand, see S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971); *Chem. Rev.*, **72**, 497 (1972).