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# KINETICS OF SOLVOLYSIS REACTIONS OF PENTAARYLANTIMONY COMPOUNDS IN 2-OCTANOL

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## Summary

Tetraphenyl-*p*-tolylantimony, *m*-chlorophenyltetraphenylantimony and *p*-methoxyphenyltetraphenylantimony have been prepared and subjected to solvolysis in 2-octanol at temperatures ranging from 50-65°. First order rate constants have been determined, and a plot of log $k \times 10^5$ vs. $\sigma$ has been found to be linear, with $\rho = 1.12$. The value for the specific rate constant of the pentaphenylantimony reaction cannot be measured directly owing to solubility problems, but it can be calculated by use of the Hammett equation. Analysis of the rate data by the method of parallel first-order reactions gives results which are in agreement with experimental data for the reaction period extending from the time at which a homogeneous solution is formed to the end of the reaction. Partial rate factors for formation of benzene and the substituted benzene have been calculated for each reaction, and these data plus the activation parameters have been used as the basis for suggested mechanisms of the solvolysis reactions. Preliminary studies have also been carried out on the effects of 2-octanoxide anion on the solvolysis reactions. In the case of the *p*-methoxyphenyltetraphenylantimony reaction, second order kinetics were observed (first order with respect to the pentaarylantimony compound and first order with respect to the 2-octanoxide anion). Although precise rates could not be obtained for the reactions of the other pentaarylantimony compounds with sodium 2-octanoxide, qualitative evidence indicated that the anion exerts a major influence in each case.

## Introduction

Wittig and Hellwinkel [1] have reported that ethoxyphenyl(2-biphenylyl)-biphenyleneantimony is produced by the action of refluxing ethanol on phenylbis(biphenylene)antimony. Briles and McEwen [2] have carried out a similar retion of pentaphenylantimony with methanol, and they obtained benzene plus methoxytetraphenylantimony (97% yield). No evidence of stereospecificity could be found by Shen, Wolf and McEwen [3] for the conversion of pentaphenylantimony—$^{14}$C to methoxytetraphenylantimony, which, in the crystal state, is known [4] to have a trigonal bipyramidal configuration with the methoxyl group occupying an apical position. Razuvaev and Osanova [5] have prepared tetraphenylphenoxyantimony by treatment of pentaphenylantimony with phenol. Recently, McEwen and Lin [6] have prepared tetraphenyl-*p*-tolylantimony and subjected this compound to solvolysis reactions in methanol, ethanol and isopropyl alcohol, respectively. The effects of the conjugate bases of the alcohols on rates of reaction and product ratios were also investigated. On the basis of these data, the suggestion was made that the simple solvolysis reactions occur mainly by an $S_N1$ (Sb) mechanism, while the reactions carried out in the presence of the respective sodium alkoxides occur mainly by an $S_N2$ (Sb—ate) mechanism. Owing to solubility problems, the rate data were essentially qualitative in nature. We have now found that the use of 2-octanol as the solvent has enabled us to overcome some of these problems, and we are therefore able to report the results of some detailed kinetics experiments.

## Results

Doleshall, Nesmeyanov and Reutov [7] have prepared methyltetraphenylantimony and ethyltetraphenylantimony by reaction of tetraphenylstibonium fluoride with the respective alkylmagnesium bromides in ether. We have now used the same method to prepare *p*-methoxyphenyltetraphenylantimony, *m*-chlorophenyltetraphenylantimony and tetraphenyl-*p*-tolylantimony. The properties of the latter compound were found to be in full agreement with those of the sample prepared previously by a different method [6].

These pentaarylantimony compounds have been subjected to solvolysis in 2-octanol, and the results are summarized in Table 1. When the concentration of

TABLE 1

KINETICS OF SOLVOLYSIS OF PENTAARYLANTIMONY COMPOUNDS ($Ph_4SbC_6H_4X$) IN 2-OCTANOL

| X | Temp. (°C ± 0.1) | $k \times 10^5$ ($s^{-1}$) | $t_H$ [a] | Yield PhH and PhX at $t_H$ (%) | Yield PhH and PhX at $t_\infty$ (%) | $\frac{PhH}{PhX}$ |
|---|---|---|---|---|---|---|
| *p*-Me | 50.0 | 3.08 | 24 h | 50 | 74 | 4.3 ± 0.1 |
| | 55.0 | 4.80 | 21 h | 67 | 87 | 4.3 ± 0.2 |
| | 65.0 | 13.3 | 20 min | 17 | 40 | 3.3 ± 0.2 |
| *p*-MeO | 50.0 | 2.76 | 110 min | 41 | 87 | 0.7 ± 0.3 |
| | 55.3 | 3.96 | 20 min | 30 | 73 | 1.1 ± 0.3 |
| | 65.0 | 7.03 | 30 min | 40 | 89 | 1.3 ± 0.3 |
| *m*-Cl | 50.0 | 15.6 | 30 min | 60 | 106 [b] | 0.9 ± 0.2 |
| | 55 3 | 18.9 | 20 min | 40 | 91 | 1.2 [c] |
| | 65.1 | 28.3 | 10 min | 50 | 96 | 0.9 [d] |

[a] The time at which the reaction mixture became a homogeneous solution. [b] A second substitution reaction is known to occur, but at a rate much slower than that of the first substitution [8]. [c] The ratio varied from 1.7 during the early period following $t_H$ to 1.2 near the end of the reaction. [d] The ratio varied from 9.0 during the early period following $t_H$ to 0.9 as calculated from the ratios of rate constants given in Table 4.

TABLE 2

ACTIVATION PARAMETERS AT 55° FOR THE SOLVOLYSIS REACTIONS OF $Ph_4SbC_6H_4X$ IN 2-OCTANOL

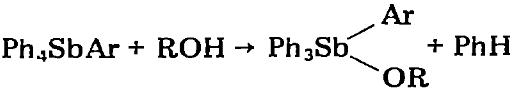
| X | $\Delta H^‡$ (kcal mol$^{-1}$) | $\Delta S^‡$ (cal mol$^{-1}$ K$^{-1}$) |
|---|---|---|
| *p*-Me | 20 | −16 |
| *p*-MeO | 12 | −42 |
| *m*-Cl | 8.0 | −51 |

*p*-methoxyphenyltetraphenylantimony in 2-octanol at 55.3° was doubled (0.152 rather than the usual 0.078 *M*), the value of the rate constant did not change ($k = 4.05 \times 10^{-5}$ $s^{-1}$ at the higher concentration vs. $3.96 \times 10^{-5}$ $s^{-1}$ at the lower concentration) even though the time required for a homogeneous solution to be formed ($t_H$) was 2.5 h at the higher concentration vs. 20 min at the lower concentration. Activation parameters were determined in the usual manner, and the results are summarized in Table 2.

The effects of sodium 2-octanoxide were investigated on the rates of solvolysis of each of the three pentaarylantimony compounds. With one equivalent of sodium 2-octanoxide present at 55°, the reactions with *m*-chlorophenyltetraphenylantimony and tetraphenyl-*p*-tolylantimony had progressed well beyond the stage of a single substitution process within a few minutes and before a homogeneous solution had been attained. Thus, no precise kinetic data could be obtained in these cases, and the ratio of benzene/substituted benzene of 3.3 in the *p*-tolyl case and 2.0 in the *m*-chlorophenyl case had little significance. In the case of *p*-methoxyphenyltetraphenylantimony, however, it was possible to obtain a specific rate constant of $1.65 \times 10^{-2}$ l mol$^{-1}$ s$^{-1}$ for the period of reaction between $t_H$ (20 min, about 80% of reaction already completed) to $t_\infty$ (20 h, 100% reaction). The ratio of benzene/anisole was 2.3 ± 0.1.

## Discussion

When a mixed pentaarylantimony compound ($Ph_4SbAr$) undergoes solvolysis in 2-octanol, two competing reactions occur:



$$Ph_4SbAr + ROH \rightarrow Ph_3Sb\begin{matrix} Ar \\ OR \end{matrix} + PhH \qquad (1)$$

$$Ph_4SbAr + ROH \rightarrow Ph_4SbOR + ArH \qquad (2)$$

(R = 2-octyl)

Although the evidence was essentially qualitative owing to solubility problems, it was nevertheless established in a previous article [6] that the rate of solvolysis of tetraphenyl-*p*-tolylantimony increases with increasing polarity of the solvent and that there is a small preference for formation of benzene over toluene. These facts led us to suggest that the solvolysis occurs essentially by an $S_N1$ (Sb) mechanism. (This could also be designated an $S_E1$ mechanism according to Ingold's [9] terminology, but we prefer to place the emphasis on the nucleophilic substitution at antimony rather than on the electrophilic substitution at carbon.)

TABLE 3

PARTIAL RATE FACTORS AT 55° FOR FORMATION OF BENZENE AND SUBSTITUTED BENZENES

| X in $Ph_4SbC_6H_4X$ | P.R.F. for PhX | P.R.F. for PhH |
|---|---|---|
| *p*-Me | 0.62 (0.77) | 0.67 (0.67) |
| *p*-MeO | 1.3 (1.3) | 0.36 (0.38) |
| *m*-Cl | 5.9 (6.9) | 1.8 (1.7) |

Owing to the fact that the solvolysis reactions in methanol, ethanol, 2-propanol and 2-octanol are essentially complete before a homogeneous solution is formed, we have not been able to obtain a direct measure of the rate of solvolysis of pentaphenylantimony relative to that of any of the compounds of type $Ph_4SbAr$. Fortunately, however, the value of the specific rate constant for the solvolysis of pentaphenylantimony in 2-octanol at 55° can be obtained by an indirect approach. From the data provided in Table 1, a Hammett plot of log $k \times 10^5$ vs. $\sigma$ can be constructed for the *m*-chloro, *p*-methyl and *p*-methoxy systems. This is linear, and the value of $\rho$ is 1.12. From this plot, we can determine that $k_0 = 7.3 \times 10^{-5}$ $s^{-1}$ for the solvolysis of pentaphenylantimony in 2-octanol at 55°.

With this value of $k_0$ in hand, we can now calculate partial rate factors for the formation of benzene and the substituted benzene at 55° for each of the compounds listed in Table 1. For example, the partial rate factor (P.R.F.) for formation of toluene from tetraphenyl-*p*-tolylantimony = $k/k_0 \times$ mole fraction toluene × statistical factor = $(4.8/7.3) \times (1/5.3) \times 5 = 0.62$. This and the other P.R.F. values are listed in Table 3.

It is possible to refine the kinetics data for the solvolysis reactions according to the known treatment [10] for parallel first-order reactions. By this treatment, it is possible to obtain specific rate constants for the production of both benzene and the substituted benzene for the solvolysis of a pentaarylantimony compound of type $Ph_4SbAr$. If only the two parallel first-order reactions are taking place, the sum of the two individual, calculated rate constants should be equal to the overall rate constant determined experimentally. In fact, as can be determined from the data presented in Tables 1 and 4, the agreement between

TABLE 4

RATE CONSTANTS CALCULATED BY THE METHOD OF PARALLEL FIRST-ORDER REACTIONS

| X in $Ph_4SbC_6H_4X$ | Temp. (°C) | $k \times 10^5$ ($s^{-1}$) for PhH formation | $k \times 10^5$ ($s^{-1}$) for PhX formation |
|---|---|---|---|
| *p*-Me | 50.0 | 2.51 | 0.57 |
| | 55.0 | 3.73 | 1.07 |
| | 65.0 | 9.90 | 3.35 |
| *p*-MeO | 50.0 | 1.41 | 1.34 |
| | 55.3 | 2.11 | 1.84 |
| | 65.0 | 4.28 | 2.75 |
| *m*-Cl | 50.0 | 6.86 | 8.74 |
| | 55.3 | 9.28 | 9.62 |
| | 65.1 | 13.2 | 15.1 |

TABLE 5

ACTIVATION PARAMETERS FOR PARALLEL FIRST-ORDER REACTIONS AT 55°

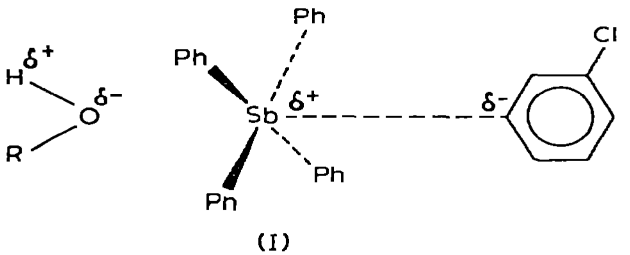
| X in $Ph_4SbC_6H_4X$ | $\Delta H^{\ddagger}$ (kcal $mol^{-1}$) | | $\Delta S^{\ddagger}$ (cal $mol^{-1}$ $K^{-1}$) | |
|---|---|---|---|---|
| | PhH | PhX | PhH | PhX |
| *p*-Me | 19.5 | 25.0 | −19 | −5 |
| *p*-MeO | 15.4 | 9.6 | −33 | −51 |
| *m*-Cl | 8.6 | 7.5 | −51 | −54 |

found and calculated values for the period of each reaction between the point at which a homogeneous solution is formed and the end of the reaction provides convincing evidence that the two competing reactions referred to earlier are the only important ones taking place. On the other hand, as might be expected, there is no agreement when an attempt is made to relate the calculated data from the start of reaction, including the heterogeneous stage, to the experimental data. This might be attributable to the occurrence of one or more additional competing reactions (besides solvolysis) during the heterogeneous stage. The additional reactions (or reaction) might very well be thermal decompositions of types previously studied [3, 11]. This would also account for the fact that quantitative yields of solvolysis products are seldom achieved.

It is also possible to calculate values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the individual reactions in any given solvolysis system. The results are pertinent to the discussion of the mechanism of the reactions, and they are summarized in Table 5.

With the aid of the data provided in Tables 1-5, it is now possible to suggest additional details of the mechanisms of the solvolysis reactions. It is convenient to discuss each solvolysis reaction separately.

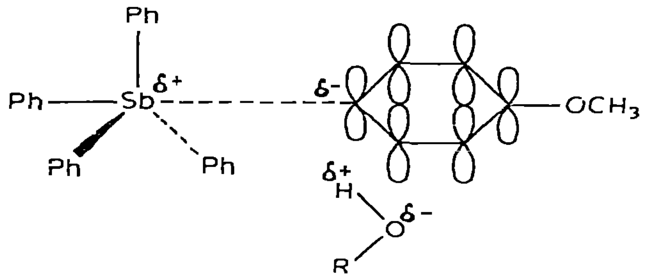
The most important facts to consider in the case of the solvolysis of *m*-chlorophenyltetraphenylantimony are (1) the very low values of $\Delta H^{\ddagger}$ for the formation of chlorobenzene and benzene; (2) the highly negative values of $\Delta H^{\ddagger}$ for the formation of chlorobenzene and of benzene; and (3) the relatively high relative rates of formation of both chlorobenzene and benzene in comparison with the formation of one molecule of benzene from pentaphenylantimony (i.e., the fundamental meaning of P.R.F. values). The best rationalization of these data incorporates relatively strong nucleophilic participation by a solvent molecule in the transition state of the fundamental $S_N1$ (Sb) reaction. A typical transition state I is shown for the departure of a *m*-chlorophenyl anion, and the



(I)

transition state for the departure of a phenyl anion would be similar. The low value of $\Delta H^{\ddagger}$ can be explained on the basis of the nucleophilic "push" exerted by the solvent molecule as a consequence of the presence of an electron-withdrawing substituent in the pentavalent antimony compound and by the presence of a relatively good leaving group, which leads to an advanced degree of breaking of the Sb—C bond in the transition state. This, in turn, leads to a somewhat greater degree of nucleophilic participation by a solvent molecule in the transition state for departure of a *m*-chlorophenyl anion than in that for departure of a phenyl anion. The highly negative value of $\Delta S^{\ddagger}$ is mainly the consequence of a solvent molecule being tied strongly into the transition state and thus losing much of its freedom of motion, but it is also attributable in part to the fact that the aryl groups have less freedom of motion in what is essentially an octahedral transition state as against that in the trigonal bipyramidal or distorted square pyramidal [12-14] configuration of the pentaarylantimony in its solution ground state. The relatively large value of the P.R.F. for chlorobenzene formation reflects the fact that the *m*-chlorophenyl anion is the most stable of all the potential aryl anions involved in the series of reactions described in this article and also the help given by the nucleophilic "push" of the solvent. The latter effect also helps increase the P.R.F. for benzene formation over that found in pentaphenylantimony (P.R.F. = 1.0 by definition) or those found in the other reactions of the $Ph_4SbAr$ compounds reported herein.

The most important facts to consider in the case of the solvolysis of *p*-methoxyphenyltetraphenylantimony are: (1) the relatively low value of $\Delta H^{\ddagger}$ for the formation of anisole and the intermediate value of $\Delta H^{\ddagger}$ for the formation of benzene; (2) the still highly negative value of $\Delta S^{\ddagger}$ for the formation of anisole (but not as negative as that for the formation of chlorobenzene in the solvolysis of the *m*-chlorophenyl compound) and the distinctly less negative value of $\Delta S^{\ddagger}$ for the formation of benzene; and, most important of all, (3) the unexpectedly high value of the P.R.F. for anisole formation and the fact that the ratio of P.R.F. values for anisole formation and benzene formation is 3.6. To explain the latter fact, we can invoke Eaborn's [15, 16] concept of electrophilic participation by a solvent molecule in the formation of anisole. Since the presence of a strongly electron-donating *p*-methoxy substituent would also discourage any strong nucleophilic participation by a solvent molecule, the transition state for anisole formation might be expected to take the form of II. The partial bonding of the proton of the alcohol to the π-cloud of the developing *p*-anisyl anion helps the formation of anisole as against benzene, and this explains the ratio of the P.R.F. values of



(II)

3.6, as well as the differences in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. In particular, since a solvent molecule is tied into transition state II, the value of $\Delta S^{\ddagger}$ should be quite negative, as it is. However, the freedom of motion of all of the groups in II would be somewhat greater than for those in I, and therefore the $\Delta S^{\ddagger}$ value for the formation of chlorobenzene in the *m*-chlorophenyl system should be more negative than that for the formation of anisole in the *p*-methoxyphenyl system, as it is. Finally, it is not unreasonable that strong nucleophilic participation by a solvent molecule (as shown in I) should be more effective in lowering $\Delta H^{\ddagger}$ than electrophilic participation (as shown in II), although one would probably not have been able to predict this in advance.

The most important facts to consider in the solvolysis of tetraphenyl-*p*-tolylantimony are (1) the relatively high values of $\Delta H^{\ddagger}$ for both benzene and toluene formation, but more so for the latter; (2) the least negative values of $\Delta S^{\ddagger}$ of all the reactions studied, and particularly that for formation of toluene; and (3) the nearly equal values of the P.R.F. for the toluene and benzene formation. These data suggest that solvation of either the nucleophilic or electrophilic type is decidedly less important for the *p*-tolyl compound than for the *m*-chloro and *p*-methoxy compounds, respectively. This is a logical development, inasmuch as the *p*-methyl substituent is only mildly electron-donating in character. Thus, it would inhibit nucleophilic participation by a solvent molecule to some degree, but, on the basis of Eaborn's results [15, 16], would not have much effect with respect to electrophilic participation by a solvent molecule. With solvent participation in the transition state at a minimum for the compounds investigated, it would be anticipated that the $\Delta H^{\ddagger}$ values would be relatively high and the $\Delta S^{\ddagger}$ values less negative than in the other cases. The lower value of $\Delta H^{\ddagger}$ for benzene formation than that for toluene formation in the solvolysis of tetraphenyl-*p*-tolylantimony reflects, in part, the greater stability of the phenyl anion over the *p*-tolyl anion and, in part, the ability of a *p*-methyl group to help stabilize the incipient triphenyl-*p*-tolylstibonium cation [6]. These two effects can also lead to a greater degree of Sb--C bond breaking in the transition state of the reaction leading to the formation of benzene than in that leading to toluene. This, in turn, causes an increase in an otherwise weak degree of nucleophilic participation by a solvent molecule in the reaction leading to formation of benzene, which therefore leads to a more negative value of $\Delta S^{\ddagger}$.

Since there is but little difference in the stabilities (ease of formation) of the phenyl and *p*-tolyl anions, the P.R.F. values for benzene and toluene formation should be about the same. The fact that both values are less than 1.0 reflects the mildly electron donating effect of the *p*-methyl substituent and the consequent diminution of nucleophilic participation by the solvent in the solvolysis. Thus, the transition states for the *p*-tolyl system come closest to that of a "pure" $S_N1$ (Sb) mechanism of the cases studied, as depicted in our previous article [6].

The data provided in Table 4 can also be used to provide a partially independent set of partial rate factors. If the values of $k$ at 55° for formation of benzene are left unchanged, while those for formation of $C_6H_5X$ are multiplied by 4 to adjust for the statistical factor, and, finally, if all of the values are now multiplied by 0.18 to adjust the scale to that used in the calculation of the original P.R.F. values given in Table 3, the new set of P.R.F. values shown in parenthesis in Table 3 results. The agreement between the two sets of P.R.F. values is remarkably good.

It would be anticipated that the situation for pentaphenylantimony would parallel that for tetraphenyl-*p*-tolylantimony. The lack of solubility of the unsubstituted compound in the various alcohols has made it impossible to confirm this is any but a qualitative sense. In that sense, however, we can state that the reactivity profile of the two compounds towards methanol, ethanol, isopropyl alcohol and 2-octanol for the heterogeneous reactions are similar. It is also worth mentioning that, if there is some degree of parallelism between the degrees of solvation of the transition states and those of the starting reagents, we would expect pentaphenylantimony and tetraphenyl-*p*-tolylantimony to be less soluble than the *m*-chloro and *p*-methoxy compounds. This is in accord with the facts.

As mentioned previously, the rates of reaction are much greater and the ratios of products are different when sodium 2-octanoxide is present in the solvolysis reaction mixture. Previously, we had suggested [6] the occurrence of an $S_N2$ (Sb—ate) mechanism when an alkoxide anion is present. The fact that we have now been able to demonstrate the occurrence of a fast second-order reaction in the solvolysis of *p*-methoxyphenyltetraphenylantimony in 2-octanol in the presence of one equivalent of sodium 2-octanoxide provides a firmer foundation for this mechanism. The corresponding $S_N2$ (Sb—ate) reactions of the *m*-chloro and *p*-methyl compounds had already passed beyond the stage of a single substitution process within a few minutes of the start of reaction and before a homogeneous solution had been formed. Evidently, the presence of the strongly electron-donating methoxy substituent slows the $S_N2$ (Sb—ate) reaction sufficiently to permit a kinetics determination to be made. However, the available data do not permit us to decide whether this is attributable to a lowering of the concentration of the ate complex in an equilibrium reaction preceding the rate-limiting ejection of an aryl anion, or whether the presence of the *p*-methoxy substituent causes a retardation of the rate-limiting ejection of an aryl anion, or both. Of course, it is also possible that attack of alkoxide anion and departure of an aryl anion are synchronous [i.e., the reaction is of the $S_N2$ (Sb) variety), but this is unlikely because of the known propensity of pentaarylantimony compounds to form ate complexes rapidly with strong bases [6, 8, 17] and also because it is unreasonable to suggest that a weaker base (2-octanoxide anion) should displace a much stronger base (an aryl anion) in a fast, synchronous process.

The question can be raised whether formation of something resembling an ate complex (actually, a conjugate acid of such a complex) represents a first step in the simple solvolysis reactions. The available evidence indicates that this is unlikely. In the first place, there is no evidence for the formation of ate complexes with pentaarylantimony compounds and related species except with strong bases [17]. Secondly, we have found that neither the apparent rate of reaction nor the ratio of benzene to toluene formed in the solvolysis of tetraphenyl-*p*-tolylantimony in propionic acid is affected by the addition of sodium propionate to the reaction mixture. Although the propionate anion is a relatively weak base, it is nevertheless a stronger one than a simple alcohol molecule. Thus, if the propionate anion does not give any evidence of forming an ate complex with a pentaarylantimony compound, it is very unlikely that an alcohol molecule will form one.

TABLE 6

SOLVOLYSIS REACTIONS OF TETRAPHENYL-*p*-TOLYLANTIMONY WITH VARIOUS SOLVENTS AT 25.0°

| Solvent | Time | Yield benzene (%) | Yield toluene (%) |
|---|---|---|---|
| Butanoic acid [a] | 2 min | 63.2 | 20.5 |
| | 6 min | 71.2 | 22.1 |
| 3-Hydroxytoluene [b] | 6 min | 49.4 | 12.8 |
| | 10 min | 73.1 | 18.0 |
| | 24 h | 79.0 | 18.0 |
| α-Hydroxytoluene [b] | 6 min | 46.2 | 11.4 |
| | 10 min | 52.9 | 16.2 |
| | 30 min | 61.9 | 16.2 |
| | 2 h | 65.7 | 18.0 |
| | 24 h | 78.2 | 18.0 |

[a] $t_H$ = 2 min. [b] $t_H$ = 6 min.

It is also pertinent that the solvolysis of tetraphenyl-*p*-tolylantimony in propionic acid is a relatively fast reaction and that the ratio of benzene to toluene produced is 3.5 rather than the values greater than 4 found with various alcohols at the lower temperatures. These observations suggest that electrophilic participation by the solvent in the solvolysis reaction increases with an increase in the acidity of the medium. Data for other solvolysis reactions are presented in Table 6.

Razuvaev, Petukhov and Osanova [18] have reported that $Ph_4PC_6D_4CH_3$-*p* undergoes reaction in refluxing ethanol to give benzene, toluene-$D_4$, triphenylphosphine oxide, diphenyl-*p*-tolylphosphine oxide and a trace of biphenyl. In a preliminary series of experiments, we have now examined the behavior of pentaphenylphosphorus in solvolysis reactions in ethanol. At 35°, with an intended concentration of 0.0489 *M* of pentaphenylphosphorus in absolute ethanol, the reaction mixture became homogeneous after 4 h. At this point, the reaction was complete, and the concentration of benzene was 0.068 *M*. No triphenylphosphine oxide and no ethyl ether [19, 20] were formed. The results were similar for a reaction carried out at 45°. While no firm conclusions about the mechanism of reaction can be reached on the basis of these data, it is nevertheless obvious that pentaphenylphosphorus is more reactive in ethanolysis than pentaarylantimony compounds, particularly with regard to the occurrence of two stages of substitution.

## Experimental

The preparation of the Grignard reagents and all of the reactions described below were carried out in a dry nitrogen atmosphere. The concentrations of the Grignard reagents were determined by iodometric titration [21]. The solvents were purified by distillation and dried over molecular sieves (Linde 3A). Elemental analyses were carried out by the Microanalysis Laboratory, University of Massachusetts.

### *Tetraphenylstibonium fluoride*

This compound was prepared by the method of Doleshall, Nesmeyanov and Reutov [7]. Its m.p. was 152-154° after crystallization from Skelly B solvent; lit. [7] m.p. 162-163° (from benzene).

### *Tetraphenyl-p-tolylantimony*

To a solution of *p*-tolylmagnesium bromide (0.035 mol) in 60 ml of anhydrous ether maintained at —20° were added 11.5 g (0.025 mol) of tetraphenylstibonium fluoride and an additional 30 ml of ether. The mixture was allowed to warm to 0° and was stirred for 20 min. A precipitate which had formed was collected by filtration and dried in vacuo. This solid was washed with ice-cold water and redried. It was then washed with 30 ml of cyclohexane, dried, and subsequently dissolved in 200 ml of warm cyclohexane, with filtration. After removal of most of the solvent from the filatrate by rotary evaporation in vacuo, 3.2 g (29%) of tetraphenyl-*p*-tolylantimony, m.p. 137-139° (lit. [6], m.p. 134—136°) crystallized. Its NMR spectrum, taken in deuteriochloroform solution, was identical with that of the sample obtained by a different method [6].

### *p-Methoxyphenyltetraphenylantimony*

A solution of 13.4 g (0.03 mol) of tetraphenylstibonium fluoride in 60 ml of anhydrous ether, contained in a 3-necked round-bottomed flask equipped with a mechanical stirrer, a condenser and a septum stopper, was cooled to —20°. To this solution was slowly added 40 ml of a 0.82 *M* solution of *p*-methoxyphenylmagnesium bromide by means of a syringe inserted into the flask through the septum stopper, the temperature of the reaction mixture being maintained at —20°. After all of the Grignard reagent had been added, the mixture was allowed to warm to 0° and was maintained at that temperature for 5 min. A precipitate which had formed was collected by filtration and dried in vacuo. The solid was dissolved in 2 l of cyclohexane/ether (90/10 by vol.), the solution filtered and most of the solvent removed by evaporation in vacuo. There was obtained 6.3 g (40%) of crystalline *p*-methoxyphenyltetraphenylantimony, m.p. 81—82°. (Found: C, 69.71; H, 5.39; Sb, 22.28. $C_{31}H_{27}SbO$ calcd.: C, 69.40; H, 5.09; Sb, 22.61%.)

The NMR spectrum of the compound was taken in deuteriochloroform solution and showed a 3 H singlet at $\delta$ 3.72 and a 24 H multiplet at 6.70—7.50. A weak signal at $\delta$ 1.4 was attributable to the presence of a trace of cyclohexane in the crystals.

### *(m-Chlorophenyl)tetraphenylantimony*

To a solution of 11.25 g of tetraphenylstibonium fluoride in 60 ml of ether was added slowly, by means of a syringe, 46 ml of a 0.61 *M* solution of *m*-chlorophenylmagnesium bromide in ether, the temperature of the reaction mixture being maintained at 0°. The mixture was stirred for 10 min and the supernatant solution removed by decantation. To this solution was added 30 ml of anhydrous Skelly F solvent. The mixture was stirred at 0° for 5 min, and a precipitate which had formed was collected by filtration. The solid was dried in vacuo, dissolved in 1 l of cyclohexane, filtered, and the solvent removed by distillation in vacuo. The residue was then crystallized from cyclohexane/Skelly B solvent (70/30 by vol.) to give 2.3 g (17%) of *m*-chlorophenyltetraphenylantimony, m.p. 97—103°. A solution of this product in diphenyl ether was subjected to VPC analysis, and was found to contain about 6-8% by weight of cyclohexane*. Found:C, 67.66; H, 5.23; Cl, 6.11. $C_{30}H_{24}SbCl \cdot 1/2C_6H_{12}$ calcd.: C, 67.89; H, 5.18; Cl, 6.07%.)

### *Kinetics*

2-Octanol was refluxed for 8 h over calcium hydride and then distilled, all operations being carried out in a nitrogen atmosphere. In a typical solvolysis experiment, 0.1260 g of *p*-methoxyphenyltetraphenylantimony was dissolved in 3.00 ml of 2-octanol which had been warmed to 55.3 ± 0.1° in a constant temperature bath. The mixture was stirred and maintained at 55.3° for 20 min, at which point a homogeneous solution resulted. Aliquots were then removed at regular intervals and quickly cooled to 0°. The aromatic hydrocarbons were analyzed by VPC, a 1 µl sample of each aliquot being injected into a Perkin—Elmer 990 gas chromatograph equipped with a 6' × 1/8" SE 30 (10%) column (helium flow 37 ml/min; injector temp. 160°; manifold, 170°; column, 118°; detector, 210°). The concentrations of hydrocarbons were determined for each aliquot by comparison of the products of peak height times retention time [24] with those of calibration curves obtained by use of solutions of known concentrations. Where necessary, corrections of benzene concentrations for cyclohexane (retention time of each = 25 min) were made, use being made of solutions of the pentaarylantimony compound in diphenyl ether, by independent VPC analyses to obtain the concentration of cyclohexane (with the help of an appropriate calibration curve). Plots of log $[C]$ vs. time, with $[C] = [C_\infty]_{(PhH\,+\,PhX)} - [C_x]_{(PhH\,+\,PhX)}$, were linear, and values of the first order rate constants were determined from the plots in the usual manner.

In the treatment of the kinetics data according to the theory of parallel first-order reactions, the reactions were considered to begin ($t = 0$) at the point of apparent homogeneity. The concentrations of each product at this point were substracted from subsequent values, giving a new set of concentration values. These were plotted as the ordinate vs. values of $(1 - e^{-k_0t})$ as the abscissa ($k_0$ is the overall first order rate constant determined as described above). Such plots were linear throughout the period in which overall reaction was amenable to kinetic analysis. Least squares refinement of such data yielded intercepts at $t = 0$ which were always less than 10% and in most cases less than 5% of the concentrations of products determined from the experimental data at $t = \infty$.

The individual rate constants for the parallel reactions were obtained by multiplying the slope of the conc. vs. $(1 - e^{-k_0t})$ plot by the quotient of the overall rate constant and the original concentration of the starting material. In calculating the rate constants for the parralel first-order reactions, the original concentration of pentaarylantimony compound was taken as the sum of the extrapolated infinite concentration values for each product. Only in the solvolyses of *m*-chlorophenyltetraphenylantimony at 55° and 65° was this calculated value different from the observed infinite concentration sum by more than ±10%.

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* Cyclohexane of crystallization has been found in other, closely related compounds. For example, pentaphenylphosphorane [22, 23] which has been crystallized from cyclohexane contains 0.5 mol of cyclohexane of crystallization.

In these two reactions, it is likely that secondary reactions are masking the actual values of the infinite concentrations of benzene and chlorobenzene (see Discussion).

For the reactions with sodium 2-octanoxide, 0.078 *M* solutions of the salt in 2-octanol were prepared by dissolution of accurately weighed amounts of clean sodium in the appropriate amounts of purified solvent. The analyses for aromatic hydrocarbons in the reactions with the pentaarylantimony compounds were carried out as described above for the simple solvolysis reactions. With the concentrations of *p*-methoxyphenyltetraphenylantimony and sodium 2-octanoxide equal, a plot of $1/[C]$ vs. time was found to be linear from the point at which a homogeneous solution was formed to the end of the reaction; $[C]$ is defined as in the simple solvolyses reactions.

### *Reaction of tetraphenyl-p-tolylantimony with propionic acid*

A typical solvolysis reaction was one in which 0.4063 g of tetraphenyl-p-tolylantimony was added to 10.0 ml of freshly distilled propionic acid, and the mixture was stirred in an ice-water bath. Aliquots (0.1 ml) were removed at regular time intervals, and a 1 μl sample of each aliquot was injected into a Varian 1200-1 hydrogen flame ionization gas chromatograph equipped with a 6' X 1/8" column containing 5% polyethylene glycol on Chromosorb W; injector t, column t and detector temperatures 140, 70 and 200° respectively. The concentrations of benzene and toluene were determined by comparison of peak areas with those obtained by use of propionic acid solutions of known concentrations of these compounds, a calibration curve being used to determine the concentrations of benzene and toluene in the reaction solutions. The reaction mixture became a homogeneous solution after 15 min. The reaction was carried out in the same manner with an equivalent amount of sodium propionate present in the reaction mixture. In either the absence or presence of sodium propionate, the yield of benzene at $t_H$ (15 min) was 70% and that of toluene 20%. After 24 h, the yield of benzene was 73% and that of toluene 20.5%.

When the same reactions were carried out in a constant termperature bath maintained at 25.0°, $t_H$ was found to be 2 min. The reaction was complete at $t_H$, the yield of benzene being 76.4% and that of toluene 22.5%, both in the absence and presence of sodium propionate.

### *Reactions of tetraphenyl-p-tolylantimony with butanoic acid, 3-hydroxytoluene and α-hydroxytoluene*

These reactions were carried out at 25.0° in the same manner as described for the propionic acid reaction. The appropriate data are provided in Table 6.

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