Registry No.—TEAF, 15077-13-1; TMAF, 2738-94-5; N,N-di(phenylethyl)-*p*-anisidine hydrochloride, 15020-04-9; N,N-di(phenylethyl)-*p*-anisidine, 14924-80-2; N-benzyl-N-*n*-propyl-*p*-anisidine hydrochloride, 15020-02-7; N-benzyl-N-*n*-propyl-*p*-anisidine, 14924-81-3; N-benzyl-N-methyl-*p*-anisidine picrate, 15020-03-8; N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, 2739-06-2; N-formyl-N,N′,N′-trimethyl-*o*-phenylenediamine, 14924-65-3; N,N,N′-trimethyl-*o*-phenylenediamine hydrochloride, 2427-05-6; N-formyl-N-methyl-*p*-hydroxyaniline, 14924-67-5; N-formyl-N-methyl-*p*-anisidine, 5279-51-6; N-formyl-N-methyl-*o*-anisidine, 14924-69-7; N-formyl-N-methyl-*m*-anisidine, 14924-70-0; N-formyl-N-*m*-propyl-*p*-anisidine, 14924-71-1; N-benzyl-N-formyl-*p*-anisidine, 14924-72-2; N-formyl-N-(2-phenylethyl)-*p*-anisidine, 15038-88-7; N-formyl-N-methyl-*p*-phenetidine, 5635-30-3; N-methyl-*p*-phenetidine hydrochloride, 15206-42-5; N-formyl-N-methylaniline, 93-61-8; N-methylaniline hydrogen oxalate, 14924-75-5; *o*-chloro-N-formyl-N-methylaniline, 14924-76-6; *p*-dimethylaminophenol, 619-60-3; N-methyl-N-*m*-methoxyphenyl-N′-phenylthiourea 14924-78-8.

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Diimide Formation in the Basic Decomposition of N,N-Dimethyl-N-phenylhydrazinium Chloride[1]

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The basic decomposition of N,N-dimethyl-N-phenylhydrazinium chloride in the presence of phenylpropiolic acid causes hydrogenation of the latter exclusively to *cis*-cinnamic acid, a stereospecificity consistent with the postulated transient formation of diimide.

Hydrazinium salts of the form, $(R_3N{-}NH_2)^+Cl^-$, can be prepared in excellent yields by reacting tertiary amines with gaseous chloramine (eq 1).[3] The anhydrous chloramine required for this reaction is made from ammonia and chlorine in a generator such as that described by Sisler.[4]

$$R_3N + NH_2Cl \longrightarrow (R_3N{-}NH_2)^+Cl^- \qquad (1)$$

These hydrazinium salts are generally stable, hygroscopic substances, unaffected by neutral solvents. In the presence of bases, however, a rather complex decomposition takes place. For example, N,N-dimethyl-N-phenylhydrazinium chloride (I) reacts with sodium ethylate in anhydrous tetrahydrofuran to yield, as identifiable products, nitrogen, hydrogen, ammonia, dimethylaniline, and N-methyl-N-phenylhydrazine. The first step in this basic decomposition is likely a deprotonation (eq 2) to the trisubstituted amine–imine II. By carrying out the deprotonation of trimethylhydrazinium chloride with potassium amide in liquid ammonia, it was possible to isolate trimethylamine–imine.[5] Similar imines of phosphorus[6] and of arsenic[7] have also been prepared, using sodamide as the deprotonating base in liquid ammonia.

$$\underset{\text{I}}{(PhN(CH_3)_2NH_2)^+Cl^-} + NaOEt \longrightarrow$$
$$\underset{\text{II}}{PhN^+(CH_3)_2N^-H} + NaCl + EtOH \qquad (2)$$

When triphenylphosphine is allowed to react with the amine–imine II, the imino group is transferred to the phosphine (eq 3) to give triphenylphosphine–imine (III). It appears doubtful, however, that this reaction proceeds *via* the intermediate formation of the imine radical, since numerous attempts to detect NH by addition across double bonds have failed.[5] The formation of large amounts of nitrogen and hydrogen during the deprotonation of I suggests, instead, that another compound of nitrogen and hydrogen forms which then easily decomposes, especially in alkaline solutions, to give nitrogen and hydrogen. Such reactivity has been observed for diimide, N_2H_2, which is formed, for example, by the careful oxidation of hydrazine. Hünig[8] and Corey[9] have demonstrated that the hydrogenation reactions observed with hydrazine in the presence of an oxidizing agent occur *via* diimide as the hydrogenating species. They showed that the hydrogenation of phenylpropiolic acid under these conditions leads exclusively to *cis*-cinnamic acid, probably through an unstable, cyclic intermediate, IV. Such a structure is consistent with the observed stereospecificity of the reaction. We

$$\text{II} + Ph_3P \longrightarrow \underset{\text{III}}{Ph_3P{=}NH} + PhN(CH_3)_2 \qquad (3)$$

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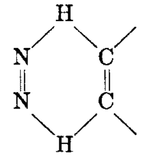

IV

have shown[10] that hydroxylamine-O-sulfonic acid in the presence of a base also causes a stereospecific hydrogenation of phenylpropiolic acid to *cis*-cinnamic acid. These findings support the assumption that here, too, the hydrogenating species is diimide. Other sources of diimide are extensively reviewed by Hünig.[11]

It was the purpose of this current work to determine if amine imines, specifically N,N-dimethyl-N- phenylamine–imine (II), also decompose to yield diimide as an intermediate. The stereospecific hydrogenation of phenylpropiolic acid to *cis*-cinnamic acid was the reaction chosen to establish this. Compound II was prepared by deprotonating I with sodium ethylate in tetrahydrofuran under anhydrous, oxygen-free conditions. Without prior isolation, II was reacted with phenylpropiolic acid. Most of the latter (*ca.* 85%) was recovered unreacted. The rest was converted to *cis*-cinnamic acid and some hydrocinnamic acid. In view of the low conversion and the difficulty in effecting a clean separation of *cis* and *trans*-cinnamic acids, it was particularly important to demonstrate the complete absence of even traces of *trans*-cinnamic acid. This was accomplished by first enriching the *cis*-cinnamic acid fraction through extraction of the product mixture with petroleum ether (60–80°), in which *cis*-cinnamic acid is considerably more soluble than is either *trans*-cinnamic acid or phenylpropiolic acid. The extracted portion appeared to be mainly *cis*-cinnamic acid, judging by the melting point and the mixture melting point with a known, pure sample. The petroleum ether extract and the residue were then examined by infrared spectroscopy and also, in the form of ethyl esters, by gas chromatographic separation. In each case, the complete absence of *trans*-cinnamic acid was verified. The chromatographic separation showed that the petroleum ether-soluble portion was mainly *cis*-cinnamic acid, with smaller amounts of hydrocinnamic acid and phenylpropiolic acid. The insoluble residue was primarily phenylpropiolic acid, with some *cis*-cinnamic acid and a trace of hydrocinnamic acid. Independent chromatographic examination of pure, known samples of esters proved that *cis,trans* isomerization did not occur under the chromatographatic conditions employed.

From these results, we can conclude that diimide is an intermediate product in the basic decomposition of N,N-dimethyl-N-phenylhydrazinium chloride. As to the mechanism of diimide formation in this decomposition, the current investigations do not yet permit any firm conclusion to be drawn.

Experimental Section

Dimethylphenylhydrazinium Chloride (I).—Anhydrous, gaseous chloramine was bubbled through pure dimethylaniline at 25° to yield a thick slurry of the hydrazinium salt in unreacted dimethylaniline. The crystals were separated by vacuum filtration and washed with benzene and with ether. To remove ammonium chloride from the product, the solids were extracted in a Soxhlet apparatus with an anhydrous mixture of ethyl acetate-methanol (90:10), in which ammonium chloride is practically insoluble. Upon cooling, the hydrazinium chloride precipitated; additional quantities were recovered by adding ether to the extract. Recrystallization from methanol solution with ether gave a pure product, mp 188–189° (lit.[3] 187–188°).

Anal. Calcd for $C_8H_{13}N_2Cl$: Cl, 20.5. Found: Cl(Volhard), 20.8.

Phenylpropiolic Acid.—Phenylpropiolic acid was prepared from the ethyl ester of *trans*-cinnamic acid.[12] To purify the product, it was repeatedly recrystallized from hot carbon tetrachloride and from hot water (mp 137–138°, lit.[12] 135–136°). Infrared examination of the pure phenylpropiolic acid indicated complete absence of cinnamic acids. As a further check on purity, the acid was esterified with ethanol and subjected to gas chromatographic separation (190°, through a 1.85-m column packed with Apiezon high-vacuum grease, hydrogen as carrier). Only one peak appeared. Synthetic mixtures of this pure ethyl phenylpropiolate with ethyl *trans*-cinnamate showed clear chromatographic separation down to less than 1% *trans*-cinnamate. Ethyl *cis*-cinnamate and ethyl hydrocinnamate have elution times less than either ethyl phenylpropiolate or ethyl *trans*-cinnamate; their chromatographic detection offered no difficulty. They were, of course, not present in the ethyl phenylpropiolate.

Hydrogenation of Phenylpropiolic Acid.—Freshly prepared sodium ethylate (5.0 g, 0.074 mole) was suspended in 150 ml of anhydrous tetrahydrofuran under a nitrogen atmosphere. After cooling the suspension to −20°, I (12.77 g, 0.074 mole) was added in portions over a 15-min period, taking great care to avoid entry of air or moisture into the reaction vessel. Finally, phenylpropiolic acid (5.37 g, 0.037 mole) was added, and the mixture was allowed to come to room temperature and stirred for 3 days, followed by 3 hr at 60°. The reaction residue, after removal of tetrahydrofuran by vacuum distillation, was dissolved in water, the upper oily layer (mainly dimethylaniline) removed, and the aqueous phase acidified at 5° with 2 *N* hydrochloric acid to precipitate the organic acids. The aqueous phase was then extracted with ether to remove final traces of organic acids.

The crystalline product (5 g) was partially molten even at room temperature. It was extracted with petroleum ether (60–80°), in which *cis*-cinnamic acid is quite soluble compared to *trans*-cinnamic acid or to phenylpropiolic acid. About 0.4 g dissolved. This substance was a slightly yellow, crystalline material, mp 35–45°. Admixed with pure *cis*-cinnamic acid (mp 42°), the melting point was 40–45°. Infrared bands (KBr disk) are: 2200 ($C\equiv C$), 1680 ($C=O$), 1630 ($C=C$ stretching), 826 cm^{-1} (*cis* out-of-plane). The $C=C$ *trans* out-of-plane frequency (970) was absent.

The infrared spectrum of the petroleum ether-insoluble portion (4.6 g) was nearly identical to that of phenylpropiolic acid. The $C=C$ stretching and out-of-plane frequencies were absent.

Both portions of the reaction product (petrol ether extract and residue) were converted to the silver salts, then esterified with ethyl iodide in ether at room temperature. The esters were subjected to vapor phase chromatographic separation, using a 1.85-m column packed with Apiezon high-vacuum grease (190°, hydrogen as carrier). Elution times were compared with those of authentic samples. Peak identification was further verified by adding small amounts of known, pure compounds, one by one, to the esterified reaction products. Summarized in Table I are the elution times for the known compounds and for the components of the petroleum ether extract and residue. Relative peak heights (direct chart readings) are also shown.

TABLE I

	Elution time, min			Relative peak heights	
Ethyl ester of	Known sample	Extract	Residue	Extract	Residue
Hydrocinnamic acid	10.0	9.8	10.0	10	1.5
cis-Cinnamic acid	11.6	11.4	11.5	82	13
Phenylpropiolic acid	15.5	15.7	15.5	8	*Ca.* 300
trans-Cinnamic acid	19.5	None	None	0	0

Registry No.—I, 80-71-0.

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