

THE ABNORMAL FINKELSTEIN REACTION. A SEQUENTIAL
IONIC-FREE RADICAL REACTION MECHANISM

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Abstract: The reaction of alkyl halides with sodium iodide in acetone (Finkelstein Reaction) may yield coupled or rearranged products via cationic intermediates.

The formation of alkyl iodides by the displacement reaction of sodium iodide in acetone (Finkelstein reaction) has been studied in great detail and cited as a classical example of the S_N2 process.¹ However, Finkelstein himself was well aware that in certain instances dimeric products are formed.² Thus, dichlorodiphenylmethane first yields 1,2-dichlorotetraphenylethane and subsequently tetraphenylethylene. Some years ago, Leffler³ reported that sodium iodide (and several other anions) in acetone reacts with tris-(p-nitrophenyl)methyl bromide forming the corresponding stable radical in solution. Among the several mechanisms considered, he suggested the possibilities of a direct S_N2 displacement forming the triarylmethyl iodide which then dissociates to radicals⁴ and of a direct oxidative displacement of iodide on the bromine to form the triarylmethyl radical directly. He discarded the possibility of a displacement on the bromide to form a carbanion which is then oxidized to the radical since carbanion traps failed to divert the course of the reaction. Ballester and coworkers⁵ reported the reaction of perchlorotoluene and related compounds to give the tetrachloroethane dimers. As part of their mechanistic considerations they suggested the possibility of first forming a carbenium ion and its reduction to a free radical. The possibility of the direct formation of the radical in an ion-molecule reaction was also mentioned. Thus, three mechanisms accounting for the formation of dimer products have been set forth. The research reported here answers the question as to which is the correct pathway.

The progress of the reaction of dichlorodiphenylmethane with sodium iodide in acetone can be followed gravimetrically or by iodometric titration. By either method the reaction is kinetically of the second order (first order in dihalide and first in iodide) for over three half-lives. The formation of tetraphenylethylene from the first formed dichloroethane is so slow that there is no problem of interference.

To examine the details of the reaction a series of bis-(p-X-phenyl) dichloromethanes were synthesized and their second order rate constants determined (Table I). In keeping with frequent observations on such displacement reactions,⁶ a Hammett $\rho\sigma$ plot is curvilinear upwards. However, in contrast to typical $S_N 2$ reactions,^{6a} the reaction is acceler-

Table I. Second Order Rate Constants for a Series of Bis-(p-X-phenyl) dichloromethanes with Sodium Iodide in Acetone (35°)

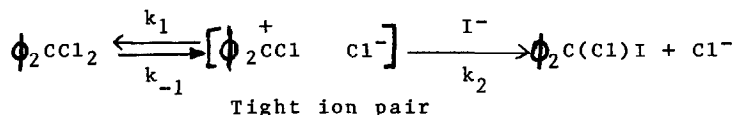
<u>X</u>	<u>k</u> (1/mole-min)	δ ($^{13}\text{C}-\alpha$) ^a
tert-Butyl	0.3	92.2
H	3.6×10^{-3}	91.9
Cl	1.7×10^{-3}	90.2
NO ₂	5.3×10^{-5}	88.2

a. Carbon-13 chemical shifts in CDCl₃ in ppm vs. TMS. The methoxyl analog was prepared but reacted too rapidly for convenient measurement (δ 92.3).

ated by the electron donating tert-butyl group and strongly retarded by the p-nitro group. Interestingly, the carbon-13 chemical shifts of the α -carbons of the dichloromethanes follow σ_p very well. The substituent effects, however, are in the opposite sense of the para-carbons in the monosubstituted benzenes. This observation is in keeping with the development of considerable positive charge in the ground state of these molecules and the expected charge alternation.⁷

The above results are reminiscent of an earlier study by Gelles, Hughes and Ingold⁸ in which triphenylmethyl chloride in nitromethane-pyridine reacts with a series of hydroxylic solvents present in limited amounts. Solvolysis products were formed in a second order process which was explained as resulting from a rate determining attack by the nucleophilic solvent upon a preformed cation ($S_N 2(C^+)$ mechanism). More recently, Snee and Larson⁹ have provided evidence to support the argument that $S_N 2$ processes proceed via attack of the nucleophile on a first formed ion pair. This position has been both attacked and defended vigorously.¹⁰

These considerations suggest a reasonable mechanism as follows:



The rate expression is

$$\text{rate} = \frac{k_1 k_2 (\text{dichloride})(\text{I}^-)}{(k_{-1} + k_2(\text{I}^-))}$$

which reduces to a second order rate expression under the conditions that $k_{-1} \gg k_2$.

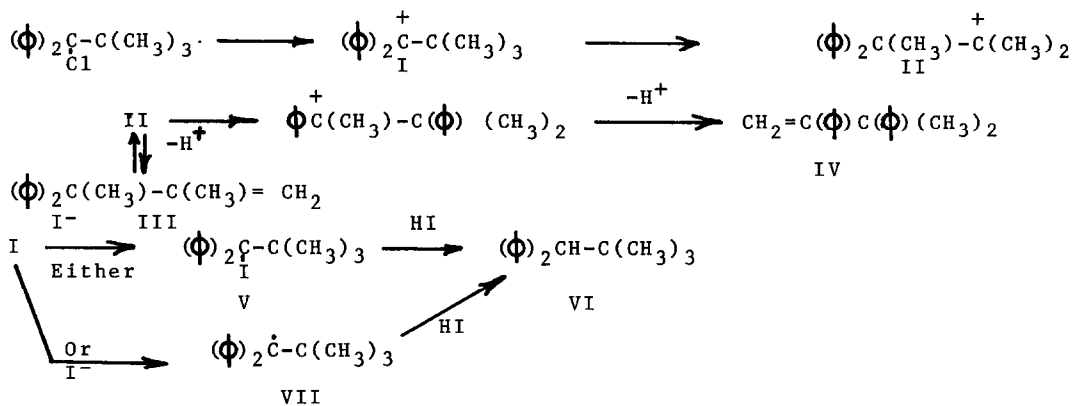
To gain further information regarding the mechanism above, the effect on the reaction rate of added lithium perchlorate (0.01M to 0.1M in eight steps favoring the low concentration end) to a solution of 0.1M dichlorodiphenylmethane and 0.3M sodium iodide was carried out at 35°. The plot of rate constant vs. added perchlorate was entirely linear

(slope 1.86×10^{-2} , intercept 4.18×10^{-3} , r 0.9999). The absence of a special salt effect is consistent with a rate determining attack by the iodide on a tight ion pair and is consistent with the postulation of Snee. ^{9,10}

The formation of the dimer product reasonably comes about by the coupling of free radicals generated by the dissociation of an unstable alkyl iodide formed as pictured above or by the more direct reduction of the cation by iodide in the k_2 step. In a related experiment, benzhydryl chloride was treated with sodium iodide in perdeuteroacetone. The course of the reaction was followed by proton NMR and clearly showed (by comparison with a known sample) the formation of benzhydryl iodide followed by its subsequent decomposition and formation of tetraphenylethane. The treatment of benzhydryl chloride with a three-fold excess of sodium iodide in refluxing acetone gives a nearly quantitative yield of tetraphenylethane.

Further evidence of the existence of a cationic intermediate in the abnormal Finkelstein reaction was given by the reaction of tert-butyl diphenylmethyl chloride (0.2M in acetone) with a three-fold excess of sodium iodide which required three days at room temperature to go to completion. Examination of the whole product by proton and ¹³C NMR showed only two products formed in equal amounts, tert-butyldiphenylmethane (VI) and 2,3-diphenyl-3-methyl-1-butene (IV). A clue to the mode of formation of the alkane was given by the observation of a small amount of byproduct mestityl oxide.

Coupling these observations with the preceding conclusions one may write:



The formation of the thermodynamically more stable IV results from a double rearrangement as shown from I. The latter is not shown as an ion pair here since this is not pertinent to the discussion. No evidence of III among the products was found under these conditions. Bateman and Marvell¹¹ had reported a number of years ago the preparation of III in good yield by the acid catalyzed dehydration of tert-butyl diphenylcarbinol. A reexamination by proton NMR of the products formed under their conditions shows a mixture of equal parts of III and IV. When this

mixture in acetone with sodium iodide is treated with hydrogen iodide, IV is recovered quantitatively.

The formation of the alkane VI results from the presence of hydrogen iodide in the reaction medium. It is well known that many alkyl iodides are reduced to their corresponding alkanes by hydrogen iodide or hydroiodic acid. Strangely, no speculations about the mechanism seem to have been made. There does not even appear to be a systematic study of structure-reactivity relations for the reaction. One can imagine a direct reduction of the alkyl iodide by hydrogen iodide via a four centered transition state, or the reduction of a preformed radical VII generated either from V or directly from I.

When the reaction of tert-butyl diphenylmethyl chloride is carried out as above but with the addition of a two-fold excess of the "proton sponge", 1,8-bis-(dimethylamino) naphthalene, a quantitative yield of olefin IV is obtained. No free iodine is observed. This result is consistent only with the formation of VI through the alkyl iodide V. We have prepared VII by the direct oxidation of the corresponding anion (Ziegler method). The radical dimerizes like triphenylmethyl and re-aromatizes the cyclohexadiene ring producing a high yield of stable hydrocarbon. In the absence of hydrogen iodide, which serves as a trap for V, the alkyl iodide reverts to the ion I forming only olefin products.

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References and Notes

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