Reactions of 2,2,2-Triphenylethyl *p*-Toluenesulfonate in Alcohol Solutions in the Presence of Base under High Pressure. Effects of Pressure on SN1- and SN2-Type Reactions

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The reactions of 2,2,2-triphenylethyl *p*-toluenesulfonate (**1**) with sodium alkoxide in methanol and ethanol solutions were studied at both 1 atm and 5000–5500 atm. In alcohol solution, solvolysis of **1** in the presence of a low concentration of base yielded quantitatively phenyl-migrated products, viz., 1,2,2-triphenylethyl alkyl ether (**2**) and triphenylethylene (**3**). However, it was found that when the concentration of base was increased, the nucleophilic substitution reaction (SN2) competed with the ionization reaction (SN1) and the products were found to be mixtures of **2**, **3**, and 2,2,2-triphenylethyl alkyl ether (**4**). The yield of the unrearranged product **4** was increased accordingly with the base concentration. However, the amount of **4** was found to be decreased by applying pressure to the system. The results indicated that the effect of pressure was greater on the solvolytic reaction than on the nucleophilic substitution reaction. These results were explained in view of different activation volumes. In the solvolytic reactions of **1**, the amount of the rearranged ether product **2** was also found to be increased over the olefin product by the application of pressure. The result was accounted for by the contraction of volume of the system and the favorable structure of the transition state in the formation of the ether as compared to that of the transition state leading to olefin. When the compound **1** was treated with NaOH in water–dioxane solution, the nucleophilic substitution product, 2,2,2-triphenylethanol (**5**), was produced along with triphenylmethane (**6**). The source of compound **6** was found to be a further reaction of **5** with NaOH through a carbon–carbon cleavage process.

In recent years, the use of high pressure for the study of organic chemistry has been increasing.[2] The pressure dependence of the rate constant of a reaction is $(\partial \ln k/\partial p)_T = -\Delta V^{\ddagger}/RT$, where $\Delta V^{\ddagger}$ is the volume of activation. If this volume is negative, i.e., the formation of the transition state complex from the reactants results in overall contraction, the rate constant k will be increased with increasing pressure.[3]

The effect of pressure on the rate of solvolytic and nucleophilic displacement reactions of alkyl halides has been investigated by a number of workers.[4,5] Generally, both reactions were found to be enhanced by applying pressure to the reaction system.

Nucleophilic substitutions (SN2) on neopentyl carbon were found to be notoriously difficult although not impossible under forcing conditions.[6,7] A phenyl group is much bulkier than a methyl group and as a consequence the nucleophilic substitution reaction on the C_1 in the 2,2,2-triphenylethyl system is expected to be much less favored than the same reaction in the neopentyl system. This possibility has never been investigated.

The solvolysis of 2,2,2-triphenylethyl *p*-toluenesulfonate (**1**) is much faster than a similar solvolysis for neopentyl *p*-toluenesulfonate, cf. about 7000 times in acetic acid.[8] Compound **1** is a highly substituted system and the relief of steric strain at C_2 in the ionization stage can account for the driving force leading to the enhanced rate. The bridged phenonium ion or the phenyl-rearranged stable tertiary carbonium ion was proposed as the transition state.[8–10] In methanol or ethanol solution **1** was solvolyzed in the presence of a low concentration of sodium alkoxide to yield quantitatively the phenyl-migrated products, viz., 1,2,2-triphenylethyl methyl ether (**2a**) or 1,2,2-triphenyldiethyl ether (**2b**) and triphenylethylene (**3**).[11] However, we have found that when the concentration of RONa was increased, the nucleophilic substitution reaction competed with the ionization reaction. Thus, the products were found to be mixtures of **2**, **3** and either 2,2,2-triphenylethyl methyl ether (**4a**) or 2,2,2-triphenyldiethyl ether (**4b**). The yield of the unrearranged product **4a** or **4b** was increased accordingly with the base concentration.

This system presents an interesting case for the study of the effects of pressure on SN1 and SN2 reactions, because the possibility of backside nucleophilic attack by solvents and normal 1,2 elimination with base are both impossible. Therefore, the solvolysis of **1** was investigated in alcohol containing NaOH or RONa at 1 atm and under high pressure.

Results

Solvolysis of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1) in the Presence of Base. Compound **1** was solvolyzed in either dioxane–water or dioxane–alcohol solution in the presence of NaOH or sodium alkoxide in the following manner. The reactants were placed in a Teflon capsule (volume 4 cm^3), which was subsequently heated to 80–100 °C for 20–25 h slightly above 1 atm pressure. When the reactions were carried out in Pyrex vessels, the base was found to react with the glass and the product distributions were found to be different from those found when the reaction was carried out in a Teflon vessel (see Experimental Section). After the solvent was removed under reduced pressure, the solid was treated with H_2O and extracted with ether. The products were then analyzed by GC and characterized by comparison with authentic samples. Typical results are summarized in Table I.

Reactions of 2,2,2-Triphenylethanol (5) with Base. In order to find the source of triphenylmethane (**6**) produced in the reactions with NaOH (see Table I), 2,2,2-triphenylethanol (**5**) was allowed to react with various concentrations of NaOH. The products were analyzed as described above and typical results are summarized in Table II. It was found that **5** reacted further with NaOH to give a carbon–carbon bond cleavage product **6**.[12] The amount of **6** was found to increase with increasing concentrations of NaOH and reaction temperature.

Reactions of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1) with Sodium Alkoxide in Alcohol under 1 Atm and High Pressure. In order to avoid complications involving the carbon–carbon cleavage of **5** with NaOH, the reactions of **1** were studied in detail in alcohol solution with the corresponding sodium alkoxide. The reactants were placed in Teflon capsules which were then heated at 80–85 °C for 20–25 h under both 1 atm pressure and also at

Table I. Effects of Base on the Solvolysis of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1)[a]

Solvent	Base (mmol)	Temp, °C	Products, %				
			2	**3**	**4**	**5**	**7**[b]
Dioxane–water[c]	NaOH (1)	90		55			45
Dioxane–water[c]	NaOH (2)	90		47		17[d]	33
Dioxane–water[c]	NaOH (3)	90		35		30[e]	30
Dioxane–MeOH[f]	MeONa (4)	100	48.2	46.6	5.2		
Dioxane–MeOH[f]	MeONa (8)	100	49.5	37.5	14.0		
Dioxane–EtOH[g]	EtONa (2)	100	37.5	59.5	3.0		
Dioxane–EtOH[g]	EtONa (4)	100	32.4	54.9	12.7		
Dioxane–EtOH[g]	EtONa (8)	100	29.4	37.4	33.2		

[a] Tosylate (0.77 mmol) was used. [b] 1,1,2-Triphenylethanol (**7**). [c] Dioxane (3 ml) and H_2O (1 ml) were used. [d] 2,2,2-Triphenyleth anol (**5**) was further treated with NaOH to yield 3% triphenylmethane (**6**). [e] Triphenylmethane produced was ~5%. [f] Dioxane (2 ml) and MeOH (2 ml) were used. [g] Dioxane (2 ml) and EtOH (2 ml) were used.

Table II. Reactions of 2,2,2-Triphenylethanol (5) with NaOH[a]

Run no.	Reaction conditions			Triphenyl-methane produced, %
	[NaOH], mol	Temp, °C	Reaction time, h	
9	0.023	80	24	7
11	0.023	100	24	23
13	0.050	100	24	30
15	0.070	100	24	45
17	0.070	130	24	100

[a] The reactions were carried out in Teflon vessels. The initial concentration of 2,2,2-triphenylethanol was 0.004 mol in a mixed solvent system composed of dioxane (50 ml)–methanol (20 ml).

5000–5500 atm using the method previously reported.[13] Control experiments established that **3** was not further reacted under the reaction conditions. The products were isolated as described above and analyzed by GC. Typical results are summarized in Table III.

Discussion

The effect of pressure on the rate of reaction in the liquid phase is known to be controlled by the volume change in the course of formation of the activated complex. Evans and Polanyi[14] suggested that the volume of activation ($\Delta V^{\ddagger}$) should be regarded as the sum of two terms. The structural term $\Delta V_1^{\ddagger}$ is the change in volume of the reacting molecules themselves when they form the transition state, while the solvation term $\Delta V_2^{\ddagger}$ is the accompanying volume change due to interactions of the surrounding molecules with the newly formed charges in the transition state.

Generally, in SN1-type reactions of alkyl halides, the rate-determining step is an ionic process, and $\Delta V^{\ddagger}$ was found to be negative, usually in the order of −15 to −25 cm^3/mol.[15] Since this ionization process implies bond cleavage, one might assume that $\Delta V^{\ddagger}$ is positive. However, at the transition state, charges exert a powerful attractive force on the nearby solvent molecules, and as a result, the molecules in the solvated hull are denser than in the bulk solvent. Thus $\Delta V^{\ddagger}$'s for these kinds of reactions generally have negative values since the $\Delta V_2^{\ddagger}$'s play decisive roles in determining the signs and magnitudes of the $\Delta V^{\ddagger}$'s.

In SN2 reactions such as the reaction of **1** with RONa, there are no additional ions produced or destroyed. In the transition state, the charge is being transferred and is probably dispersed somewhat. A fair number of such reactions have been studied and nearly all have volumes of activation between −5 and −10 cm^3/mol.[16] These negative volumes were accounted for by decreasing the structural volume $\Delta V_1^{\ddagger}$.

The solvolysis rate of **1** in dioxane–ethanol was found to be greatly enhanced by applying pressure. The reaction products were quantitatively the phenyl-rearranged compounds, **2** and **3**. The activation volume for this system was found to be about −14 cm^3/mol.[11] The sign and magnitude of this value are similar to those for the solvolysis of alkyl tosylate in which the transition states were suggested to have a large degree of charge delocalization.[17] The structure of the transition state for the solvolytic reaction of **1** may be considered to be a carbonium ion highly stabilized by resonance and in which the charge is dispersed throughout the phenyl rings. Thus, the activation volume appears to be somewhat smaller than those associated with the solvolysis of other alkyl tosylates.

The reaction of **1** in alcohol–dioxane with a high concentration of RONa yielded the phenyl-unrearranged product **4** as well as the rearranged products **2** and **3**. The variance of the proportion of the unrearranged product formed with varying base (NaOH and RONa) concentrations over a considerable range suggests that product **4** resulted only from nucleophilic attack of RONa on C_1 (Table I). Since the direct measurement of $\Delta V^{\ddagger}$ for the SN2 reaction of **1** is difficult because of the accompanying solvolytic reaction, the reaction products were isolated and analyzed in order to find the pressure effects on the SN2 reaction.

As has been shown in Table III, the amounts of the rearranged products were increased at the expense of SN2 substitution products by applying pressure on the system, cf. the relative ratio of SN1 to SN2 reactions in ethanol–dioxane with 1 and 2 N sodium ethoxide under 5500 atm were increased respectively three- and fivefold over those under 1 atm. These results indicate that the pressure effect on the SN1 reaction of **1** is more pronounced than on the SN2 reaction. This may be accounted for by the development of a highly ionic character at the transition state for the SN1 reaction and in which the solvation term $\Delta V_2^{\ddagger}$ for this reaction plays a decisive role. Thus, the phenyl-rearranged products were increased by applying pressure.

The amount of ether production in the solvolytic reaction was found to be increased compared to olefin formation by applying pressure to the system; cf., the ratio of ether to olefin formation was increased from 3.3 to 10.5 in methanol with 16 mmol of MeONa and from 0.79 to 1.44 with 8 mmol of EtONa under 5500 atm (Table III). This phenomenon may be accounted for by tight solvation under pressure and probably the oxygen atom of the alcohol is more closely attracted to the carbonium ion under high pressure than it would be at 1 atm. Therefore, the structure of the transition state under high pressure has rather more favorable conditions for ether formation in contrast with

Table III. Effects of Pressure on S_N1 and S_N2 Reactions of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1)[a] with Sodium Alkoxide in Alcohol

		Reaction products, %							
		1 atm[b]				5500 atm			
Alcohol	Base (mmol)	2	3	4	S_N1/S_N2[c]	2	3	4	S_N1/S_N2[c]
MeOH	MeONa (4)	48.2	46.6	5.2	18.2	50.0	46.2	3.8	25.3
MeOH	MeONa (8)	49.5	37.5	14.0	6.2	52.3	38.7	9.0	10.0
MeOH	MeONa (16)	52.6	15.8	31.6	2.2	79.1	7.5	13.4	6.5
EtOH	EtONa (2)	37.5	59.5	3.0	32.3	62.0	37.0	<1.0	>99.0
EtOH	EtONa (4)	32.4	54.9	12.7	6.7	60.9	34.5	4.6	21.0
EtOH	EtONa (8)	29.4	37.4	33.2	2.0	53.6	37.3	9.2	9.9

[a] Tosylate (0.77 mmol) was used for all reactions. All reactions were carried out at 80–85 °C. [b] The pressure was slightly higher than 1 atm in order to conduct the reaction above boiling points of the solvents. [c] The ratio of S_N1 to S_N2 reaction products.

Table IV. Reactions of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1) with Sodium Alkoxide in Methanol or Ethanol in the Pyrex Glass Vessel

			Products, %		
Solvent	Base (mmol)	Temp, °C	2	3	4
Dioxane–MeOH	MeONa (8)	100	50.8	48.1	1.1
Dioxane–MeOH	MeONa (16)	100	54.2	19.4	26.4
Dioxane–EtOH	EtONa (4)	100	33.0	60.5	6.5
Dioxane–EtOH	EtONa (8)	100	36.8	45.0	18.2

olefin formation. In addition, the formation of ether involves the combination of solvent and an ion, and as a result the volume of the system is expected to decrease. On the other hand, the volume for olefin formation remains almost unchanged. Therefore, formation of the substitution product is more favorable than that of the elimination reaction under high pressure.

Experimental Section

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected. The infrared absorption spectra were determined on a Perkin-Elmer Model 521 spectrophotometer and were calibrated using 6.23-μ (1603 cm^{-1}) band of polystyrene film. Nuclear magnetic resonance spectra were obtained with Varian A-60 and/or Varian HR-220 spectrometers using Me_4Si as internal standard in chloroform-*d* or carbon tetrachloride. Vapor phase chromatography analyses were performed on an Aerograph A-700 instrument, with a 10% SE-30 silicone rubber on Chromosorb W (80–100 mesh, 10 ft × 0.25 in. aluminum column). In quantitative analyses, areas under the peaks in the chromatogram were measured using either the cut-and-weigh method or with a K and E Model 4236M planimeter.

Materials. 2,2,2-Triphenylacetic acid, triphenylethylene, and 1,1,2-triphenylethanol were purchased from Aldrich Chemical Co., Milwaukee, Wis. Dioxane of reagent grade was purified by distillation and stored over sodium wire. In all cases, NMR and VPC were used to ensure a high degree of purity.

Preparation of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1). 2,2,2-Triphenylacetic acid was reduced directly with lithium aluminum hydride in THF in the usual manner,[19] producing the ethanol in 45% yield (0.10-mol scale), with mp 105–106 °C after recrystallization from methanol (lit. mp 107 °C). The toluenesulfonate, mp 106 °C, was prepared in 48% yield by the standard procedure.[20] Its NMR spectrum consisted of aromatic peaks between δ 7.0 and 7.6 (m, 19 H), CH_2 peak at δ 4.9 (s, 2 H), and CH_3 peak at δ 2.4 (s, 3 H).

Typical Reaction Procedures of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1) with Sodium Alkoxide in Methanol or Ethanol Solutions. A mixture of 0.43 g (0.01 mol) of 1 and various concentrations of sodium alkoxide or sodium hydroxide in 2 ml of alcohol and 2 ml of dioxane was prepared in a drybox. The solution thus prepared was placed in a Teflon capsule (1.8 cm i.d., 2 cm long), and the system was pressurized to 5000–5500 atm at 80–85 °C for 20–25 h.[18] The reaction mixture was quenched with H_2O, extracted with ether, and then dried over anhydrous magnesium sulfate. After removal of the solvent on a rotary evaporator, the concentrated product mixture was analyzed by VPC. Retention times of each peak were in good agreement with those of authentic samples, 2, 3, and 4. Compounds 2 and 4 were synthesized by the method of Williamson.[21] Each compound was identified by NMR, ir, and VPC.

In a control experiment, a solution of 2.56 g (0.01 mol) of triphenylethylene (3) in 4 ml of 50% absolute ethanol–50% dioxane (v/v), with 8 mmol of sodium ethoxide was placed in a Teflon capsule and subsequently pressurized at 120 °C for 48 h under 5000–5500 atm. NMR and VPC showed the presence only of the starting material 3.

Typical Reaction Procedures of 2,2,2-Triphenylethanol (5) with Sodium Hydroxide. Compound 5 was treated with 0.023 mol of NaOH at 100 °C for 24 h in a Teflon vessel. Twenty-three percent of triphenylmethane was produced and was identified by NMR.

Reactions of 2,2,2-Triphenylethyl *p*-Toluenesulfonate (1) with Sodium Alkoxide in Methanol or Ethanol in a Pyrex Glass Vessel. When reactions of 1 with various concentrations of sodium ethoxide in methanol or ethanol were done in Pyrex glass vessels, typical results are shown in Table IV. The S_N2 product 4 was found to be decreased compared to that of the reaction carried out in a Teflon vessel (see Table I). The result indicated that RONa had reacted with Pyrex glass and decreased the base concentration.

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Registry No.—1, 808-85-5; 5, 896-32-2; NaOH, 1310-73-2; MeONa, 124-41-4; EtONa, 141-52-6; 2,2,2-triphenylacetic acid, 595-91-5.

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Reaction of 1,1-Dibenzoyl-2,2-dimethylhydrazine with Methyl *p*-Toluenesulfonate

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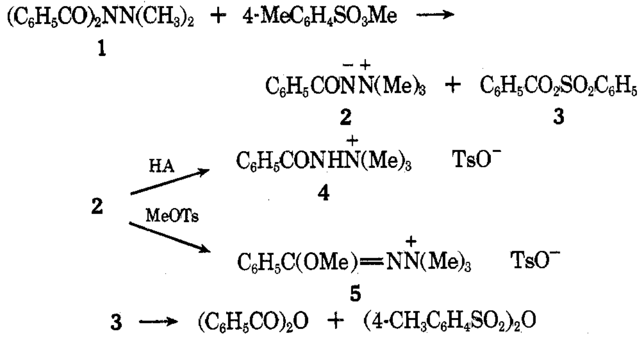
Reaction of 1,1-dibenzoyl-2,2-dimethylhydrazine with 2 equiv of methyl *p*-toluenesulfonate at 120–130 °C afforded a mixture containing 1,1,1-trimethyl-2-benzoylhydrazinium *p*-toluenesulfonate, 1,1,1-trimethyl-2-α-methoxybenzylidenehydrazinium *p*-toluenesulfonate, benzoic anhydride, and *p*-toluenesulfonic acid. The reaction apparently proceeds via the intermediate formation of 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt [$C_6H_5CO\bar{N}N^+(Me)_3$] and benzoyl *p*-toluenesulfonate.

Hinman has reported that 1,1-dibenzoyl-2,2-dimethylhydrazine (**1**) affords debenzoylated products on reduction with lithium aluminum hydride[1] and hydrogenolysis with Raney nickel.[2] This paper reports additional examples of deacylation reactions of **1**.

We have found **1** to be unreactive to alkylation with methyl iodide but reaction with 2 equiv of methyl *p*-toluenesulfonate at 120–130 °C afforded a mixture of salts consisting of 1,1,1-trimethyl-2-benzoylhydrazinium *p*-toluenesulfonate (**4**) and 1,1,1-trimethyl-2-α-methoxybenzylidenehydrazinium *p*-toluenesulfonate (**5**). The **4**:**5** ratio varied from 0.4 to 1.5 with the O-methylated material (**5**) predominating when the reaction was conducted on a degassed reaction mixture utilizing methyl *p*-toluenesulfonate that had been freed of acid impurities. Nonionic products were found to consist of benzoic anhydride and *p*-toluenesulfonic acid. Ethyl benzoate and benzoic acid (probably originating from benzoic anhydride) were also isolated when the reaction mixture was worked up in ethanol.

The structure of salt **5** was established by its synthesis from the reaction of 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt (**2**) with methyl *p*-toluenesulfonate.[3] Salt **4** was recovered unchanged after prolonged treatment with methyl *p*-toluenesulfonate at 120 °C.

The above results suggest that reaction of **1** and methyl *p*-toluenesulfonate initially affords 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt (**2**) and benzoyl *p*-toluenesulfonate (**3**). Once formed, **2** may then competitively undergo either O-methylation to give **5** or protonation (most likely by *p*-toluenesulfonic acid) to give **4**. The mixed anhydride (**3**) was prepared by the method of Overberger and Sarlo[4] and was found to be thermally unstable. When heated at 120 °C **3** was transformed to benzoic anhydride and *p*-toluenesulfonic acid, which are products also isolated from the reaction of **1** and methyl *p*-toluenesulfonate. The latter results may be accounted for by disproportionation[5] of **3** to *p*-toluenesulfonic anhydride and benzoic anhydride followed by selective hydrolysis of *p*-toluenesulfonic anhydride by moisture.[6]



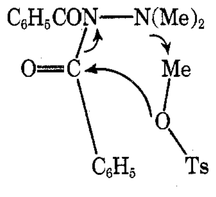
$$\underset{\mathbf{1}}{(\mathrm{C_6H_5CO})_2\mathrm{NN(CH_3)_2}} + 4\text{-}\mathrm{MeC_6H_4SO_3Me} \longrightarrow \underset{\mathbf{2}}{\mathrm{C_6H_5CO\overset{-}{N}\overset{+}{N}(Me)_3}} + \underset{\mathbf{3}}{\mathrm{C_6H_5CO_2SO_2C_6H_5}}$$

$$\mathbf{2} \xrightarrow{\mathrm{HA}} \underset{\mathbf{4}}{\mathrm{C_6H_5CONH\overset{+}{N}(Me)_3}} \quad \mathrm{TsO^-}$$

$$\mathbf{2} \xrightarrow{\mathrm{MeOTs}} \underset{\mathbf{5}}{\mathrm{C_6H_5C(OMe){=}N\overset{+}{N}(Me)_3}} \quad \mathrm{TsO^-}$$

$$\mathbf{3} \longrightarrow (\mathrm{C_6H_5CO})_2\mathrm{O} + (4\text{-}\mathrm{CH_3C_6H_4SO_2})_2\mathrm{O}$$

We have been unable to isolate the aminimide **2** from a reaction involving molar equivalents of **1** and methyl *p*-toluenesulfonate. The latter experiment afforded a mixture consisting of 30% of **5** and 13% of **4** (based on recovered **1**). Thus, the evidence for the intermediacy of **2** must be based on the isolation of its transformation products, **4** and **5**. A possible pathway for the conversion of **1** to **2** may involve a cyclic transition state in which N-methylation and debenzoylation occur in a concerted manner as indicated below.



We have also found that **1** is converted to *n*-butyl benzoate (54%) and 1,1-dimethyl-2-benzoylhydrazine in refluxing 1-butanol.[7]

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. NMR spectra were determined on a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane as an internal standard.

Reaction of 1,1-Dibenzoyl-2,2-dimethylhydrazine (1) with Methyl *p*-Toluenesulfonate. Identification of 1,1,1-Trimethyl-