heptafluorobutyranilide was obtained in 21% yield as colorless needles, m.p. 97°. The product was identical with the amide prepared directly from *p*-anisidine.

Products from N-Phenylmalonamic Acid.—Treatment of this amic acid with trifluoroacetic or heptafluorobutyric anhydrides gave a colorless powder in yields of 60–80% (calculated as dehydration product). The melting point varied with different preparations (210°, 186–190° dec.) and appeared to depend on the rate of heating. The infrared spectrum contained bands at 3.08 and 5.95 μ.

Anal. Calcd. for $C_9H_7NO_2$ (malonanilic acid–water): C, 67.07; H, 4.38; N, 8.69. Found: C, 66.63; H, 5.05; N, 8.49, corresponding to $C_9H_8NO_2$.

The products from thionyl chloride were colored, amorphous solids with broad melting range (205–220°). Attempted hydrolysis of an orange sample by boiling potassium hydroxide solution formed on acidification hydrogen sulfide and a green precipitate. The green solid had an infrared spectrum differing from that of the orange solid only in the sharpness of the carbonyl absorption.

Camphorisoimides and Related Compounds.—The literature procedures[12] were followed for the preparation of compounds in this series. N-Methyl-α-camphoramic acid was obtained by direct reaction of aqueous methylamine with suspended *d*-camphoric anhydride. N-Methylcamphorimide was prepared by heating the α-amic acid above its melting point and then distilling the melt. The yellow distillate did not solidify at room temperature; the infrared spectrum had four carbonyl bands indicating a mixture of camphoric anhydride (5.52, 5.65 μ) and the imide (5.80, 6.00 μ). One crystallization from ether and two from absolute ethanol gave needles, m.p. 38–40° (lit. m.p. 40–42°) having only the imide carbonyl bands. N-Methyl-β-camphoramic acid was obtained by dehydration of the α-amic acid to imide followed by hydrolysis of the crude imide. The β-amic acid was separated from α-amic acid, formed in smaller amounts, by fractional crystallization. The α-amic acid was dehydrated by heating with acetyl chloride followed by treatment with aqueous hydroxide to liberate the free isoimide; N-methyl-α-camphorisoimide was isolated in 16% yield as fine crystals (from ether), m.p. 132–133°. The β-amic acid was dehydrated with phosphorus oxychloride to a neutral product (9% yield) having four carbonyl bands indicating imide (5.80, 5.98 μ) and, presumably, β-isoimide (5.63, 5.90 μ).

Reaction of Isoimides with Piperidine.—The method was that of Mustafa, *et al.*[36] The products were not the amine adducts of the maleisoimides as shown by insolubility in acid and by infrared bands at 3.02 (N—H) and 5.97 μ (amide C═O) and absence of the original isoimide bands.

(a) **Piperidide of N-(*p*-methoxyphenyl)maleamic acid** was obtained in 40% yield as pale yellow crystals (from aqueous ethanol), m.p. 151.0–154.0°. The low yield resulted from the presence of amic acid in the sample of maleisoimide, indicated by the precipitation of the piperidinium salt of N-(*p*-methoxyphenyl)maleamic acid in 42% yield immediately on addition of piperidine; this salt was identified by comparison of its infrared spectrum with that of the salt prepared directly from the amic acid and piperidine.

Anal. Calcd. for $C_{16}H_{20}N_2O_3$: C, 66.64; H, 6.99; N, 9.72. Found: C, 66.54; H, 6.96; N, 9.85.

(b) **Piperidide of N-(1-naphthyl)maleamic acid** was obtained in 86% yield as off-white needles (from acetone), m.p. 150.0–152.0°.

Anal. Calcd. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54, N, 9.09. Found: C, 73.82; H, 6.38; N, 9.10.

(c) **α-Piperidyl-N-(1-naphthyl)succinimide.**—The piperidine adduct of N-(1-naphthyl)maleimide was prepared for comparison with the diamide obtained from the isoimide. The product was obtained in 74% yield as a semisolid which after several recrystallizations from 95% ethanol gave colorless crystals, m.p. 147–151°. The infrared spectrum had no N–H absorption and a sharp imide band at 5.86 μ, with shoulders at 5.66 and 5.95 μ.

Anal. Calcd. for $C_{19}H_{20}N_2$: C, 74.00; H, 6.54; N, 9.09. Found: C, 74.04; H, 6.77; N, 9.08.

Infrared Measurements.—Qualitative spectra were obtained in Nujol mulls on a Perkin-Elmer Infracord spectrophotometer, Model 137-B. Quantitative spectra were determined in purified dioxane[43] in an 0.0252-mm. cell on a Perkin-Elmer Model 21 spectrophotometer.

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[43] L. F. Fieser, "Experiments in Organic Chemistry;" 3rd Ed.; D. C. Heath and Co., Boston, Mass., 1955, p. 285.

Novel Method for the Preparation of Acid Anhydrides by Means of Diphenylmercury and Tertiary Phosphine

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The reactions of phenylmercuric acetate with triethyl phosphite or tri-*n*-butylphosphine have been investigated. Further, a novel method for the preparation of acid anhydrides by means of diphenylmercury and tri-*n*-butylphosphine has been studied. The reactions of two moles of carboxylic acids with one mole each of diphenylmercury and of tri-*n*-butylphosphine gave the corresponding carboxylic acid anhydrides in high yields along with mercury, benzene, and tri-*n*-butylphosphine oxide. Similarly, pyrophosphates or sulfonic acid anhydride were prepared in high yields by the reactions of two moles of phosphoric monoesters or sulfonic acid with one mole each of diphenylmercury and of tri-*n*-butylphosphine. The mechanisms of these reactions are discussed.

It recently has been found that mercuric and mercurous carboxylates are reduced by means of triethyl phosphite or tertiary phosphines to give mercury and the corresponding acid anhydrides in good yields.[1]

$$(RCO_2)_2Hg + R_3'P \longrightarrow Hg + (RCO)_2O + R_3'P{=}O$$
$$R' = C_2H_5O\text{–},\ n\text{-}C_4H_9\text{–},\ C_6H_5\text{–}$$

In the present study, the reduction of phenylmercuric acetate by the trivalent phosphorus compounds was tested first under the assumption that it would, when reduced, yield mercury and acetophenone. Indeed, an exothermic reaction was observed when the acetate reacted with triethyl phosphite at room temperature. Mercury and acetophenone, however, were not obtained, but ethyl acetate was produced in 74% yield along with a large amount of white crystals (I), m.p. 163–166°. These white crystals (I) were shown to be diethyl phenylmercuric phosphonate by means of elemental analysis and infrared absorption spectrum which has characteristic bands attributable to phosphorus–oxygen double bonds (1260 cm.$^{-1}$) and to a monosubstituted benzene ring (1600, 730 and 695 cm.$^{-1}$).

This reaction may proceed through an initial formation of adduct II of phenylmercuric acetate, and triethyl phosphite; this, subsequently, is transformed into III, conceivably by way of an internal nucleophilic displacement. The intermediate (III) thus formed has

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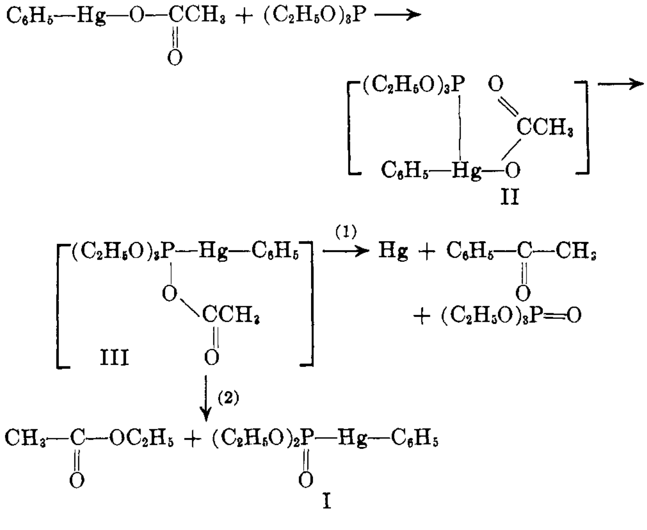
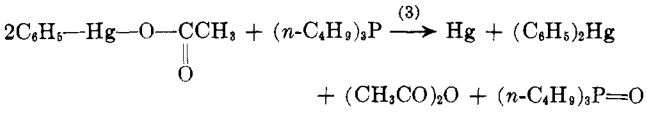
[1] T. Mukaiyama, H. Nambu, and I. Kuwajima, *J. Org. Chem.*, **28**, 917 (1963).

two possible pathways of decomposition, namely (1) the formation of mercury, acetophenone, and triethyl phosphate by electrophilic attack of an acetyl group on a phenyl group and (2) the formation of ethyl acetate and diethyl phenylmercuric phosphonate (I) by nucleophilic attack of an acetoxyl group on an ethyl group—*i.e.*, the Arbuzov type reaction—as described in the following scheme. Since the decomposition of III occurs more readily by the Arbuzov type reaction, the two products mentioned previously may result.

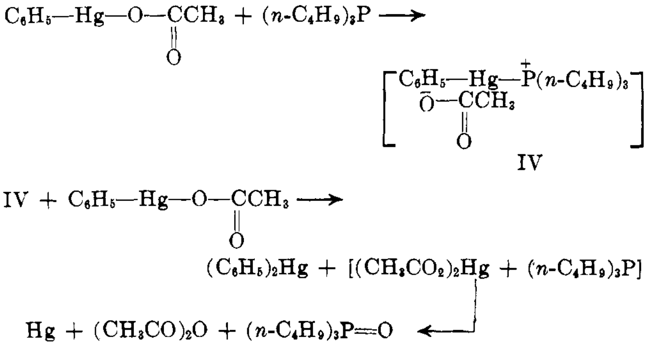


On the other hand, when tri-*n*-butylphosphine, which can not undergo the Arbuzov type reaction, was used in place of triethyl phosphite, mercury (46%), diphenylmercury (34%), acetic anhydride (31%), and tri-*n*-butylphosphine oxide (45%) were obtained, and tri-*n*-butylphosphine (40%) was recovered. However, when the reaction of two moles of phenylmercuric acetate with one mole of tri-*n*-butylphosphine was examined, mercury (80%), diphenylmercury (62%), acetic anhydride (49%), and tri-*n*-butylphosphine oxide (86%) were obtained, and tri-*n*-butylphosphine was not recovered.



$$2C_6H_5\text{—}Hg\text{—}O\text{—}\underset{\underset{O}{\|}}{C}CH_3 + (n\text{-}C_4H_9)_3P \xrightarrow{(3)} Hg + (C_6H_5)_2Hg + (CH_3CO)_2O + (n\text{-}C_4H_9)_3P{=}O$$

This reaction can be explained in the following manner. The phosphonium acetate (IV), which may be derived from the reaction of phenylmercuric acetate with tri-*n*-butylphosphine, reacts further with phenylmercuric acetate to yield diphenylmercury and mercuric acetate. Of the two compounds thus formed, the latter is successively reduced by tri-*n*-butylphosphine to give mercury and acetic anhydride.



$$C_6H_5\text{—}Hg\text{—}O\text{—}\underset{\underset{O}{\|}}{C}CH_3 + (n\text{-}C_4H_9)_3P \longrightarrow \left[C_6H_5\text{—}Hg\text{—}\overset{+}{P}(n\text{-}C_4H_9)_3 \quad \overset{-}{O}\text{—}\underset{\underset{O}{\|}}{C}CH_3\right] \quad \text{IV}$$

$$\text{IV} + C_6H_5\text{—}Hg\text{—}O\text{—}\underset{\underset{O}{\|}}{C}CH_3 \longrightarrow (C_6H_5)_2Hg + [(CH_3CO_2)_2Hg + (n\text{-}C_4H_9)_3P] \longrightarrow Hg + (CH_3CO)_2O + (n\text{-}C_4H_9)_3P{=}O$$

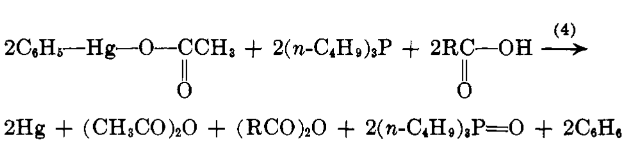
When equimolar amounts of phenylmercuric acetate and tri-*n*-butylphosphine reacted in the presence of an equimolar amount of carboxylic acid, the anhydride of the carboxylic acid was obtained along with mercury, acetic anhydride, tri-*n*-butylphosphine oxide, and benzene (see Table I).

TABLE I

THE REACTIONS OF PHENYLMERCURIC ACETATE AND TRI-*n*-BUTYLPHOSPHINE IN THE PRESENCE OF CARBOXYLIC ACIDS

	Yield, %				
Carboxylic acid	$(RCO)_2O$	$(CH_3CO)_2O$	Hg	$(n\text{-}C_4H_9)_3P{=}O$	C_6H_6
Acetic acid	82	82	92	90	86
Propionic acid	62	62	89	92	100

[a] These reactions were carried out at 60–65° for two hours without solvent.



$$2C_6H_5\text{—}Hg\text{—}O\text{—}\underset{\underset{O}{\|}}{C}CH_3 + 2(n\text{-}C_4H_9)_3P + 2R\underset{\underset{O}{\|}}{C}\text{—}OH \xrightarrow{(4)} 2Hg + (CH_3CO)_2O + (RCO)_2O + 2(n\text{-}C_4H_9)_3P{=}O + 2C_6H_6$$

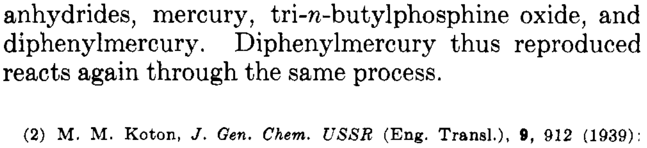
The reaction was extended further to the preparation of various carboxylic acid anhydrides in yields ranging from 74 to 87% by treating two moles of carboxylic acids with one mole each of diphenylmercury and of tri-*n*-butylphosphine (see Table II).

TABLE II

THE REACTIONS OF DIPHENYLMERCURY AND TRI-*n*-BUTYLPHOSPHINE IN THE PRESENCE OF CARBOXYLIC ACIDS

				Yield, %		
Carboxylic acid	Reaction solvent	Time, hr.	Temp., °C.	Anhydride	Hg	$(n\text{-}C_4H_9)_3P{=}O$
Acetic	Benzene	2.0	80	80	94	86
Propionic	Benzene	2.0	80	80	92	95
Butyric	Benzene	2.0	80	87	94	89
Benzoic	Dioxane	4.0	100	74	85	87
Phthalic	[a]			78	71	92

[a] In the case of phthalic acid, a white precipitate, m.p. 142–143°, was obtained by refluxing the benzene solution for 2 hr. Its mercury and phosphorus content could not be analyzed by the methods of A. Koten and R. Adams, *J. Am. Chem. Soc.*, **46**, 2764 (1924), and D. F. Boltz and M. G. Mellon, *Anal. Chem.*, **19**, 873 (1947). But, when it was pyrolyzed at 180°, mercury, phthalic anhydride, and tri-*n*-butylphosphine oxide were obtained. Assuming the precipitate to be a 1:1:1 adduct of the three starting materials, the yields were calculated.



$$(C_6H_5)_2Hg + (n\text{-}C_4H_9)_3P + 2R\underset{\underset{O}{\|}}{C}\text{—}OH \xrightarrow{(5)} Hg + (RCO)_2O + (n\text{-}C_4H_9)_3P{=}O + 2C_6H_6$$

These two types of reactions (4 and 5) are regarded as proceeding through an initial formation of phenylmercuric carboxylates which result by the reaction of diphenylmercury with carboxylic acids.[2] The subsequent reduction of phenylmercuric carboxylates by tri-*n*-butylphosphine yields the corresponding acid anhydrides, mercury, tri-*n*-butylphosphine oxide, and diphenylmercury. Diphenylmercury thus reproduced reacts again through the same process.

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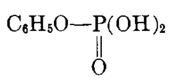
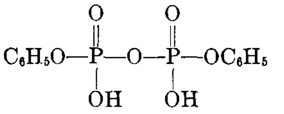
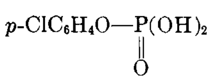
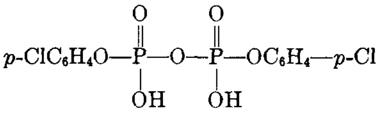
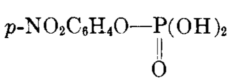
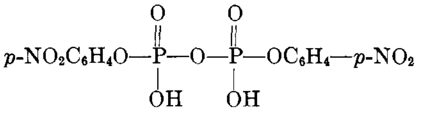
(2) M. M. Koton, *J. Gen. Chem. USSR* (Eng. Transl.), **9**, 912 (1939); *Chem. Abstr.*, **34**, 392^6 (1940).

TABLE III

THE REACTIONS OF DIPHENYLMERCURY, TRI-*n*-BUTYLPHOSPHINE, AND THE MONOESTERS OF PHOSPHORIC ACID OR *p*-TOLUENESULFONIC ACID

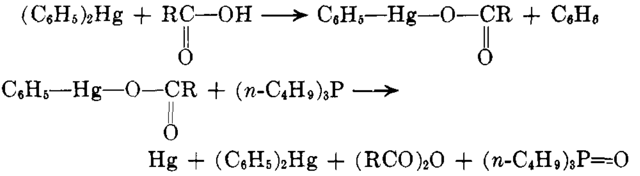
Acid	Anhydride	Yield, %	Hg, %	$(n\text{-}C_4H_9)_3P=O$, %
 $C_6H_5O\text{—}\underset{O}{\underset{\|}{P}}(OH)_2$	 $C_6H_5O\text{—}\underset{OH}{\overset{O}{P}}\text{—}O\text{—}\underset{OH}{\overset{O}{P}}\text{—}OC_6H_5$	86[a]	85	78
 $p\text{-}ClC_6H_4O\text{—}\underset{O}{\underset{\|}{P}}(OH)_2$	 $p\text{-}ClC_6H_4O\text{—}\underset{OH}{\overset{O}{P}}\text{—}O\text{—}\underset{OH}{\overset{O}{P}}\text{—}OC_6H_4\text{—}p\text{-}Cl$	92[b]	89	83
 $p\text{-}NO_2C_6H_4O\text{—}\underset{O}{\underset{\|}{P}}(OH)_2$	 $p\text{-}NO_2C_6H_4O\text{—}\underset{OH}{\overset{O}{P}}\text{—}O\text{—}\underset{OH}{\overset{O}{P}}\text{—}OC_6H_4\text{—}p\text{-}NO_2$	95[c]	95	83
$p\text{-}CH_3C_6H_4SO_3H$	$p\text{-}CH_3C_6H_4SO_2\text{—}O\text{—}SO_2C_6H_4\text{—}p\text{-}CH_3$	76	93	88

[a] R_f 0.74 (*n*-PrOH:NH$_3$:H$_2$O = 6:3:1). [b] R_f 0.79 (*n*-PrOH:NH$_3$:H$_2$O = 6:3:1). [c] R_f 0.90 (5% Na$_2$HPO$_4$:*i*-AmOH = 2:1), C. E Carter, *J. Am. Chem. Soc.*, **72**, 1466 (1950).

TABLE IV

THE REACTIONS OE DIPHENYLMERCURY, TRI-*n*-BUTYLPHOSPHINE, AND CARBOXYLIC ACIDS IN THE PRESENCE OF ALCOHOLS OR AMINES

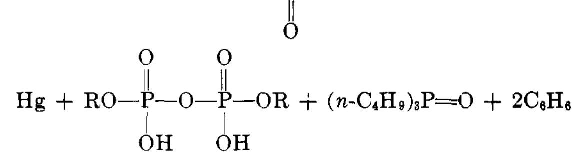
Acid	ROH or RNH$_2$	Solvent	Time, hr.	Yield, %		
				Hg	$(n\text{-}C_4H_9)_3P=O$	Esters or amides
Acetic	$C_6H_5CH_2OH$	Dioxane	10	88	83	$CH_3CO_2CH_2C_6H_5$ 83
Propionic	$C_6H_5CH_2OH$	Dioxane	10	85	70	$C_2H_5CO_2CH_2C_6H_5$ 75
Butyric	$C_6H_5CH_2OH$	Benzene	10	88	82	$C_3H_7CO_2CH_2C_6H_5$ 79
Benzoic	C_2H_5OH	Benzene	10	85	80	$C_6H_5CO_2C_2H_5$ 76
Acetic	$C_6H_5NH_2$	Benzene	5.0	89	87	$CH_3CONHC_6H_5$ 80
Benzoic	$C_6H_5NH_2$	Benzene	5.0	92	85	$C_6H_5CONHC_6H_5$ 83



$$(C_6H_5)_2Hg + R\underset{O}{\underset{\|}{C}}\text{—}OH \longrightarrow C_6H_5\text{—}Hg\text{—}O\text{—}\underset{O}{\underset{\|}{C}}R + C_6H_6$$

$$2C_6H_5\text{—}Hg\text{—}O\text{—}\underset{O}{\underset{\|}{C}}R + (n\text{-}C_4H_9)_3P \longrightarrow Hg + (C_6H_5)_2Hg + (RCO)_2O + (n\text{-}C_4H_9)_3P=O$$

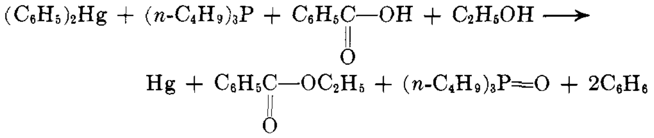
Further, it was established that the reaction of monoesters of phosphoric acid or of *p*-toluenesulfonic acid with tri-*n*-butylphosphine and diphenylmercury gave *sym*-diesters of pyrophosphate or *p*-toluenesulfonic acid anhydride in high yields.



$$(C_6H_5)_2Hg + (n\text{-}C_4H_9)_3P + 2RO\text{—}\underset{O}{\underset{\|}{P}}(OH)_2 \longrightarrow Hg + RO\text{—}\underset{OH}{\overset{O}{P}}\text{—}O\text{—}\underset{OH}{\overset{O}{P}}\text{—}OR + (n\text{-}C_4H_9)_3P=O + 2C_6H_6$$

$$(C_6H_5)_2Hg + (n\text{-}C_4H_9)_3P + 2p\text{-}CH_3\text{—}C_6H_4\text{—}SO_3H \longrightarrow Hg + (p\text{-}CH_3\text{—}C_6H_4\text{—}SO_2)_2O + (n\text{-}C_4H_9)_3P=O + 2C_6H_6$$

When a solution of equimolar amounts of diphenylmercury, tri-*n*-butylphosphine, benzoic acid, and ethanol was refluxed for eight hours, ethyl benzoate was obtained in 76% yield along with mercury (85%) and tri-*n*-butylphosphine oxide (80%).



$$(C_6H_5)_2Hg + (n\text{-}C_4H_9)_3P + C_6H_5\underset{O}{\underset{\|}{C}}\text{—}OH + C_2H_5OH \longrightarrow Hg + C_6H_5\underset{O}{\underset{\|}{C}}\text{—}OC_2H_5 + (n\text{-}C_4H_9)_3P=O + 2C_6H_6$$

Similarly, various carboxylic esters were produced in good yields by the reactions of diphenylmercury and tri-*n*-butylphosphine.

When aniline was used in place of alcohol in the preceding experiment, the corresponding anilides were obtained in good yields (see Table IV).

Furthermore, it became apparent that the reaction proceeds more readily when di-*p*-anisylmercury is used in place of diphenylmercury. These reactions are examined further.

Experimental

Materials.—Phenylmercuric acetate (m.p. 147–148°) and diphenylmercury (m.p. 121°) were prepared by the methods of Seide, *et. al.*,[3] and Blicke and Smith.[4]

Reaction of Phenylmercuric Acetate with Triethyl Phosphite.—When triethyl phosphite (3.4 g., 0.02 mole) was added all at once to phenylmercuric acetate (6.7 g., 0.02 mole) with vigorous shaking at room temperature, the reaction soon started with liberation of heat. After the reaction mixture was heated at 100° for 4 hr. with occasional shaking, the solid which was deposited was filtered. The filtrate was distilled, giving ethyl acetate, 1.3 g. (74%), b.p. 74–76°, and triethyl phosphate, 0.2 g. (5.5%), b.p. 90–92° (10 mm). Then the solid was dissolved in anhydrous dioxane and a trace of mercury was filtered off. The filtrate was evaporated *in vacuo* and a white crystal was obtained. It was washed with a small volume of anhydrous dioxane and dried *in vacuo*, yielding 5.2 g. (62%), m.p. 163–166°.

Anal. Calcd. for $C_{10}H_{15}O_3PHg$: P, 7.44; Hg, 48.1. Found: P, 7.21; Hg, 48.4.

Reaction of Phenylmercuric Acetate with Tri-*n*-Butylphosphine.—A solution of phenylmercuric acetate (6.7 g., 0.02 mole) and tri-*n*-butylphosphine (2.0 g., 0.01 mole) in 30 ml. of anhydrous benzene was refluxed for half an hour. Then the liberated mercury (1.65 g., 82%) was filtered off and the filtrate was concentrated. By the addition of petroleum ether to the residue, diphenylmercury, 2.2 g. (62%), m.p. and m.m.p. 115–117°, was obtained. After it was filtered off, the filtrate was concen-

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(3) O. A. Seide, S. M. Scherlin, and G. J. Bras, *J. prakt. Chem.*, **138**, 55 (1933).

(4) F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, **51**, 3479 (1929).

trated and distilled. Acetic anhydride, 0.5 g. (49%), b.p. 136–137°, and tri-*n*-butylphosphine oxide, 1.9 g. (86%), b.p. 123–125° (0.2 mm.), were obtained.

Reaction of Phenylmercuric Acetate with Tri-*n*-Butylphosphine and Acetic Acid.—A mixture of phenylmercuric acetate (6.7 g., 0.02 mole), tri-*n*-butylphosphine (4.0 g., 0.02 mole), and glacial acetic acid (1.3 g., 0.02 mole) was heated with stirring at 65° for 2 hr. Mercury (3.4 g., 86%) was separated and the filtrate was distilled. Benzene, 1.4 g. (90%), b.p. 80–82°, acetic anhydride,[5] 1.63 g. (82 × 2%), b.p. 70–72° (92 mm.), and tri-*n*-butylphosphine oxide, 3.8 g. (94%), b.p. 123–125° (0.2 mm.), were obtained.

Reaction of Diphenylmercury and Tri-*n*-Butylphosphine with Acetic Acid.—A solution of diphenylmercury (5.3 g., 0.015 mole), tri-*n*-butylphosphine (3.0 g., 0.015 mole), and glacial acetic acid (1.8 g., 0.03 mole) in 10 ml. of anhydrous benzene was refluxed for 2 hr. Then the liberated mercury (2.84 g., 94%) was filtered off and the filtrate was concentrated. The residue was distilled, giving acetic anhydride, 1.38 g. (80%), b.p. 134–136°, and tri-*n*-butylphosphine oxide, 2.6 g. (86%), b.p. 123–125° (0.2 mm.).

By a similar procedure, propionic, butyric, and benzoic anhydrides were obtained (see Table II).

Reaction of Diphenylmercury and Tri-*n*-Butylphosphine with Phthalic Acid.—A solution of diphenylmercury (5.3 g., 0.015 mole), tri-*n*-butylphosphine (3.0 g., 0.015 mole), and phthalic acid (2.5 g., 0.03 mole) in 10 ml. of anhydrous benzene was refluxed for 2 hr. Then a trace of liberated mercury was filtered off and the filtrate was cooled. The resulting white precipitate, 6.95 g., m.p. 128–133°, was filtered and the filtrate was concentrated *in vacuo*. An additional white precipitate, 2.35 g., m.p. 125–128°, was obtained. These were combined and recrystallized twice from benzene, m.p. 142–143°.

When 4.60 g. of these crystals was heated at 180° for 20 min., mercury, 0.90 g., was liberated and the residue solidified. This solid was washed with a small volume of dry ether and phthalic anhydride, 0.73 g., m.p. and m.m.p. 130–132°. From the filtrate, tri-*n*-butylphosphine oxide, 1.28 g., b.p. 123–135 (0.2 mm.), was obtained.

Reaction of Diphenylmercury and Tri-*n*-Butylphosphine with Phenyl Dihydrogen Phosphate.—A solution of diphenylmercury (3.5 g., 0.01 mole), tri-*n*-butylphosphine (2.0 g., 0.01 mole), and phenyl dihydrogen phosphate (3.4 g., 0.02 mole) in 15 ml. of anhydrous benzene was refluxed for 3 hr. After the liberated mercury, 1.70 g. (85%), was filtered off, a solution of barium chloride ($BaCl_2 \cdot H_2O$, 5 g.) in 20 ml. of water and pyridine (10 ml.) was added to the cold filtrate and allowed to stand in a refrigerator for about 30 min. The white precipitate was washed twice with acetone, dried, and then thoroughly washed with 50 ml. of water. The undissolved precipitate was filtered and dried *in vacuo* over phosphorus pentoxide, yielding 4.50 g. (86%) of barium diphenyl pyrophosphate, R_f 0.74 (n-PrOH:NH_3:H_2O = 6:3:1). From the filtrate, tri-*n*-butylphosphine oxide, 1.70 g. (78%), b.p. 121–122° (0.8 mm.), was obtained.

By a similar procedure, *sym*-di-*p*-chlorophenyl pyrophosphate and *sym*-di-*p*-nitrophenyl pyrophosphate were obtained.

Reaction of Diphenylmercury and Tri-*n*-Butylphosphine with *p*-Toluenesulfonic Acid.—Diphenylmercury (3.5 g., 0.01 mole), tri-*n*-butylphosphine (2.0 g., 0.01 mole), and *p*-toluenesulfonic acid (3.4 g., 0.02 mole) were dissolved in 15 ml. of anhydrous benzene and refluxed for 3 hr. Then the liberated mercury, 1.86 g. (93%), was filtered off and the filtrate was evaporated *in vacuo*. On addition of 0.9 g. (0.01 mole) of aniline to the residue, a white precipitate deposited. It was filtered off and washed with a small volume of water and dried *in vacuo*; 1.88 g. (76%) of *p*-toluenesulfonyl anilide, m.p. and m.m.p. 100–102°, was obtained. From the filtrate, tri-*n*-butylphosphine oxide, 1.92 g. (88%), b.p. 120–122° (0.2 mm.), was isolated.

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[5] Acetic anhydride, derived from two sources, can not be determined separately; consequently, it is assumed that equal volumes are obtained from them.

Mechanisms of Hydrolysis of Several Atom-Bridged Bicyclic Anhydrides, N-Methylimides, and Lactones

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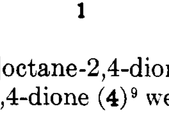
Several atom-bridged bicyclic carbonyl compounds were synthesized. The saponification or hydrolysis rates of these and related compounds were determined. Ground state strains were assessed by determining the position of the monomer–polymer equilibrium. The rates were interpreted using a postulate of Bruice and Pandit about the location of the transition states. Because these cage structures reacted readily in most cases, a configuration of the transition state wherein the hydroxyl ion is colinear with the carbonyl oxygen was rejected.

Interest in the mechanisms of hydrolysis and saponification reactions[1] prompted determination of the rates of these reactions for several atom-bridged bicyclic compounds prepared earlier[2] and for several new ones.

Results

Preparation of Compounds.—Ethyl 3-hydroxycyclopentanecarboxylate was prepared according to Vaughan[3] and Toki.[4] When heated with a trace of litharge,[2] ethanol was eliminated and the lactone, 2-oxabicyclo[2.2.1]heptan-3-one (**1**), distilled as a waxy solid.[5] 2-Oxabicyclo[3.2.1]octan-3-one (**2**) was prepared by Baeyer–Villiger oxidation of norcamphor.[6,7] 3-Oxabicyclo[3.2.1]octane-2,4-dione (**3**)[8] and 3-oxabicyclo[3.2.2]nonane-2,4-dione (**4**)[9] were prepared from corresponding dicarboxylic acids by literature procedures. N-Methyl-3-azabicyclo[3.2.1]octane-2,4-dione (**5**) and N-methyl-3-azabicyclo[3.3.1]nonane-2,4-dione (**6**) were prepared by treating *cis*-cyclopentane-1,3-dicarboxylic acid and *cis*,-



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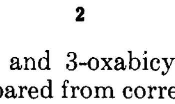

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