53.46; H, 3.99. Found: C, 53.75; H, 3.70. **7n**-OBs had mp 135–136°. **9n**-OBs had mp 168–169.5°.

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Involvement of a Solute in a Transition State without Any Effect on Rate. The Role of Added Pyridine in Methanolysis of Triphenylmethyl Chloride in Benzene Solution[1]

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Abstract: The role of added pyridine in the methanolysis of triphenylmethyl (trityl) chloride in dilute dry benzene solutions at 25° is now clear. The rate of methanolysis in the presence of excess pyridine is first order in stoichiometric methanol below 0.005 M methanol, and first order in trityl chloride. Methanol in solutions more concentrated than 0.1 M in pyridine is appreciably associated with pyridine according to infrared and vapor-pressure data. Nevertheless, the rate of methanolysis is independent of pyridine concentration, and unchanged when pyridine is replaced by the very much more hindered 2,6-di-*t*-butylpyridine. Therefore, tritylpyridinium chloride (I) is not an intermediate, when pyridine is present. However, pyridine is involved: it prevents catalysis and reversal by HCl, by forming pyridinium chloride; it prevents otherwise serious adsorption of methanol on and reaction with the glass walls of the vessel; and it is a constituent of the transition state without HCl, to an extent that depends on pyridine concentration but has no effect on the rate. No kinetically significant amount of I is formed from reaction of trityl chloride and pyridine in benzene solution under ordinary conditions because the equilibrium is unfavorable. The "tritylpyridinium chloride" reported in the literature is a complex of triphenylcarbinol and pyridinium chloride, associated through a weak hydrogen bond in the solid state.

The methanolysis of triphenylmethyl (hereafter called trityl) chloride in benzene solution containing excess pyridine produces trityl methyl ether.

$$(C_6H_5)_3CCl + CH_3OH \xrightarrow{\text{slow}} (C_6H_5)_3COCH_3 + HCl$$

$$HCl + C_5H_5N \xrightarrow{\text{fast}} C_5H_5NHCl$$

Pyridine has been added to suppress reversal of the first reaction by combining with hydrogen chloride.[2] This also suppresses catalysis of the slow step by hydrogen chloride. Trityl chloride and pyridine do not react to a kinetically significant extent under these conditions in benzene at 25°,[3] and the rate of the reaction of trityl chloride with methanol in benzene is independent of the nature or concentration of tertiary amine when pyridine, 2,6-lutidine, triethylamine, or tribenzylamine is present, provided that any one of these amines is used in excess over the hydrogen chloride produced.[2]

Ingold and coworkers, on the other hand, stated that the reaction of trityl chloride in benzene solution with tertiary amines, *e.g.*, with pyridine to form tritylpyridinium chloride (I), although reversible, "goes forward extensively, at a rate comparable with the rate of chlorine exchange of trityl chloride with a saline radiochloride,"[4] which is much faster than the methanolysis. Leffek and Waterfield in 1967[5] reported additional kinetic data, which they interpreted as showing that pyridine very rapidly forms a "tetrahedral complex" with trityl chloride, markedly changing the reactivity of the trityl chloride.

In order to evaluate the role of pyridine in these reactions critically, 2,6-di-*t*-butylpyridine was used in the present reinvestigation of methanolysis of trityl chloride in benzene solution at 25°. 2,6-Di-*t*-butylpyridine reacts with protonic acids, but, because of extraordinarily high steric hindrance, it fails to react with Lewis acids or with alkyl halides such as methyl iodide at 1 atm.[6] Therefore, no reaction is likely between trityl chloride and 2,6-di-*t*-butylpyridine. If the formation of tritylpyridinium chloride (I) or of any tetrahedral complex of pyridine and trityl chloride were involved either in the rate-determining step or in a prior equilibrium step when pyridine is present, the rate of methanolysis of trityl chloride in the presence of 2,6-di-*t*-butylpyridine should be orders of magnitude

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[1] Supported in part by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905.

[2] C. G. Swain and E. E. Pegues, *J. Am. Chem. Soc.*, **80**, 812 (1958); C. G. Swain, *ibid.*, **70**, 1119 (1948).

[3] A. E. Tschitschibabin [*J. Russ. Phys. Chem.*, **33**, 249 (1902); *Chem. Zentralbl.*, **73**, No. 1, 1301 (1902)] first reported that even neat pyridine and I do not react unless equivalent water is added, whereupon a complex of pyridine and triphenylcarbinol is formed.

[4] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 356; E. D. Hughes, C. K. Ingold, S. F. Mok, and Y. Pocker, *J. Chem. Soc.*, 1238 (1957).

[5] K. T. Leffek and R. G. Waterfield, *Can. J. Chem.*, **45**, 1497 (1967). A difficulty with their mechanism (their eq 2–4) used to explain slight retardation by tetrabutylammonium chloride is that it violates the principle of microscopic reversibility. A simpler interpretation is that this salt also suppresses catalysis by hydrogen chloride by complexing with hydrogen chloride.

[6] H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953); **88**, 986 (1966).

less than that in the presence of pyridine. The rates of methanolysis of trityl halides in benzene with these amines were measured by the isotopic tracer technique using methanol labeled with tritium.[2] Concentrations were below 0.005 *M* methanol, so that the total kinetic order of the reaction was second (first order in trityl halide and first order in methanol). Results are given in Table I.

Table I. Second-Order Rate Constants for Methanolysis of Trityl Halides in Benzene at 25°

$(C_6H_5)_3$-CCl,[a] *M*	$CH_3OH \times 10^4$, *M*	C_6H_5N, *M*	2,6-$(t\text{-}C_4H_9)_2$-C_5H_3N, *M*	$k_2 \times 10^5$, M^{-1} sec^{-1}
0.089	16.4	0.0048		8.54
0.124	9.26	0.020		6.68
0.0625	8.19	0.040		6.64
0.0770	7.41	0.080		6.67
0.0762	20.0	0.081		8.08
0.0961	23.1	0.100		8.02
0.089	16.4	0.710		6.25
0.089	16.4	1.24		6.38
0.0625	8.19		0.038	6.06
0.0937	8.19		0.038	6.98
0.0937	40.9		0.038	7.78
0.020[a]	8.20	0.020		840[a]
0.020[a]	8.20		0.0146	870[a]

[a] Last two rows for $(C_6H_5)_3CBr$ instead of $(C_6H_5)_3CCl$.

Table I shows that the second-order rate constant for trityl chloride is identical within experimental error with the two amines (av $k_2 = 7.3 \times 10^{-5}$ M^{-1} sec^{-1}). The rate of methanolysis of trityl bromide is over one hundred times that of the chloride, but is again independent of the nature of the amine present. These results disprove the involvement of tritylpyridinium chloride (I) or of any tetrahedral complex of pyridine and trityl chloride as an important intermediate in the methanolysis of trityl chloride in benzene solutions containing pyridine, because the great difficulty in forming an analogous intermediate with 2,6-di-*t*-butylpyridine should lead to a transition state closely resembling the intermediate, with an energy accordingly sensitive to the structure of the amine (not found). Therefore, the published reinterpretations[4,5] of work on methanolysis in our laboratories[2] cannot be correct.

Tritylpyridinium Chloride (I). The kinetics above prove that tritylpyridinium chloride (I) is not a kinetically significant intermediate in benzene solution under any of the conditions used.[2-5] Nevertheless, I does exist. It has recently been synthesized by reaction of trityl chloride and pyridine under high pressure, and is stable at 25° when the pressure is removed.[7] Tritylpyridinium bromide or perchlorate can be isolated as colorless salts from reaction of trityl bromide or perchlorate and pyridine even at atmospheric pressure. The reason why the concentration of pyridine does not influence the rate of methanolysis of trityl chloride in benzene solution is simply that the equilibrium of trityl chloride and pyridine to give I is so unfavorable that less than a few per cent of the molarity of trityl chloride is ever present as I. Nevertheless, species such as I are much stabler and in much higher concentration than triarylcarbonium ions, which are easily distinguished by their color from the visibly colorless triarylmethylammonium ions. For example, the reaction of trianisylmethyl chloride with pyrrole in benzene solution at 25° demonstrates accumulation and subsequent decay of red ionic trianisylmethyl chloride, but kinetic analysis establishes that there is a mobile equilibrium between this cation and pyrrole to give the visibly colorless triarylmethylammonium ion (trianisylmethylpyrrolium ion) with an equilibrium constant of 100 in favor of the latter.[8] Similarly, it has been found from spectroscopic and conductivity measurements[9] that the equilibrium between ionic trityl bromide and pyridine to give the visibly colorless tritylpyridinium bromide in 1,1,2,2-tetrachloroethane at 20° has a constant between 1.1×10^5 and 6.6×10^5 M^{-1}. Although such constants are large, this still does not represent kinetically significant accumulation of triarylmethyl halide in any ionic form in solution at our pyridine concentrations, because the prior equilibrium between covalent and ionic triarylmethyl halide is so extremely unfavorable in these low dielectric aprotic solvents.

Complexing between Methanol and Pyridine in Reactant and Transition States. The zero-order dependence of rate of methanolysis on pyridine does *not* mean that pyridine is never in the transition state under our conditions. To justify that further deduction one would have to show that no appreciable part of the reactant methanol is complexed with pyridine under any of our conditions. Virtually any degree of involvement in and stabilization or destabilization of the transition state by pyridine would still be consistent with the observed independence of rate on type and concentration of amine, depending on what sort of complexing exists between methanol and the amine in the initial reactant state of the solution. In fact, we find that under some of our conditions (though not under most) more than half of the methanol is complexed with pyridine. This leads to the surprising conclusion that the methanol–pyridine complex has reactivity identical with free methanol. Evidently pyridine can be a constituent of the transition state, but it then stabilizes it to the identical extent that it stabilizes methanol in the initial reactant state in the solution. This illustrates the indispensability of studying association among reactants before attempting to deduce the gross composition of a transition state from kinetic data.

With 1.24 *M* pyridine and 0.0016 *M* methanol, over 80% of the methanol is complexed (see Experimental Section). With 2,6-lutidine or other more strongly basic amines, the extent of complexing should be even greater. Such complexing alters the rate less than 10%.[2] This provides an example, unique as far as we are aware, of complexing or involvement of a reactant in a transition state without change in rate.

We picture the association of pyridine in the transition state, when it occurs, as involving a hydrogen bond between pyridine and the methanol molecule that ultimately forms the covalent O–C bond. Such a hydrogen bond need not be different in strength from that between pyridine and methanol in the initial

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[7] Y. Okamoto and Y. Shimakawa, submitted for publication.

[8] C. G. Swain, L. E. Kaiser, and T. E. C. Knee, *J. Am. Chem. Soc.*, **77**, 4681 (1955).

[9] G. Briegleb, W. Rüttiger, and W. Jung, *Angew. Chem., Intern. Ed. Engl.*, **2**, 545 (1963).

reactant state. The absence of any net effect on the rate is thus attributed to fortuitous perfect cancellation of activity coefficient changes (or equivalent free-energy changes) due to such complexing (see Experimental Section for further details).

One may object that failure of the rate to decrease because of complexing of methanol at the higher pyridine concentrations might be due to a fortuitously exactly cancelling increase in rate constant due to a medium effect, because pyridine is then a substantial fraction of the total solvent. This appears to us to be merely rephrasing our same interpretation in an alternate way. The rate can certainly be reexpressed as a single term involving the activities of methanol, trityl chloride, and a transition state, or as a sum of two terms, only one of which explicitly involves pyridine as an additional reactant and extra component of the transition state. However, in either treatment, the observed fact that added pyridine does not change the rate, in spite of cutting down the concentration and activity of free methanol (CH_3OH), forces one to the same remarkable conclusion: the reason why pyridine does not affect the rate is that it is equally strongly complexed in reactant state and transition state.

Reaction between Methanol and Glass. Pyridine or other tertiary amines have another curious but helpful effect in kinetic studies of methanolysis in benzene solution in glass reaction vessels. They greatly decrease adsorption of methanol on the walls, evidently by themselves becoming hydrogen bonded instead to hydroxyl groups on the glass surface. In the absence of amines, when benzene solutions with low concentrations of methanol (4×10^{-4} to 4×10^{-3} M) are allowed to stand in 100- or 250-ml Pyrex volumetric flasks for 24 hr at 25°, 10–50% of the methanol disappears from the solution. Similar adsorption of methanol on glass surfaces from carbon tetrachloride solutions has been reported,[10] and methanol solutions or vapor react with Pyrex to produce trimethyl borate.[11] However, when 0.02 M pyridine was mixed with the benzene first, no loss of methanol from 10^{-4} to 10^{-3} M solutions in benzene was observed. Methan-*t*-ol was again used as a tracer in these studies. Sixfold increases of surface area (by use of Pyrex glass wool) or substitution of polyethylene bottles as reaction vessels had no influence on the rate of methanolysis of trityl chloride when 0.0048 M or higher concentrations of pyridine were present. Polyethylene vessels do not absorb methanol even in the absence of amines.

Complex (II) between Triphenylcarbinol and Pyridinium Chloride. "Tritylpyridinium chlorides" (mp 167, 171, 174°) have been reported by several investigators.[12] To facilitate the search for such compounds under our conditions of methanolysis, the infrared spectra of trityl chloride and pyridine both in benzene solution and in pyridine solution were recorded (no methanol present). However, the spectra of the solutions 10 min after mixing were identical with those taken after 48 hr under a nitrogen atmosphere, and the trityl chloride was recovered quantitatively by evaporation of benzene and pyridine. Moreover, every attempt to synthesize I from trityl chloride by conventional procedures (without pressure) was unsuccessful.[7,13] However, when a benzene solution of trityl chloride and pyridine was allowed to stand at room temperature for several days, a small growth of fine white crystalline material (II) was observed on the glass surface of the vessel. The crystal formation did not increase, even after 2 months. However, the rate and extent of crystal formation increased rapidly if the vessel was opened and the contents were exposed to the atmosphere, or if water was added. The crystals, after being separated and dried, melted at 177.5° (without apparent decomposition), in contrast to trityl chloride, mp 113°, pyridinium chloride, 83°, and triphenylcarbinol, 162°. The crystals decomposed into pyridine, water, and trityl chloride on being heated to 200–250° under reduced pressure. When treated with methanol, trityl methyl ether was obtained, while water gave triphenylcarbinol. Microanalysis fitted the molecular formula $C_{24}H_{22}ClNO$. This product (II) apparently corresponds to the compounds reported as tritylpyridinium chloride.[12]

The crystals were insoluble in carbon tetrachloride and carbon disulfide, but slightly soluble in chloroform. The infrared spectrum of II in chloroform solution was completely superimposable on the sum of the spectra of triphenylcarbinol and pyridinium chloride in the same solvent. However, the spectrum in the solid state (in potassium bromide pellet or Nujol mull) showed one difference from those of triphenylcarbinol and pyridinium chloride in the 3-μ region: the band characteristic of OH stretching was shifted to a slightly lower frequency, from 3480 to 3360 cm^{-1}. Such a shift is usually associated with hydrogen bond formation.[14] The crystalline compound (II) was synthesized also from a chloroform solution of an equimolar mixture of pure triphenylcarbinol and pyridinium chloride by evaporating the solvent, mp 176.5°, undepressed by mixture with the sample from trityl chloride, also identical infrared spectra in KBr or Nujol.

The structure of the crystalline material (II) is thus strongly indicated to be a complex of triphenylcarbinol and pyridinium chloride, associated through a weak hydrogen bond in the solid state. A simplified or condensed representation might be $(C_6H_5)_3COH\text{---}Cl^-\text{---}HN^+C_5H_5$. The carbinol hydrogen bond is so weak that the complex breaks down into its constituents in chloroform solution, since the infrared spectrum of the compound in chloroform is simply the sum of the spectra of triphenylcarbinol and pyridinium chloride. Triphenylcarbinol and hydrogen chloride are produced from trityl chloride only by water that is added or enters the system fortuitously.

Preparation of similar complex compounds from other aryl alcohols and tertiary ammonium chlorides

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[10] K. M. Sancier, *J. Phys. Chem.*, **61**, 1127 (1957).

[11] R. P. Porter, *ibid.*, **61**, 1260 (1957).

[12] Prepared from trityl chloride and pyridine, mp 167–167.5°, by J. F. Norris and L. R. Culver, *Am. Chem. J.*, **29**, 134 (1903); with mp 171°, by E. v. Meyer and P. Fischer, *J. Prakt. Chem.*, [2] **82**, 523 (1910); and with mp 173–174° by C. A. Kraus and R. Rosen, *J. Am. Chem. Soc.*, **47**, 2744 (1925). It was also obtained with mp 174° from a pyridine solution of triphenylcarbinol and hydrogen chloride by B. Helferich and H. Dehe, *Ber.*, **58**, 1605 (1925); this product was shown to contain the elements of one molecule of water by B. Helferich and H. Sieber, *Ber.*, **59**, 600 (1926), and the melting point (170–175°) and Helferich's conclusion were later confirmed (without reference to Helferich) by E. D. Hughes, *J. Chem. Soc.*, 75 (1933). See also ref 3.

[13] All published attempts to react trityl halides with trimethylamine were also unsuccessful; *cf.* L. W. Jones and M. W. Seymour, *J. Am. Chem. Soc.*, **50**, 1150 (1928), and ref 12.

[14] L. J. Bellamy, "Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1954, p 83.

was attempted. From chloroform solutions of triphenylcarbinol and 2,6-lutidinium chloride, and benzhydrol and pyridinium chloride, white crystals were obtained, mp 199 and 95–96°, respectively. From a solution of benzyl alcohol and pyridinium chloride, no crystalline material was isolated. Table II records the characteristic OH stretching peaks of these compounds and the shift for each complex relative to the parent alcohol.

Table II. O–H Stretching Frequencies of Aryl Alcohols and Their Complexes with Pyridinium Chlorides in Nujol Mull

Compound	OH, cm^{-1}	$\Delta\nu$, cm^{-1}
Triphenylcarbinol	3480	
Triphenylcarbinol–pyridinium chloride	3360	120
Triphenylcarbinol–2,6-lutidinium chloride	3340	140
Benzhydrol	3330	
Benzhydrol–pyridinium chloride	3280	50

Preparation of "addition compounds" of one molecule of tetraphenyl glycol with various tertiary ammonium chlorides has been reported by Schönberg and coworkers; similarly, Wieland and Maier reported complex formation from trityl hydroperoxide and pyridinium chloride.[15] The structures of these complexes in the solid state are probably analogous to the structure of the triphenylcarbinol–pyridinium chloride (II) described in this investigation.

Experimental Section

Reactants. Benzene was reagent grade, dried by distilling 10% to remove the water–benzene azeotrope. The main fraction was stored over sodium wire. Methanol was reagent grade, dried over Drierite, and distilled. Pyridine (Mallinckrodt reagent) and 2,6-lutidine (Eastman pure) were dried over calcium hydride and distilled. 2,6-Di-*t*-butylpyridine was prepared by the method of Brown and Kanner,[6] n^{25}D 1.5730, bp 96–98° (15 mm) (lit.[6] bp 100–101° (23 mm)). Trityl chloride was from Matheson Coleman and Bell, once or twice recrystallized from a benzene–light petroleum ether (bp 30–60°) mixture, mp 111–112°. Trityl bromide was prepared from dry hydrogen bromide and triphenylcarbinol (Eastman pure, purified by recrystallization from ethanol, mp 162°); it was recrystallized from benzene–light petroleum ether mixture, mp 154–155°.

Tritium-labeled methanol was synthesized as described previously.[2] Picolinic acid (Eastman, 20 g) was recrystallized from benzene containing 0.005 ml of tritium-labeled water (HOT, 3 Ci/mole), mp 138°, dried under vacuum, and decarboxylated quantitatively at 165–180°. The resulting pyridine-2-*t* was distilled from calcium hydride through a semimicro column, bp 114.5°, n^{25}D 1.5070. The tritium-labeled water was prepared from T_2 gas and H_2O using platinum.[16]

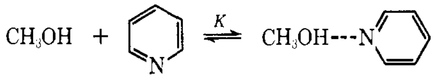
Kinetic Procedure. The procedure for kinetic measurements was similar to that previously reported[2] with one exception. Aliquots of low base concentration were treated with water containing pyridine to prevent the solution from becoming acidic during the extraction with water. A typical kinetic run is shown in Table III. A 15-ml aliquot was extracted with 10 ml of water, and exactly 1.00 ml of the water solution was dissolved in 65 ml of scintillation solution for counting radioactivity by a Packard Tri-carb liquid scintillation spectrometer. The scintillation solution contained 4 g of Arapahoe scintillation grade 2,5-diphenyloxazole and 15 mg of Matheson diphenylhexatriene dissolved in 770 ml of reagent toluene and 230 ml of absolute ethanol.

Table III. Kinetic Data for the Reaction of 2.31 × 10^{-3} *M* Methanol with 0.0961 *M* Trityl Chloride in Benzene Solution Containing 0.100 *M* Pyridine at 25°

Time, min	Unreacted CH_2TOH, av counts/2 min	Reaction, %
0	25,400	0.0
135	23,500	7.1
440	19,900	21.5
1190	14,700	42.0
1470	13,000	48.9
1820	10,600	58.4
2540	7,600	70.0
3160	5,900	76.8

Complexing between Methanol and Pyridine. In order to study the hydrogen bond formation between low concentrations of methanol and pyridine in benzene solution, the infrared spectrum of 1.1 *M* methanol-*d* in benzene was measured in a Perkin-Elmer 21 double beam spectrophotometer. The characteristic peaks for the OD stretching frequency appeared at 2480 and 2645 cm^{-1}. The former peak was assigned to the associated OD stretching frequency and the latter to the free OD frequency.[17] In the infrared spectrum of 0.1 *M* methanol-*d* in benzene, the peak for the associated OD almost disappeared and the characteristic peak for the free OD remained sharp. Thus, at low concentrations of methanol (<0.1 *M*) in benzene solution most of the methanol exists as a nonassociated species. However, this peak was mostly shifted by adding pyridine (0.7 *M*) or 2,6-lutidine (0.7 *M*) to 2460 or 2420 cm^{-1}, respectively. These results show that methanol is predominantly associated with pyridine or 2,6-lutidine through a hydrogen bond in benzene solution.

The equilibrium constant *K* between methanol and the complex



of methanol and pyridine was measured as 5.9 ± 0.6 M^{-1} by a dynamic vapor pressure method[18] using pyridine labeled with tritium in the α position. A fixed volume of benzene-saturated air was passed through each solution to carry over equilibrium pyridine vapor into 25 ml of liquid scintillation solution containing acid. Sample data are recorded in Table IV. The scintillation solutions were stored in Pyrex volumetric flasks, and were 8 × 10^{-6} to 5 × 10^{-3} *M* in pyridine. The amount of pyridine removed from the initial solutions by the known volume of air swept through did not exceed 0.03% of that in the original solutions. The equilibrium constant was calculated on the assumption that the solutions obey Henry's law, that one molecule of pyridine is associated with one molecule of methanol, and that the vapor pressure of the complex is much lower than that of either methanol or pyridine.

Table IV. Complexing between Pyridine and Methanol in Benzene at 25°

Pyridine, *M*	Methanol, *M*	Pyridine, counts/min × 10^{-3}	*K*, M^{-1}
0.0130	0.000	202, 210, 192	
0.0129	0.063	143, 140, 155	6.4
0.0118	0.250	79, 85, 75	5.4

Adsorption of pyridine from benzene solution onto Pyrex glass walls, though useful in methanolysis to prevent loss of methanol, does not remove a serious amount of pyridine from solution. The concentrations of these very dilute benzene solutions of pyridine-2-*t* in Pyrex volumetric flasks appeared to remain constant (by counting) over several days at 25°.

Reaction between Pyridine and Trityl Halides. A benzene solution of 0.5 *M* trityl chloride and 0.5 *M* pyridine was allowed to

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(15) A. Schönberg and R. Michaelis, *J. Chem. Soc.*, 1571 (1936); A. Schönberg and A. Mustafa, *ibid.*, 385 (1948); H. Wieland and J. Maier, *Ber.*, 64, 1205 (1931).

(16) C. G. Swain and A. J. Kresge, *J. Am. Chem. Soc.*, **80**, 5281 (1958).

(17) *Cf.* W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941); W. Gordy, *ibid.*, **9**, 215 (1941); M. Tamres, S. Searles, E. M. Leighly, and D. W. Mohrman, *J. Am. Chem. Soc.*, 76, 3984 (1954).

(18) C. G. Swain and John F. Brown, Jr., *ibid.*, **74**, 2691 (1952).

stand for 48 hr at 25°. After distilling off solvent under vacuum, I was recovered in quantitative yield, mp 109–111°, not depressed by mixture with authentic pure trityl chloride, carbon and hydrogen both correct within 0.25%. Even when trityl chloride and bromide were refluxed with pyridine for 48 hr under nitrogen in benzene solution or in the absence of benzene, the unreacted halides were recovered quantitatively. When the mixtures were heated in sealed tubes at 150–200° for 48 hr, unreacted halides and tarlike material were isolated.

Isolation and Physical Properties of II. A benzene solution (200 ml) of trityl chloride (0.3 *M*) and pyridine (0.5 *M*) was allowed to stand for several days at room temperature. The prismatic fine crystalline material (0.010 g) obtained from the solution was filtered, washed three times with dry benzene, and dried in a desiccator under reduced pressure, mp 177.5° without decomposition.

Anal. Calcd for $C_{24}H_{22}NOCl$: C, 76.68; H, 5.90; N, 3.73; Cl, 9.43. Found: C 76.51; H, 5.48; N, 3.98; Cl, 9.15.

A Perkin-Elmer Model 21 double beam spectrophotometer was used to measure the infrared spectra in chloroform, potassium bromide pellet, and Nujol mull. No $C-N^+$ peak analogous to that in benzylpyridinium chloride could be detected.

X-Ray analysis of the crystalline material, mp 177.5°, was attempted.[19] Preliminary data showed that the crystal was triclinic with a measured density (Berman balance using toluene) of 1.252 g/ml. The unit cell volume is about 988 Å^3 and, assuming two molecules per unit cell, the density is 1.26 g/ml.

Decomposition of II. The crystalline material (mp 176.5°) synthesized from trityl chloride and pyridinium chloride (1.5 g) was heated gradually to 200–250° under 0.2–0.3 mm. A white solid material condensed on the cold part of the glass apparatus, while liquid material was collected farther on in a cold trap (−78°). Water was detected as a part of the liquid by reaction with calcium hydride and cupric sulfate. After drying the liquid over Drierite, pyridine was identified as another component by infrared. The melting point of the white solid was 105–110° before and 110–112° after recrystallization from *n*-hexane. There was no depression when the compound was mixed with pure trityl chloride, and this solid was identified as trityl chloride also by infrared spectrum.

The crystalline material (0.1 g) was mixed with 1 ml of water at room temperature (heterogeneous). After the aqueous solution was filtered, the insoluble white solid was washed with water and ethyl alcohol. It melted at 160–161°, and showed no depression on mixing with pure triphenylcarbinol (161–162°). The infrared spectrum of the white solid in chloroform solution was identical with that of pure triphenylcarbinol. The crystalline material (0.1 g) was dissolved in 5 ml of absolute methyl alcohol and allowed to stand overnight. After distilling off the solvent (4 ml), solid material precipitated from the solution upon cooling. The compound was isolated and washed with methyl alcohol, mp 83–84°. No depression was found on mixing it with pure trityl methyl ether (84°) prepared from a methyl alcohol solution of trityl chloride and pyridine. The infrared spectra were superimposable.

Other Molecular Complexes of Triphenylcarbinol or Pyridinium Chloride. A chloroform solution (20 ml) of 1.8 g of benzhydrol and 1.2 g of pyridinium chloride was prepared and allowed to stand overnight. When part of the chloroform (17 ml) was distilled off and the solution cooled, white crystalline material precipitated, mp 95–96°.

Anal. Calcd for $C_{18}H_{18}NOCl$: C, 72.11; H, 6.05; N, 4.67; Cl, 11.83. Found: C, 71.68; H, 5.82; N, 4.46; Cl, 11.96. From triphenylcarbinol and 2,6-lutidinium chloride, a complex compound was obtained, mp 199°.

Anal. Calcd for $C_{26}H_{26}NOCl$: C, 77.30; H, 6.49; N, 3.47; Cl, 8.78. Found: C, 77.12; H, 6.56; N, 3.60; Cl, 8.62.

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[19] The X-ray studies were performed by Dr. Jerry Silverman, Air Force Cambridge Research Laboratories.

Covalent Addition of Bisulfite Ion to 2-Amino-1-methylpyrimidinium Ion

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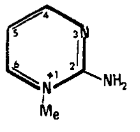
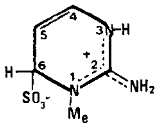
Abstract: Nmr and uv spectral data are presented to show that two 1:1 covalent adducts are formed by addition of bisulfite ion to 2-amino-1-methylpyrimidinium ion (I) in water. One of these products is shown from its X-ray diffraction pattern to be 2-amino-1,6-dihydro-1-methylpyrimidinium-6-sulfonate (II) and the other is believed to be 2-amino-3,4-dihydro-1-methylpyrimidinium-4-sulfonate (III). In dilute aqueous solutions at 32° the initial reaction yielded a 1.3:1 ratio of the products II and III. However, this was a kinetically controlled "pseudo-equilibrium" and a subsequent slow interconversion of isomers yielded an equilibrium mixture containing a 0.8:1 mixture of the isomers II and III. An interesting feature of this system was that only isomer II could be crystallized out of concentrated aqueous solutions of the bisulfite adducts or obtained as a solid following flash evaporation of an equilibrium mixture at 25°.

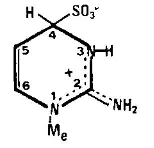
Covalent addition of bisulfite ion across cyclic imino groups (>C=N–) in nitrogen-containing heteroaromatics is now a well-recognized reaction. For example, covalent bisulfite adducts of pyridines,[2] pyrimidines,[3] pteridines,[4] and quinazolines[5] have been characterized and quantitative data on some of these systems[3,4d] have been reported. The present article deals with the structures and yields of products formed by covalent addition of bisulfite ion to 2-amino-1-methylpyrimidinium ion (I). This compound was known[3] to add bisulfite ion reversibly in aqueous



I



II



III

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