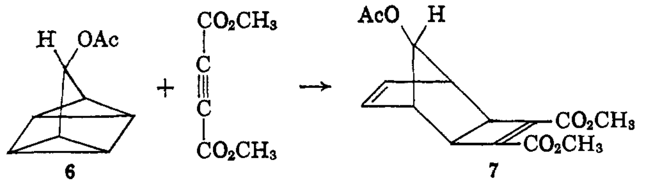
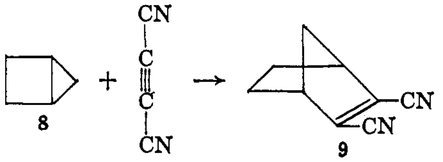


a 1:1 adduct. Adducts have been observed with a variety of other dienophiles and will be discussed in detail in a later paper.

We propose that this behavior of quadricyclane demonstrates a novel "diene-like" activity with a striking preference for *exo* attack by dienophiles. Gassman and Mansfield[6] have reported that bicyclo[2.1.0]pentane



(**8**) reacts slowly with dicyanoacetylene to give 2,3-dicycanobicyclo[2.2.1]hept-2-ene (**9**). This reaction is promoted in part by the strain energy built into the bicyclopentane system. A closely related reaction was reported recently by Cairncross and Blanchard[7] for bicyclobutanes.

[6] P. G. Gassman and K. Mansfield, *Chem. Commun.*, 391 (1965).

[7] A. Cairncross and E. P. Blanchard, Jr., *J. Am. Chem. Soc.*, **88**, 496 (1966).

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Direct Nucleophilic Substitution at the Central Carbon Atom of Triarylmethyl Substrates[1]

Sir:

The literature records no clear-cut example of nucleophilic substitutions on triarylmethyl substrates by the S$_N$2 mechanism.[2] In this communication we report experimental results showing that if sufficiently deactivated substrates[3] and suitable conditions are used, the direct substitution mechanism may be made to compete effectively with, or even take over completely, the ionization mechanism.

The results deal with the kinetics of isotopic exchange between ionic chloride (tetraethylammonium chloride-^{36}Cl) and 4,4′,4″-trinitrotriphenylmethyl or 4,4′-dinitrotriphenylmethyl chloride in acetone. The experiments were carried out in the presence of a constant electrolyte concentration which was maintained at the preset value (0.01 or 0.1 *M*) by adding tetraethylammonium perchlorate. These working conditions effectively minimize the ambiguities which often arise in the borderline region of nucleophilic substitution.[5] The kind of experiment is illustrated in Table I which reports two series of runs for the tri-*p*-nitro substrate where the total electrolyte concentration was 0.01 (the first four entries) and 0.1 *M* (the last four entries), respectively.

The data of Table I as well as those similarly obtained for the same substrate in acetonitrile solvent, and for the di-*p*-nitro substrate in acetone, all fit satisfactorily the simple rate equation for concurrent first- and second-order processes: $\text{rate}/[\text{R–Cl}] = k_1 + k_2[\text{Et}_4\text{NCl}]$. Table II records the sets of k_1 and k_2, and their standard deviations, each obtained in 4–7 kinetic runs covering an approximately tenfold change of the nucleophile concentration.

Other significant observations are the following. (a) In the tri-*p*-nitro substrate (0.01 *M*) the rate of exchange is not affected by the presence of *m*-dinitrobenzene (up to 0.05 *M*). (b) Ionic azide (Bu$_4$NN$_3$) in acetone reacts with tri-*p*-nitrophenylmethyl chloride by a second-order process: at 80° the rate constant is 5.06×10^{-1} M^{-1} sec^{-1}, *i.e.*, about 500 times faster than the chloride exchange.

The first-order contribution to the rate appears to arise from a rate-determining ionization. Thus, while k_1 is nil within experimental error for the more deactivated substrate (tri-*p*-nitro) in the less polar medium (acetone, 0.01 *M* electrolyte), it becomes significantly greater than zero when the polarity of the medium is increased, either by increasing the electrolyte concentration to 0.1 *M* or by substituting acetone for acetonitrile, or when the substrate is made less deactivated (di-*p*-nitro). The experiments, however, tell nothing as to which particular ionization stage[6] may be involved.

Table I. First-Order Specific Rates of Isotopic Exchange between (4-NO$_2$–C$_6$H$_4$)$_3$CCl and Et$_4$N^{36}Cl in Acetone at 80° in the Presence of Et$_4$NClO$_4$

Et$_4$N^{36}Cl, $M \times 10^3$	0.945	1.91	4.91	9.92	0.957	1.91	4.89	9.91
Et$_4$NClO$_4$, $M \times 10^3$	8.99	7.96	4.98	...	98.9	98.0	95.0	90.0
Rate × 10^6/[R–Cl], sec^{-1}	1.16	2.03	4.94	10.7	0.643	0.952	2.21	3.83

The second-order term cannot arise from a positive salt effect on the first-order ionization process since the *over-all* exchange rate actually decreases with increasing salt concentration (Table I). Inspection of Table II shows the decrease is due to a diminishing importance of the second-order contribution with increasing salt.

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[1] Supported by Consiglio Nazionale delle Ricerche, Rome.

[2] For a discussion of nucleophilic substitution reactions on triarylmethyl systems see (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 81; (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., Chapter VII.

[3] The need of having strong electron-attracting groups in the aryl moiety has recently been recognized by Patai and Zabicki[4] who used 4,4′,4″-trinitrotriphenylmethyl chloride in a recent study of S$_N$ reactions.[4] However, their choice of acetic acid as the medium and the use of powerful electrophilic cations (lithium, silver, and mercury) in the nucleophilic salts were hardly suitable to fostering S$_N$2-type reactions which in fact were not observed.[4]

[4] S. Patai and Zabicki, *J. Chem. Soc.*, 5479 (1961).

[5] (a) A. Fava, A. Iliceto, and A. Ceccon, *Tetrahedron Letters*, 685, (1963); (b) A. Ceccon, I. Papa, and A. Fava, *J. Am. Chem. Soc.*, in press.

[6] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and C. G. Robinson, *ibid.*, **78**, 328 (1956).

Table II. Isotopic Exchange between Nitro-Substituted Triphenylmethyl Chlorides and Labeled (^{36}Cl) Tetraethylammonium Chloride in Acetone at 80°

R	Total salt, M^a	10^6k_1, sec^{-1}	10^4k_2, M^{-1} sec^{-1}
$(p\text{-NO}_2\text{C}_6\text{H}_4)_3\text{C}$-	0.01	0.0 ± 0.07	10.6 ± 0.13
	0.10	0.32 ± 0.09	3.65 ± 0.16
	0.01^b	0.46 ± 0.04	2.60 ± 0.06
$(p\text{-NO}_2\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_5\text{C}$-	0.01	0.5 ± 0.2	18.9 ± 0.4
	0.10	3.46 ± 0.05	12.1 ± 0.1

^{a} M = [Et$_4$NCl] + [Et$_4$NClO$_4$]. ^{b} Acetonitrile.

In the tri-*p*-nitro substrate the value of k_2 is reduced by a factor of three in going from 0.01 to 0.1 M electrolyte, nearly the same factor which is observed for a substrate, *p*-nitrobenzyl chloride, which undergoes a *bona fide* bimolecular substitution.[7] Thus the second-order term arises from a path which includes the nucleophile in the rate-determining transition state. In view of the particular nature of the substrates, several processes can be envisioned: (1) a one-step direct displacement on the central carbon atom; (2) a two-step process involving a slow displacement on an ion pair formed in a preliminary fast equilibrium

$$\text{RCl} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{R}^+\text{Cl}^- \qquad \text{fast}$$

$$^*\text{Cl}^- + \text{R}^+\text{Cl}^- \overset{k_2'}{\rightleftarrows} \text{R}^{+*}\text{Cl}^- + \text{Cl}^- \qquad \text{slow}$$

(3) a two-step process involving the slow attack by chloride on the chlorine atom of the substrate

$$\text{R—Cl} + {}^*\text{Cl}^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} \text{R}^- + \text{ClCl}^*$$

followed by a fast back reaction which may occur on either chlorine;[8] (4) a two-step process involving slow attack by chloride on chlorine to give a radical pair

$$\text{RCl} + {}^*\text{Cl}^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} \text{R}\cdot + {}^*\text{ClCl}\cdot^-$$

followed by a fast recombination reaction.[8]

Mechanism 4 is proposed in view of the recent findings of Kornblum and co-workers.[9] However, *m*-dinitrobenzene[9] up to a molar ratio 5:1 produces no significant decrease of the rate, indicating that this mechanism does not contribute appreciably in the present case.

Mechanism 3 is suggested in view of the great stability associated with nitro-substituted triphenylmethyl carbanions. However, it can be dismissed in the present case since the structural effect on k_2 would predict the tri-*p*-nitro compound to react faster than the di-*p*-nitro one, while in fact it does not (Table II).

Of the two remaining possibilities we believe, at least for the trinitro substrate, a choice can be made in favor of 1 against 2.[10] This is based on the salt and solvent effects which are in agreement with mechanism 1 and opposite to what one can reasonably guess for mechanism 2. The transition state of the latter would in fact resemble an ion triplet, Cl$^-$R$^+$Cl$^-$, the stability of which, relative to the initial state, is expected to be favored by an increased polarity of the medium.[11] The structural effect is not inconsistent with mechanism 1 since bond breaking may well be predominant in these bimolecular substitutions.[5b]

Besides the medium effects, the great reactivity of azide relative to chloride ion offers a strong argument for mechanism 1 against 2. The latter, owing to the ion-triplet character of the transition state, would be expected to exert little discrimination between different nucleophiles. Instead, tri-*p*-nitrotriphenylmethyl chloride appears to discriminate strongly between azide and chloride ions, $k_{\text{N}_3^-}$-k_{Cl^-} being about 500.

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(7) The pertinent data are (U. Miotti, unpublished results): acetone; 25°; *p*-nitrobenzyl chloride 0.01 M, Et$_4$N^{36}Cl 1.04 × 10^{-3} M, and Et$_4$NClO$_4$ 9.0 × 10^{-3} M, k_2 = 9.13 × 10^{-3} M^{-1} sec^{-1}; Et$_4$N^{36}Cl 1.28 × 10^{-3} M and Et$_4$NClO$_4$ 98.9 × 10^{-3}M, k_2 = 4.08 × 10^{-3} M^{-1} sec^{-1}.

(8) Although in both mechanisms 3 and 4 the species at the right-hand-side have been written as being separated, the back reaction could conceivably occur while the product species have not yet diffused away and are contained in the same solvent cage.

(9) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **87**, 4520 (1965).

(10) H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965), have presented suggestive albeit not conclusive evidence for the operation of mechanism 2 in the reaction of 2-octyl mesylate in aqueous dioxane.

(11) Another way, perhaps more convincing, of saying the same thing is that in mechanism 2 the observed second-order rate coefficient is compounded of an equilibrium constant for ion-pair formation ($K = k_1/k_{-1}$) and of a rate constant, k_2', for direct displacement on an ion pair, $k_2 = Kk_2'$. Then the observed salt and solvent effect would result from the combination of the effects on K (large increase with increasing polarity) and k_2' (small decrease with increasing polarity).

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Nondissociative Electron Attachment Reactions in γ Radiolysis of Solutions of Cyclic Perfluorocarbons in Alkanes

Sir:

Recently considerable attention has been given to the role of halogenated hydrocarbons as electron scavengers in systems undergoing radiolysis. Pulsed radiolysis of aqueous solutions has been used to establish the rates of reaction of hydrated electrons in the alkyl halides[1] and monohaloacetates.[2] Hamill[3] and his co-workers have studied the electron-capturing ability of several halogen- and acetoxy-substituted hydrocarbons in organic glasses undergoing radiolysis. Evidence has been obtained for electron capture by the solutes in all those cases where the electron affinity of the halogen or acetoxy group exceeded the bond dissociation energy of the carbon–halogen or carbon–acetoxy bond.[3d] In the liquid-phase radiolysis of CCl$_4$ and CHCl$_3$ solution in cyclohexane, the decrease in hydrogen yield was attributed by Stone and Dyne[4] to either excitation energy transfer or electron capture by solute.

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(1) A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **69**, 289 (1965).

(2) M. Anbar and E. J. Hart, *ibid.*, **69**, 271 (1965).

(3) (a) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962); (b) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962); (c) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963); (d) J. B. Gallivan and W. H. Hamill, *Trans. Faraday Soc.*, **61**, 1960 (1965).

(4) J. A. Stone and P. J. Dyne, *Can. J. Chem.*, **42**, 669 (1964).