Table II

The Reaction of Ethylmagnesium Bromide and Diethylmagnesium with 1-Hexyne in Tetrahydrofuran

$C_4H_9C{\equiv}CH$: organometal, molar ratio	Br : Mg	Relative reactivity
1:1	0	350
10:1	0	330
10:1	1.00	134
10:1	1.05	105
10:1	1.17	80

is little dependence of the rate of reaction on the molar concentration of reactants.

Experimental

The gas-collecting system and the determination of rates was the same as previously described.[3] Ethers were purified by distilling from ethylmagnesium bromides prepared in them. 1-Hexyne was purchased from Farchan Research Laboratories, redistilled, and sealed in vials until ready for use. Magnesium turnings were from an unknown lot purchased from Eastman Organic Chemicals. Analysis of the metal was not known.

Diethylmagnesium was prepared by the dioxane precipitation method.[10] The solvents were removed *in vacuo*. The light green solid remaining was redissolved in dry tetrahydrofuran forming a light yellow solution. It contained less than 0.3 mole % of bromine.

A tetrahydrofuran solution of magnesium bromide was prepared by treating bromine with magnesium in dry tetrahydrofuran. The solution was analyzed for total magnesium and bromine content. The preparation of magnesium bromide in ether was previously described.[11]

The Grignard reagents were prepared from ethyl bromide in the appropriate ethers. With the exception of ether and tetrahydrofuran, the bromine to magnesium ratios of the formed solution were sufficiently close to 1.08 so that they did not require adjustments with solutions of magnesium bromide in the appropriate ethers.

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(10) C. R. Noller and W. R. White, *J. Am. Chem. Soc.*, **59**, 1354 (1937).

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Perhalo Ketones. IV.[1] The Reaction of Perhaloacetones with Phosphorus Pentachloride

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The perhalofluorochloroacetones are not readily susceptible to attack by reagents that normally lead to replacement of the carbonyl oxygen.[3] This inertness is in marked contrast with their considerable reactivity toward nucleophiles[4] and other polar functions.[5]

This study has indicated that these perhaloacetones are resistant to the action of phosphorus pentachloride under conditions which lead to replacement of the carbonyl oxygen even in highly substituted ketones. They were recovered unchanged after refluxing with phosphorus pentachloride, either in the presence or absence of inert solvents. Although pentachloroacetone is converted to heptachloropropane with PCl_5 at 180° in 6–8 hr.,[6] the perhaloacetones gave extremely low yields at 200° for 24 hr. with excess reagent in a rocking autoclave. Not until temperatures of 250° or higher were employed did substantial reaction occur, except in the case of hexachloroacetone which reacted at 230°. At 275–300° fair yields of the corresponding perhalopropanes were obtained (Table I) in 5 hr. Since the unreacted ketones are either readily soluble in aqueous base,[7] or react with it, the perhalopropanes were obtained in high purity. These compounds have previously been prepared only by multistep syntheses.

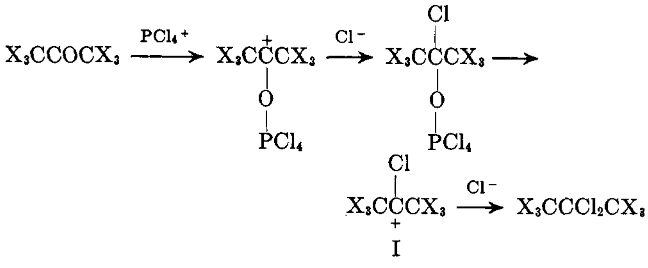
Table I

Preparation of Perhalopropanes

Perhalopropane formed	B.p., °C.	% yield[a]	% fluorine Calcd.	% fluorine Found
$F_3CCCl_2CF_3$	33–34[b]	31	51.7	51.6
$F_3CCCl_2CF_2Cl$	72[c]	50	40.2	40.0
$ClF_2CCCl_2CF_2Cl$	112–113[d]	61	29.8	29.9
$ClF_2CCCl_2CFCl_2$	152[d]	48	21.2	21.1
$Cl_2FCCCl_2CFCl_2$	194[e]	62	12.9	13.2
$Cl_3CCCl_2CCl_3$[f]	270–271[g]	85		

[a] Based on the amount of ketone used. [b] J. T. Maynard, *J. Org. Chem.*, **28**, 113 (1963). [c] A. L. Henne, A. M. Whaley, and J. K. Stevenson, *J. Am. Chem. Soc.*, **63**, 3478 (1941). [d] A. L. Henne and M. W. Renoll, *ibid.*, **61**, 2489 (1939). [e] A. L. Henne and E. C. Ladd, *ibid.*, **60**, 2491 (1938). [f] Run at 230°. [g] F. Kraft and V. Merz, *Ber.*, **8**, 1296 (1875). Product gives an infrared spectrum identical with that of sample purchased from Aldrich Chemical Co.

This resistance of the perhaloacetones to phosphorus pentachloride is attributed to the negative inductive effect of the halogen clusters surrounding the carbonyl group,[8] which reduces electron availability at the carbonyl oxygen and inhibits attack by the chlorophosphonium ion, PCl_4^+.[9] It would also make the formation of the carbonium ion I difficult, since departure of the oxygen atom with its pair of bonding electrons would be electronically unfavorable.



$$X_3CCOCX_3 \xrightarrow{PCl_4^+} X_3C\underset{\substack{|\\ O\\ |\\ PCl_4}}{\overset{+}{C}}CX_3 \xrightarrow{Cl^-} X_3C\underset{\substack{|\\ O\\ |\\ PCl_4}}{\overset{\substack{Cl\\ |}}{C}}CX_3 \longrightarrow X_3C\underset{\substack{+\\ \mathrm{I}}}{\overset{\substack{Cl\\ |}}{C}}CX_3 \xrightarrow{Cl^-} X_3CCCl_2CX_3$$

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(1) Paper I: B. Sukornick, *Org. Syn.*, **40**, 103 (1960); Paper II: P. Eaton, E. J. Carlson, P. Lombardo, and P. Yates, *J. Org. Chem.*, **25**, 1225 (1960); and Paper III: B. Farah and S. Horensky, *ibid.*, **28**, 2494 (1963).

(2) To whom inquiries should be sent.

(3) H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960).

(4) See, for example, (a) S. Andreades, U. S. Patent 3,030,409 (1962); (b) S. Andreades, U. S. Patent 3,040,085 (1962); (c) I. L. Knunyants, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 927 (1962).

(5) See, for example, (a) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961); (b) J. F. Harris and D. D. Coffman, *ibid.*, **84**, 1553 (1962).

(6) P. Fintsch, *Ann.*, **297**, 314 (1897).

(7) (a) W. K. Pearlson, "Fluorine Chemistry," Vol. I, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1950, p. 482; (b) C. Woolf, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 1957, p. 23M.

(8) E. T. McBee, Y. S. Kim, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3154 (1962); H. P. Braendlin and E. T. McBee, *Advan. Fluorine Chem.*, **3**, 1 (1963).

(9) For an elegant discussion of the mechanism of the reaction of phosphorus pentachloride with ketones, see (a) M. S. Newman and L. L. Wood, *J. Am. Chem. Soc.*, **81**, 4300 (1959); (b) M. S. Newman, G. Fraenkel, and W. N. Kirn, *J. Org. Chem.*, **28**, 1851 (1963).

Experimental

Typical Procedure.—The ketone (0.5 mole) and phosphorus pentachloride (1.0 mole) were sealed in a stainless steel autoclave, and the mixture was heated at 275–300° for 5 hr. with shaking. The vessel was then cooled to room temperature and the contents were transferred to a separatory funnel containing 1 kg. of crushed ice. The mixture was shaken and the lower layer was withdrawn. It was washed three times with 50-ml. portions of 5% sodium hydroxide solution, dried over calcium chloride, and distilled.

The Effects of Hydrogen Bonding on the Absorption Spectra of Some Substituted Benzaldehyde Tosylhydrazone Anions

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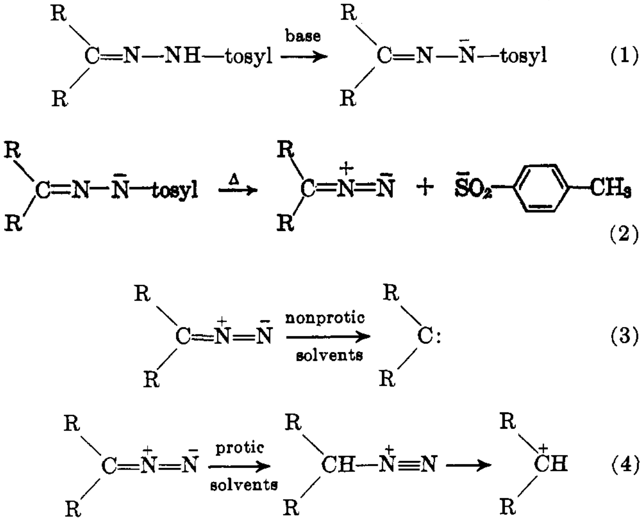
The decomposition reaction of the anions of aryl- and alkylsulfonylhydrazones, referred to as the Bamford–Stevens reaction, has attracted considerable attention in the past few years.[1-4] The reaction affords a convenient way of generating carbenes when it is carried out in aprotic media (eq. 1–3), while the decomposition in protic solvents leads to products formed *via* an ionic mechanism (eq. 1, 2, and 4). The intermediates in both cases are aryl- or alkyldiazomethanes. In the case of the tosylhydrazones of some aromatic aldehydes and ketones, the alkaline decomposition reaction proceeds at sufficiently low temperatures that the diazo compound may be conveniently isolated.[5] During the course of some synthetic work using this reaction we observed large differences between the absorption spectra of the anion of the tosylhydrazone of *p*-nitrobenzaldehyde in protic and nonprotic solvents. Similar observations had been made earlier by Burawoy and co-workers[6,7] in their studies of the effects of hydrogen bond formation on the absorption spectra of many aromatic substances having hydrogen bond donor and acceptor sites. They showed that where the effect of hydrogen bonding with the solvent is to reduce the polarity of the solute molecule a blue shift of the $\pi \rightarrow \pi^*$ absorption band (K-band) is observed. A relevant example is the blue shift which occurs in the absorption spectrum of the *p*-nitrophenol anion on changing the solvent from pyridine to water.[7] In this case hydrogen bonding localizes the negative charge on the oxygen, thereby decreasing the dipole moment of the anion and stabilizing its ground state and causing a shift of the primary band to shorter wave lengths.



Brealey and Kasha[8] have also discussed the effect of hydrogen bonding on electronic absorption spectra. They showed that the blue shifts observed in the $n \rightarrow \pi^*$ absorption bands (R-bands) of pyridazine and benzophenone upon changing from hydrocarbon to hydroxylic solvents are mainly due to hydrogen bonding, which stabilizes the ground state more than the excited state of the molecule.

This paper reports our findings of a hypsochromic shift of the primary absorption bands of several anions of substituted benzaldehyde tosylhydrazones upon changing from aprotic to protic solvents. It was also found that the rate at which the anions decompose is retarded by the same solvent changes.

Experimental

Spectra.—Spectra were measured on a recording spectrophotometer, using 1-cm. quartz cells.

Solvents.—Solvents used were all Spectroquality, with the exception of N,N-dimethylformamide (DMF), which was reagent grade. Distilled water was used.

Toluene-*p*-sulfonylhydrazones.—The toluene-*p*-sulfonylhydrazones were prepared in ethanol solutions and were recrystallized from methanol–water mixtures. The *p*-diethylamino compound was prepared in an ethanol–acetic acid solution. The aldehyde tosylhydrazones which are shown in Table I were prepared.

Excess diethylamine was added to 10^{-4} *M* solutions of the tosylhydrazones to obtain the anion solutions, except in solutions of the *p*-diethylamino compound, in which alcoholic NaOH was used.

The spectral absorption data are given in Tables II and III where λ_{max} refers to the wave length of the primary absorption band. The *p*-nitrobenzaldehyde tosylhydrazone was studied most thoroughly, since it displayed the greatest shift.

***p*-Nitrophenyldiazomethane.**—*p*-Nitrobenzaldehyde tosylhydrazone (1 g.) was dissolved in 10 ml. of DMF. Diethylamine (1 ml.) was added and the solution was allowed to stand at room temperature for about 1 hr. On the addition of water, *p*-nitrophenyldiazomethane, m.p. 80° dec., separated and was recrystallized from acetone; yield 59%, λ_{max}^{EtOH} 370 mμ (log ϵ 4.29). In the infrared spectrum a strong band at 4.84 μ ($>CN_2$[9]) was observed. The identical compound was also prepared by the oxidation of p-$O_2NC_6H_4CH{=}NNH_2$ with active manganese dioxide.

Anal. Calcd. for $C_7H_5N_3O_2$: C, 51.5; H, 3.1. Found: C, 51.6; H, 3.1.

***p*-Nitrobenzaldehyde N-Methyltoluene-*p*-sulfonylhydrazone.**—*p*-Nitrobenzaldehyde N-methyltosylhydrazone was prepared in 80% yield according to Dornow and Bartsch,[2] by alkylation of the tosylhydrazone with diazomethane. It melted at 165°

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