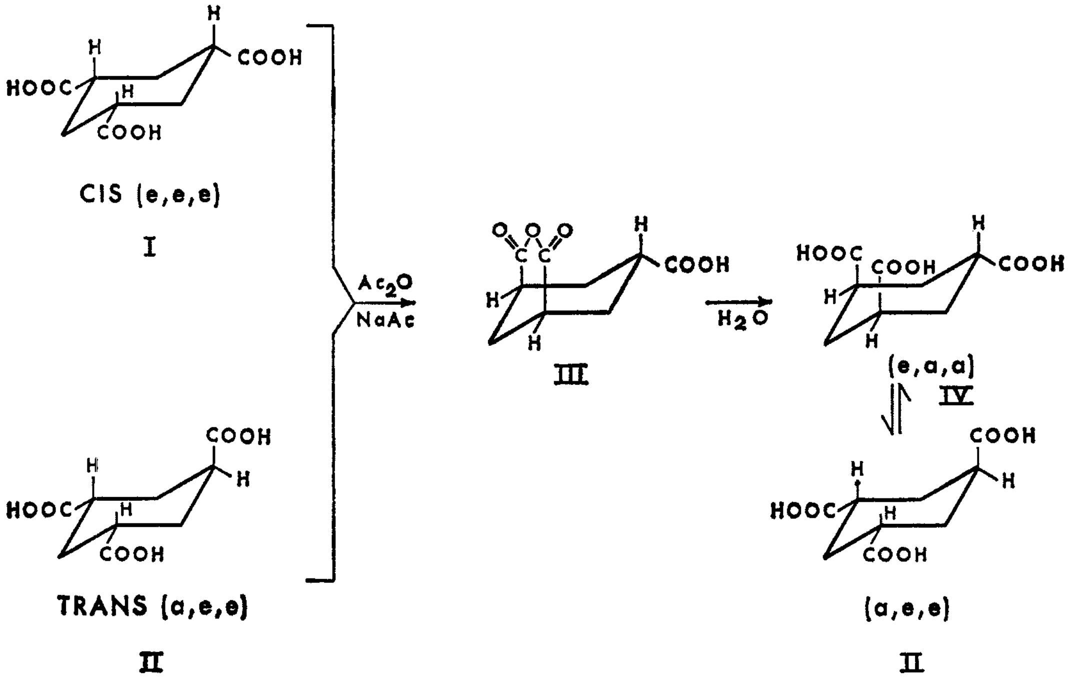
Scheme I

Preparation of *trans*-1,3,5-Cyclohexanetricarboxylic Acid



(a,a)-cyclohexanedicarboxylic acid is formed as shown by gas chromatography of the equilibrated mixture after esterification. Armitage, *et al.*,[6] suggests that this third epimer of 1-*t*-butyl-3,5-cyclohexanedicarboxylic acid assumes the skew-boat conformation.

Experimental Section

Hydrogenation of Trimesic Acid.—A slurry of trimesic acid (three parts) in water (five parts) was hydrogenated at 150° and 1500 psig using as catalyst 5% palladium on carbon in the amount of 5% based on trimesic acid. Hydrogen uptake ceased in 3 hr. Catalyst was filtered from the otherwise homogeneous product. In order to preserve isomer ratio, the total solids (mp 175–206°, acid number 762 (theory 778), were recovered by evaporation of solvent rather than by crystallization. The solids were esterified with diazomethane[3] and analyzed by gas chromatography on a 10-ft column of silicone grease–Carbowax 6000 on Chromosorb W with the temperature programmed from 80 to 210°. The product consisted of 76.6% *cis* isomer, 21.4% *trans* isomer, and 2.0% dibasic acids.

***cis*-1,3,5-Cyclohexanetricarboxylic Acid.**—The hydrogenation product was dissolved in the minimum quantity of boiling ethanol, and toluene was added to decrease solubility. The crystals obtained on cooling were washed with chilled ethanol–toluene, and recrystallized in the same manner. The dried crystals melted at 218–219°; analysis showed that the product consisted of 1.5% *trans* isomer, 98% *cis* isomer, and 0.5% dibasic acids.

Anal. Calcd for $C_9H_{12}O_6$: C, 49.9; H, 5.55. Found: C, 50.2; H, 5.58.

***trans*-1,3,5-Cyclohexanetricarboxylic Acid.**—The hydrogenation product (5 g) was refluxed with 20 ml of acetic anhydride and 1 g of sodium acetate for 4 hr. The base was removed by refluxing 2 hr with 10 ml of acetyl chloride. Excess acetyl chloride was removed by distillation to an overhead temperature of 132°. The liquid mixture containing some sodium chloride crystals was poured into 400 ml of water. Evaporation to 5 ml and cooling gave a crystal crop, which was recrystallized from water, mp 208–210°. Analysis by esterification and gas chromatography showed 95.9% *trans* isomer, 2.5% *cis* isomer, and 1.7% dibasic acids.

Anal. Calcd for $C_9H_{12}O_6$: C, 49.9; H, 5.55. Found: C, 50.3; H, 5.58.

Thermal Equilibration.—Two-gram samples of the hydrogenation product and each of the pure isomers were heated in test tubes in a thermostatically controlled aluminum block at 240° for 24 hr. The molten samples were rapidly chilled to below their freezing point of 218°. The pulverized products were analyzed by esterification and gas chromatography, all products had substantially the same composition: 54.9 (± 0.3)% *trans* isomer, 43.5 (± 0.6)% *cis* isomer, and 1.6 (± 0.7)% dibasic acids.

Registry No.—I, 16526-68-4; II, 16526-69-5.

Phosphonitrilic Chloride as Activator of Carboxylic Acids. Formation of Amides and Hydrazides[1]

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Considerable advances have been made in the study of the chemical behavior of phosphonitrilic halides during the last decade.[2]

The simplest and best known member of this family of compounds, hexachlorocyclotriphosphatriazene **1**, reacts readily with a variety of compounds, like amines, alcohols, and phenols, to yield substitution products. The high reactivity of the halogen atoms and the observation that the high-temperature reaction of **1** with sodium benzoate resulted in the formation of benzonitrile and benzoic anhydride[3] prompted us to examine the possibility of using **1** or other phosphonitrilic chlorides as activators of carboxylic acids. It was expected that the reaction of an acid or its

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[1] Work done with financial support of the Italian National Research Council (C. N. R.)

[2] See, for recent surveys, R. A. Shaw, *Chem. Ind.* (London), 1737 (1967); N. L. Paddock, *Quart. Rev.*, **18**, 168 (1964).

[3] I. I. Bezman and W. R. Reed, *J. Amer. Chem. Soc.*, **82**, 2167 (1960).

TABLE I

Acids[a]	Amines	Moles	$(PNCl_2)_3$, mol	Procedure	Solvent	Product	From	Yield,[b] %
α-Naphtylacetic	Aniline	6	0.3	A,B	THF, benzene, acetone	α-Naphtylacetanilide	CH_2Cl_2–heptane	73
α-Naphtylacetic	Cyclohexylamine	5	1.0	A,B	THF, benzene, acetone	N-Cyclohexyl-α-naphthylacetamide	Heptane	82
Palmitic	Cyclohexylamine	5	1.0	A,B	THF, benzene, THF–water 80:20	N-Cyclohexylpalmitamide	CH_2Cl_2–heptane	80
Benzoic	Aniline	6	1.0	B	THF, benzene, THF–water 80:20	Benzanilide	EtOH–water	83
Salicilic	NH_3	12	1.0	C	THF, benzene	Salicilamide	EtOH–water	60
p-Nitrocinnamic	Cyclohexylamine	7	0.5	B	THF, benzene, diethylene dioxide	N-Cyclohexyl-p-nitrocinnamide	CH_2Cl_2–heptane	70
12-Ketostearic	Cyclohexylamine	6	0.5	B	THF, benzene	N-Cyclohexyl-12-ketostearamide	Heptane	65
Thiophen-2-carboxylic	Aniline	8	1.0	B	THF, benzene, diethylene dioxide	N-Phenylthiophen-2-carboxamide	CH_2Cl_2–heptane	75
α-Phenylcinnamic	Cyclohexylamine	12	1.0	C	THF, benzene, diethylene dioxide	N-Cyclohexyl-α-lithocolicamide	CH_2Cl_2–heptane	75
Lithocolic	Dimethylamine	6	1.0	B	THF, benzene, diethylene dioxide	N,N′-Dimethyllithocolicamide	EtOH–water	63

[a] One mole. [b] Yields calculated on acid employed.

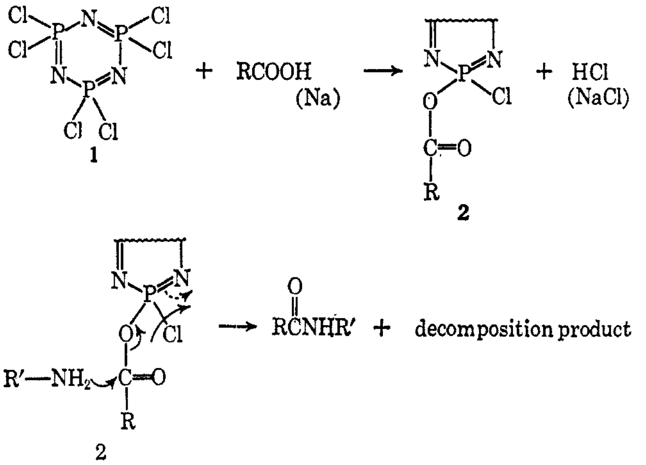
TABLE II

Acids[a]	Hydrazides	Moles	$(PNCl_2)_3$, mol	Procedure	Solvent	Product	From	Yield,[b] %
Palmitic	Hydrazine	6	1.0	A,B	THF, benzene	Palmitoylhydrazide	MeOH	75
Benzoic	Hydrazine	10	1.0	C	THF, benzene, cyclohexane	Benzoylhydrazide	MeOH–water	65
Phenylacetic	Phenylhydrazine	6	1.0	A,B	THF	Phenylacetophenylhydrazide	MeOH–water	65
α-Phenylcinnamic	Phenylhydrazine	6	1.0	B	THF	α-Phenylcinnamylphenylhydrazide	EtOH	60
Salicylic	Phenylhydrazine	10	0.5	B	THF, benzene	Salicylphenylhydrazide	EtOH	67
α-Naphthylacetic	p-Toluenesulfonylhydrazine	8	0.5	B	THF, benzene	N-p-toluenesulfonyl-N′-α-naphthylacetylhydrazide	EtOH	73

[a] One mole. [b] Yields calculated on acid employed.

salt with **1** would lead to an intermediate such as **2** (Scheme I); this, in turn, was expected to react with amines and hydrazines to yield the corresponding amides and hydrazides analogous to compounds of the type RCOOX=Y.[4]

SCHEME I



In fact, reaction of **1** with salts of carboxylic acids, followed by treatment of the reaction mixture with an excess of a primary or secondary amine, produced amides in very good yields. The reaction could be run in a variety of solvents (benzene, cyclohexane, tetrahydrofuran, tetrahydrofuran–water, ethyl acetate). Preformed sodium salts of carboxylic acids could be employed, but equivalent results were obtained by treating the free acid *in situ* with 1 equiv of triethylamine or a suitable primary or a secondary amine.

When a slurry of the sodium salt of the carboxylic acid was added to 0.35–1 equiv of **1** (calculated on a mole to mole basis), the precipitate of sodium chloride appeared at once.

A six- to tenfold excess of amine was then added and work-up of the reaction mixture yielded the corresponding amide.

The whole operation required no more than 20 min. Table I gives a list of amides prepared. Analogously, we prepared a number of hydrazides (Table II).

Our results indicated that **1** can be used as an activator in the conversion of the carboxylic function. The possibility of using a variety of solvents for the reaction, the simplicity of the operations involved, the high yields even with polyfunctional acids together with mild conditions, and the ready availability of the reagent **1** recommend the new route to amides and hydrazides.

Work is in progress to elucidate the mechanism of formation of the carboxy derivative from **1** as well as to widen the scope of the synthesis.

Experimental Section

Materials.—Hexachlorocyclotriphosphatriazene (1) was purchased from Albright and Wilson, England, and used without further purification. Thin layer chromatography to test the purity of the synthetic products was performed on Merck silica gel G.

Procedure A.—The sodium salt of the carboxylic acid (1 mol) was stirred in the solvent of choice (tetrahydrofuran, benzene, cyclohexane, tetrahydrofuran–water 80:20, ethyl acetate) with 0.35–1 mol of 1 at room temperature during 5–10 min; then a six- to tenfold excess of amine (or hydrazine) was added, and stirring was continued for 5–10 min.

A saturated solution of sodium bicarbonate was added and the mixture was extracted with diethyl ether. The organic layer was washed with water, dilute hydrochloric acid, and water again and dried over sodium sulfate.

The solvent was evaporated and the compound obtained was then purified by crystallization or by chromatography on silica gel.

Procedure B.—A solution of 1 mol of the acid and 1 mol of triethylamine in the solvent of choice (*vide supra*) was added

(4) J. Rudinger, *Pure Appl. Chem.*, **7**, 335 (1963).

to 0.35–1 mol of **1** dissolved in the same solvent and was then treated as in procedure A.

Procedure C.—A solution of 1 mol of the acid and 1 mol of the amine to be used for the preparation of the amide in the solvent of choice (*vide supra*) was added to 0.35–1 mol of **1** dissolved in the same solvent and was then treated as in procedure A.

Registry No.—**1,** 940-71-6.

Acknowledgment.—We wish to thank Mr. G. Baccolini, who carried out some of the experiments, and Mr. G. Valentini for obtaining the elemental analyses.

Diaryliodosyl Salts[1]

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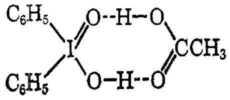
In 1935, Masson, Race, and Pounder[2] reported the self-condensation of iodoxybenzene in the presence of hydroxide ion to yield the first member of a new class of compounds called by the authors "diphenyliodyl hydroxide." It was isolated as an impure, unstable, amorphous solid which formed a moderately stable amorphous carbonate and a stable, crystalline acetate. Salts derived from strong acids were not isolated. Salts of carbonic and acetic acids were reported to be hydrogen-bonded cyclic complexes, such as "diphenyliodyl acetate" (I).[2,3] Strong acids, it was reasoned, do not readily undergo chelation or coordination and therefore the "diphenyliodyl salts" of strong acids undergo hydrolysis with consequent decomposition of the unstable hydroxide.

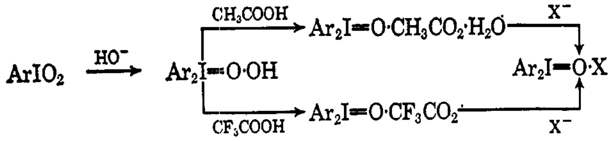


I

A study of this class of compounds which we have renamed "diaryliodosyl salts" has been initiated, and the synthesis and properties of several of these compounds are reported here.

Synthesis.—The method of preparation is a modification of that of Masson, *et al.*[2] according to Scheme I.

SCHEME I



$X = F, Cl, Br, and IO_3$

These compounds are colorless, nonvolatile, infusible solids. They are listed in Table I along with their respective decomposition points and yields. Solubility characteristics are described in the Experimental Section.

TABLE I

DIARYLIODOSYL SALTS

Diaryliodosyl salt	X (compd no.)[j]	Dec pt, °C	Yield,[a] %
$Ph_2I{=}O \cdot X$	$CH_3CO_2 \cdot H_2O$	114[b]	50[d]
	(1)	114 dec[c]	75,[e] 50[f]
	CF_3CO_2 (2)	158 exp[i]	95[f]
	F (3)	197 exp	54[g]
	Cl (4)	181 exp	44[g]
	Br (5)	144 exp	49[g]
$p\text{-}(MeC_6H_4)_2I{=}O \cdot X$	IO_3 (6)	131–133 dec	78[f]
	CF_3CO_2 (7)	159 dec	65
	F (8)	170 exp	48[f]
$p\text{-}(FC_6H_4)_2I{=}O \cdot X$	CF_3CO_2 (9)	175 exp	14[f]
			36[h]
	F (10)	185 exp	53[g]
	Cl (11)	163 exp	44[g]

[a] Yields are of the unrecrystallized product. [b] Reported value (ref 2). [c] Observed value. [d] Reported yield (ref 2). [e] Observed yields; the higher was obtained by treating the carbonate with acetic acid, while the lower was obtained when the diphenyliodosyl hydroxide was neutralized directly with acetic acid. [f] Yield is based on starting iodoxy compounds. [g] Yield is based on parent diaryliodosyl trifluoroacetate. [h] Yield is based only on reacted *p*-fluoroiodoxybenzene; that is, on unrecovered starting material. (The *p*-fluoro group therefore not only retards the reaction but causes the iodoxy compound to be consumed in a different way.) [i] Explodes. [j] Registry no. are as follows: 2, 16317-00-3; 3, 16451-39-1; 4, 16503-27-8; 5, 16451-40-4; 6, 16317-04-7; 7, 16394-32-4; 8, 16451-41-5; 9, 16394-33-5; 10, 16451-42-6; 11, 16451-43-7.

Chemical Properties.—Diaryliodosyl salts are easily reduced to the corresponding iodonium salts by iodide, bisulfite, and hydrogen peroxide. Chloride and bromide are rapidly oxidized under acidic conditions probably according to the following equation.[2]

$$Ph_2I{=}O \cdot X + X^- + 2H^+ \longrightarrow Ph_2I^+ + X_2 + H_2O$$

4,4′-Dimethyldiphenyliodosyl fluoride and iodate are hygroscopic, forming hydrates on prolonged contact with air. The fluoride forms a monohydrate as confirmed by elemental analysis. Hydration of the iodate was not studied quantitatively. Attempted dehydration of diphenyliodosyl acetate was unsuccessful. More vigorous conditions than drying to constant weight at 25° and 2-mm pressure caused decomposition.

Ultraviolet Spectra.—Ultraviolet spectra of iodoxybenzene and diphenyliodosyl salts have previously not been reported, while those of iodobenzene[4–7] and diaryliodonium salts [7,8] have been studied in the 400–200-mμ region. Diphenyliodosyl salts and iodoxybenzene exhibit bands which are much broader than those of diphenyliodonium salts and iodobenzene; otherwise there are no distinguishing features. The spectrum of diphenyliodosyl trifluoroacetate, in water, has a band with a plateau extending from 216 to 227 mμ (log ε 4.12). Diphenyliodonium trifluoroacetate exhibits a

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[1] This paper is largely based on part I of a dissertation submitted by P. Bodlaender in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, 1967.

[2] I. Masson, E. Race, and F. E. Pounder, Jr., *J. Chem. Soc.*, 1669 (1935).

[3] C. G. Le Fevre and R. J. W. Le Fevre, *ibid.*, 3373 (1950).

[4] K. Bowden and E. A. Braude, *ibid.*, 1071 (1952).

[5] H. E. Ungnade, *J. Amer. Chem. Soc.*, **75**, 434 (1952).

[6] W. F. Forbes, *Can. J. Chem.*, **37**, 1979 (1959).

[7] F. M. Beringer and I. Lillien, *J. Amer. Chem. Soc.*, **82**, 5135 (1960).

[8] H. Irving, G. P. A. Turner, and R. W. Reid, *J. Chem. Soc.*, 2082 (1960).