

g. of the free thiophenol was added 0.3 cc. of bromine in 10 cc. of benzene and the mixture then allowed to stand for forty-eight hours. Evaporation of the benzene left yellowish granules and a little red oil. On exposure to the air the oil largely solidified. Although the product had first shown definite indications of the presence of considerable amounts of some other products, the procedure resulted in the ultimate identification of about 97% of the product as hexabromodiphenyl disulfide.

Product Formed by Bromine with Thiophenol in Glacial Acetic Acid.—Thiophenol (5.7 g.) was dissolved in 50 cc. of glacial acetic acid. To this was added 11.4 cc. of bromine and it was then allowed to stand for several hours, part of the time in sunlight. The solution was then cooled in an ice-bath, the solid filtered off, washed five times with cold acetic acid and then five times with water. After drying, the solid was recrystallized from alcohol; m. p. 91–93°. The melting point, crystalline form and analysis correspond to the 4,4'-dibromodiphenyl disulfide of Hübner and Alsberg.¹¹

Anal. Calcd. for $(C_6H_4BrS)_2$: Br, 42.50. Found: Br, 42.87.

Summary

1. The salts of 2,4,6-tribromothiophenol, as well as the free thiophenol, react in a perfectly normal manner with halogens and alkyl halides to give the disulfide or thio ethers in nearly quantitative yield. The products contain nothing analogous to the amorphous polydihalogenophenylene oxides obtained from the trihalogenated phenols and phenolates.

2. The first stage in the reaction of both phenolates and thiophenolates is probably the formation of metal halide plus an unstable product containing halogen directly attached to oxygen or sulfur.

3. The first known member of the series of trihalogenated thiophenols has been prepared. From this eight derivatives have been prepared and characterized.

¹¹ Hübner and Alsberg, *Ann.*, **156**, 328 (1870).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

KETENES FROM ACYLPHTHALIMIDES AND OTHER SUBSTITUTED AMIDES

BY CHARLES D. HURD AND MALCOLM F. DULL

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Acetylcarbazole is known¹ to regenerate carbazole on heating above its melting point. Propionylcarbazole,² *n*-nonoylcarbazole³ and palmitylcarbazole show a similar instability on fusion. Although carbazole was identified in all cases, no attention was directed to the fate of the acyl radicals.

If the elements of carbazole, $(C_6H_4)_2NH$, are subtracted from those of acetylcarbazole, $(C_6H_4)_2NCOCH_3$, the elements of ketene remain. Whereas

¹ Graebe and Glaser, *Ann.*, **163**, 351 (1872).

² Oddo, *Mem. accad. Lincei*, [v] **14**, 510 (1923).

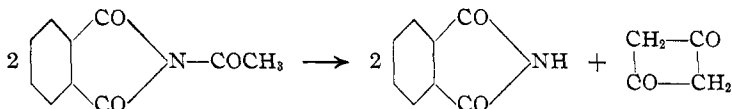
³ Copisarow, *J. Chem. Soc.*, **113**, 816 (1918).

ketene was not found, its dimer was formed when dry acetylcarbazole was refluxed. Ketene dimer is considered⁴ to be cyclobutanedione, $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \quad | \\ \text{CO}-\text{CH}_2 \end{array}$.

The ketene detachment from this acetyl derivative of carbazole was due, in part at least, to the weakness of carbazole as a base, since the acetyl derivative of ammonia, namely, acetamide, gave no incontrovertible evidence⁵ of ketene as a product of pyrolysis. Therefore, other acyl derivatives of neutral or acidic trivalent nitrogen compounds were also tested for similar ketene production.

Acetyldiphenylamine, diacetamide and acetylphthalimide were taken. The first of these, despite its structural similarity to acetylcarbazole, was unchanged after 24 hours of refluxing (290°) or after passage through tubes at 500 or 600°. Diacetamide was less stable, giving good yields of acetic acid and acetonitrile⁶ as it was passed rapidly through a tube at 635°. No evidence was obtained for ketene or its dimer: $(\text{CH}_3\text{CO})_2\text{NH} \rightarrow \text{CH}_3\text{CN} + \text{CH}_3\text{CO}_2\text{H}$.

Acetylphthalimide, previously described by Aschan⁷ to be an active acetylating agent, was found to decompose at a refluxing temperature into phthalimide and to give remarkably good yields of ketene dimer, yields which were considerably better than from acetylcarbazole. This constitutes a very satisfactory new method for synthesizing ketene dimer



Although acetylphthalimide resembled acetylcarbazole in giving rise to ketene dimer, the former (when not especially dried) simultaneously produced acetic acid whereas the latter gave acetone. The acetic acid points to ketene as its precursor, whereas the acetone comes from the cyclobutanedione. Acetylphthalimide decomposed much more readily than acetylcarbazole, a fact which may explain why ketene exists for a moment in the first case but not in the second.

Ketenes from Other Acylphthalimides.—*n*-Propionyl-, *n*-butyryl- and *n*-caproyl-phthalimide were studied in the hope of obtaining, respectively, methylketene, ethylketene and *n*-butylketene or their dimers, but instead only decomposition products of these substances were isolated. *n*-Butyrylphthalimide, which was found to decompose spontaneously on keeping for a few hours, pyrolyzed into phthalimide, butyric anhydride,

⁴ Chick and Wilsmore, *J. Chem. Soc.*, 97, 1978 (1908); Staudinger and Bereza, *Ber.*, 42, 4908 (1909).

⁵ Hurd, Dull and Martin, *THIS JOURNAL*, 54, 1974 (1932).

⁶ The same products in a sealed tube experiment at 250° were reported by Hentschel, *Ber.*, 23, 2396 (1890).

⁷ Aschan, *ibid.*, 19, 1398 (1886).

di-*n*-propyl ketone and carbon dioxide. The butyric anhydride is traceable through ethylketene and water whereas dipropylketone and carbon dioxide are traceable through the dimer of ethylketene and water. The source of such a quantity of water is not apparent for no more than traces should have been present. With acetylphthalimide which was dried in the same way as the butyrylphthalimide (air dried), some water was also present as evidenced by the production of acetic anhydride and acetone but even so, considerable ketene dimer was isolated as such.

Propionylphthalimide, which was purified and dried in such a way that water should have been completely excluded prior to its pyrolysis, behaved like the butyrylphthalimide. Propionic anhydride, diethyl ketone and carbon dioxide were formed between 220–320°. These products point to methylketene and its dimer as intermediates but neither could be isolated as such. Some water was even identified as such in the later stages of the pyrolysis. Its presence has no adequate explanation. Similarly, propionylcarbazole yielded distillation products which were analogous to those obtained from propionylphthalimide, namely, diethyl ketone and propionic anhydride.

Caproylphthalimide, on pyrolysis, gave rise to caproic acid and to an indifferent product which was a trimer of *n*-butylketene. Similar trimers were obtained by Wedekind⁸ by the action of tertiary bases on acid chlorides.

***iso*-Butyrylphthalimide and Dimethylketene.**—When *iso*-butyrylphthalimide, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NCOCH}(\text{CH}_3)_2$, was heated to 225°, free dimethylketene was formed in substantial amounts. Even in its present state this method is considerably simpler than the existing method⁹ for the synthesis of dimethylketene and, undoubtedly, the yield from the new method will be increased with further study.

Diphenylacetylphthalimide, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NCOCH}(\text{C}_6\text{H}_5)_2$, underwent pyrolysis into diphenylketene and phthalimide.

Comparison of the Methods with Existing Ones

Ketene Dimer.—At present this is best prepared by the slow polymerization of liquid ketene. Although gaseous ketene may be prepared easily from acetone, its liquefaction requires either solid carbon dioxide or liquid air temperatures, preferably the latter. Nothing of this nature is required in the preparation of ketene dimer from acetylphthalimide (or acetylcarbazole), for it is a direct product. Since acetylphthalimide may be prepared merely by refluxing phthalimide with acetic anhydride, the simplicity of the method is striking.

⁸ Wedekind, *Ann.*, **323**, 246 (1902).

⁹ Staudinger, *Ber.*, **39**, 968 (1908).

Dimethylketene.—To make an ether solution of dimethylketene, Staudinger¹⁰ converted *iso*-butyric acid into α -bromo-*iso*-butyryl bromide, which, in ether solution, was dehalogenated with zinc. Ether and dimethylketene are inseparable by distillation. For pure dimethylketene, it was necessary to synthesize dimethylmalonic anhydride and to subject it to pyrolysis. It is obvious that the present method is simpler than either of these for *iso*-butyrylphthalimide is readily synthesized from *iso*-butyryl chloride and potassium phthalimide. From it, dimethylketene may be prepared without contamination by a solvent.

Diphenylketene.—The most satisfactory method for this preparation is the pyrolysis of azibenzil.¹¹ However, azibenzil is difficult to prepare, involving as it does the preparation of benzil hydrazone and dehydrogenation of the latter with mercuric oxide. In contrast, diphenylacetylphthalimide may be synthesized rapidly from diphenylacetyl chloride and potassium phthalimide. This compensates for the lower yield of diphenylketene which is obtained. It is believed that considerably better yields of diphenylketene and of dimethylketene may be developed with further study of the acylphthalimides.

Experimental Part

Preparation of Materials.—Acetyldiphenylamine¹² and acetylphthalimide¹³ were prepared, respectively, in 88 and in 72–78% yields by literature methods. The former, crystallized from xylene and from alcohol, melted at 99°. Acetylphthalimide, after recrystallization from a hot benzene-petroleum ether solution, melted at 135–139° instead of 132–135° (Aschan's value).

Acetylcarbazole.—Graebe and Glaser¹⁴ prepared this by heating acetic anhydride and carbazole in a sealed tube. With the following directions, developed in part by Mr. R. W. McNamee, the sealed tube was avoided.

Carbazole (200 g.) was refluxed with an excess of acetic anhydride (600 cc.) for twenty hours. This hot mixture was poured, with stirring, into one liter of water at 75°. The oily layer was separated, washed with sodium carbonate solution, with cold water till the mass solidified, and then crystallized from alcohol (500 cc. of alcohol for each 100 g. of acetylcarbazole). Decolorizing charcoal was used. The purified crystals were dried in air. They weighed 208 g. (83.3% yield) and melted at 69°.

Propionylcarbazole was also synthesized by refluxing for twenty-four hours 100 g. of carbazole and 300 cc. of propionic anhydride. The purification procedure was the same as with acetylcarbazole. An eighty gram (60%) yield of pure propionylcarbazole was isolated, m. p. 89.5°. Previously, Oddo¹⁵ synthesized this compound from propionyl chloride and magnesium carbazole.

¹⁰ Staudinger and Klever, *Ber.*, **39**, 968 (1908); Staudinger and Ott, *ibid.*, **41**, 2208 (1910).

¹¹ Schroeter, *ibid.*, **42**, 2345 (1909).

¹² Kaufmann, *ibid.*, **42**, 3480 (1909).

¹³ Aschan, *ibid.*, **19**, 1398 (1886).

¹⁴ Graebe and Glaser, *Ann.*, **163**, 351 (1872).

¹⁵ Oddo, *Mem. accad. Lincei*, [v] **14**, 510 (1923).

Diacetamide.—Titherley's procedure¹⁶ was modified. He suspended two moles of acetamide in benzene and treated it with one mole of acetyl chloride. We obtained better results by melting the acetamide (141 g.) and adding it slowly to 1.6 moles of a benzene (200–250 cc.) solution of acetyl chloride (100 g.) which was shaken constantly. Titherley's purification procedure was used. Yields were 35–45 g. (30–37%); m. p. 78–79°.

Propionylphthalimide.—A mixture of 100 g. of phthalimide and 250 cc. of propionic anhydride was refluxed for twelve hours. Crystals formed on cooling which were filtered off, dissolved in hot benzene and caused to crystallize by the admixture of petroleum ether. The fine yellow needles which were obtained in 72% yield (90 g.) melted at 143–144°.

Anal. (Kjeldahl) Subs., 0.2973, 0.3104: cc. of 0.2138 *N* acid, 6.90, 7.01. Calcd. for $C_{11}H_9O_3N$: N, 6.89. Found: N, 6.94, 6.76.

***n*-Butyrylphthalimide** was prepared by the interaction of 50 g. of potassium phthalimide and 45 g. of *n*-butyryl chloride in 450 cc. of dry benzene. Only at the start was warming required. When complete, it was filtered and worked up in a manner identical to that described below for caproylphthalimide. The yield of dry crystals was 23 g. or 39%. Even when freshly crystallized from alcohol or from ethyl acetate, the compound had a pronounced odor of butyric acid. The crystals softened at 70–72° but did not melt completely until the melting point of phthalimide was reached. On standing overnight in a corked bottle the crystals changed into an amorphous powder and acquired a pronounced acid odor.

Caproylphthalimide.—To a suspension of 25 g. of potassium phthalimide in 250 cc. of dry benzene there was added 25 g. of caproyl chloride. The solution was warmed to start the reaction, which completed itself in ten minutes. The potassium chloride was filtered off and the filtrate evaporated at room temperature. The dry residue was extracted for five minutes with 250 cc. of alcohol¹⁷ at 30°. The solution was filtered rapidly by suction and the filtrate placed in a refrigerator until crystallization of the caproylphthalimide was complete, but not sufficiently long to permit separation of unchanged phthalimide. The large, lustrous, plate-like crystals were collected on a filter and air-dried; m. p. 78.5–79.5°; yield, 20 g. or 60%.

Anal. (Kjeldahl) Subs. 0.3177, 0.3097: cc. of 0.2138 *N* acid, 6.01, 6.00. Calcd. for $C_{14}H_{18}O_3N$: N, 5.72. Found: N, 5.77, 5.76.

Iso-butyrylphthalimide was prepared by the general procedure used for caproylphthalimide, taking 43 g. of potassium phthalimide, 50 g. of *iso*-butyryl chloride and 450 cc. of dry benzene. The product separated from alcohol in plate-like crystals; m. p. 96–98°; yield, 23 g. (45.7%).

Anal. (Kjeldahl) Subs. 0.3215, 0.3124: cc. of 0.2138 *N* acid, 6.96, 6.87. Calcd. for $C_{12}H_{14}O_3N$: N, 6.45. Found: N, 6.48, 6.58.

Diphenylacetylphthalimide.—The calculated quantity of diphenylacetyl chloride (23 g.) was refluxed vigorously for five minutes with a suspension of 18.5 g. of potassium phthalimide in 350 cc. of dry benzene. After filtering and evaporating to the consistency of a thin paste, petroleum ether was added and the whole chilled in a refrigerator for four hours. The crude crystals (13–15 g.) of diphenylacetylphthalimide thus pro-

¹⁶ Titherley, *J. Chem. Soc.*, 79, 411 (1901).

¹⁷ In some cases alcohol cannot be used to extract or to crystallize the acylphthalimides because it is a reaction solvent. Then ethyl acetate may be used, but usually the compounds are too soluble in it for convenience. If ethyl acetate is used, it should be free from alcohol.

duced were contaminated with phthalimide. Purification was effected by crystallization from absolute ethyl acetate. Ordinary ethyl acetate gave trouble, probably due to its alcohol content. Diphenylacetylphthalimide melted at 170–171°. It was rather insoluble in cold alcohol; with warm alcohol it gave phthalimide and ethyl diphenylacetate.

Anal. Subs. 0.3111, 0.3009: cc. of 0.2138 *N* acid; 4.32, 4.36. Calcd. for $C_{22}H_{15}O_2N$: N, 4.14. Found: N, 4.16, 4.19.

Pyrolysis of Diacetamide.—Using the flow method previously described for acetamide,¹⁸ diacetamide vapors were passed through a Pyrex tube (1.6 cm.) at 630–640°. An empty, ice-cold flask was placed between the furnace outlet and the aniline flask. Ketene was not formed since no acetanilide was found. With a 2.2 seconds contact time, 50 g. of diacetamide was passed during ten minutes. Only 1 g. was recovered; 27–27.5 g. of acetic acid and 18–19 g. of acetonitrile were formed. At 510° and 6.2 sec., at least one-third of the diacetamide remained unchanged.

Experiments with Acylphthalimides and Acylcarbazoles

General Procedure.—Quantities ranging from 15 to 75 g. of these amides were heated to gentle refluxing in a 125- or 250-cc. distilling flask, the side arm of which delivered into an empty 25-cc. distilling flask kept at 0°. The uncondensed vapors were conducted from this flask into a flask which contained 10 cc. of aniline.

Acetyl Derivatives

Acetylphthalimide started to decompose at 240° and at 284° the reaction became so vigorous that heating was stopped. Then heating was resumed up to 325° for one to four hours. In several runs, using 50 g., about 10 g. of distillate and only about 0.5 g. of acetanilide were identified. Consistently the distillate contained 3.5–4.5 g. (30–38% yield) of ketene dimer, b. p. 125–127°, and 5–5.5 g. of lower boiling material, three-fourths of which was acetic acid. The ketene dimer was identified by reaction with aniline, producing acetoacetanilide. The latter melted at 84°.

To remove traces of water (as evidenced by acetic acid formation) from the acetylphthalimide, 800 cc. of toluene was added to 150 g. of the material and 200 cc. of the toluene distilled from it at 20 mm. One liter of petroleum ether was poured into the residual solution and the precipitated acetylphthalimide filtered by suction in an atmosphere of dry air. Heating 70 g. of this material for an hour or 50 g. for five hours gave, respectively, 9.2 and 8.7 g. of pure ketene dimer. These values represent 53 and 75% of the theoretical. Only traces of acetic acid were produced.

Acetylcarbazole.—This material started to decompose at 200°, the temperature gradually increasing to 356°. Heating 75 g. for six to seven hours gave 3–3.1 g. of ketene dimer (b. p. 125–127°, and yielding acetoacetanilide with aniline) and 1–1.2 g. of acetone (b. p. 56–57°, and yielding benzylideneacetone, m. p. 111–112°, with benzaldehyde). There was no acetanilide and little or no acetic acid. The yield of ketene dimer was 20%.

When 75 g. of acetylcarbazole was heated at 110° and 15 mm. for three hours to dry it, subsequent pyrolysis for three hours gave rise to a 5.6 g. (37%) yield of ketene dimer and only 0.1 g. of acetone.

Acetyldiphenylamine.—When 75 g. of this amide was refluxed for twenty-four hours, only a few drops of distillate were collected. The amide changed in part to a black tar, but much was recoverable. No ketene or ketene dimer appeared. Following this, 50 g. was passed during twelve to fifteen minutes through a Pyrex combustion

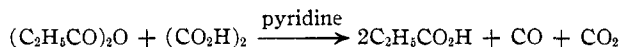
¹⁸ Hurd, Dull and Martin, *THIS JOURNAL*, **54**, 1974 (1932).

tube at 500 or at 600° with a recovery of 45–46 g. of the original amide. Apparently no ketene was formed nor was ammonia evolved. Some charring was observed.

Propionyl Derivatives

Propionylphthalimide.—This compound started to decompose at 220°, the temperature gradually being increased to 322°. The heating was maintained for three hours, but most of it was completed in thirty minutes. Besides phthalimide, the reaction products were diethyl ketone and propionic anhydride, equal weights of the last two substances being formed. After one and one-half hours, droplets of water appeared in the side arm of the condensing flask. This water was characterized by its melting point and by its ability to dissolve anhydrous copper sulfate to a blue solution. In a series of pyrolyses using 15-g. portions, there was formed 1.2–1.5 g. of diethyl ketone (38–47% yield) and 1.2–1.4 g. (25–29%) of propionic anhydride. The ketone was collected by distillation at 101–104° and was identified as 2,6-diphenyl-3,5-dimethyl-tetrahydro- γ -pyrone,¹⁹ m. p. 106°, its reaction product with benzaldehyde and alcoholic potassium hydroxide. The distillate collected between 160–170° was considered to be propionic anhydride since it was neutral to litmus but dissolved slowly in water to give an acid reaction. It gave propionanilide by reaction with aniline and it analyzed as an acid anhydride.

Analysis of Propionic Anhydride.—Whitford²⁰ showed that acetic anhydride reacted quantitatively with anhydrous oxalic acid and dry pyridine to evolve carbon monoxide and carbon dioxide. We found that the method was also adaptable for the quantitative determination of propionic anhydride. With pure propionic anhydride a 100% value was established



Using this method of analysis on the total distillate (8.3 g.) from a 50-g. sample, 21% of propionic anhydride or 1.24 g. was established whereas in the run under consideration, 2.0 g. of distillate was found between 160–178°.

Manner of Drying.—In these experiments the propionylphthalimide was dried in several ways without materially changing the result. Thus, 50 cc. of benzene or 50 cc. of toluene or 50 cc. of xylene was distilled from the 15-g. sample using diminished pressures so that distillation temperatures, respectively, of 40, 75 and 100° were attained. All water was undoubtedly removed by this method, but, as stated above, water was formed during the pyrolysis. Hence, neither methylketene or its polymer were isolated as such. In other similar experiments, propionylphthalimide was dried by heating it in an oven for four hours at 105° before use.

Gas Formed.—In one experiment on a 50-g. sample, 12.3 liters (standard conditions) of gas was collected. Analysis showed 81.9% of CO₂, 6.7% CO, the remainder being nitrogen. This represents 2.0 g. of carbon dioxide, which is equivalent to 3.9 g. of diethyl ketone; actually 2.9 g. of distillate was collected between 101–104°.

Propionylcarbazole.—Decomposition of a 40-g. sample started at 240° and the temperature was increased to 361°. After four hours, 5.1 g. of liquid had distilled. Carbon dioxide was evolved during the pyrolysis. The distillate was very similar to the one from propionylphthalimide and consisted of diethyl ketone and propionic anhydride.

***n*-Butyrylphthalimide.**—Fifteen grams of air-dried material was heated in the usual way. It yielded 3.6 g. of distillate, which contained 1.7 g. of dipropyl ketone

¹⁹ Vorländer and Hobohm, *Ber.*, **29**, 1352 (1896).

²⁰ Whitford, *THIS JOURNAL*, **47**, 2939 (1925).

(b. p. 143–147°), 0.2 g. of butyric acid (b. p. 147–188°), and 1.4 g. of butyric anhydride (b. p. 188–195°).

Caproylphthalimide.—The following is a typical run out of several which were performed. Caproylphthalimide was recrystallized from ethyl acetate and dried in a vacuum desiccator over sulfuric acid for four days or longer. Pyrolysis of 25 g. of it (140–230°) during twenty minutes yielded about half a liter of carbon dioxide. The distillate contained phthalimide and caproic acid, separation of these two being effected by solution of both in petroleum ether and precipitation of phthalimide from the solution at 0°. Distillation of the petroleum ether filtrate yielded 1.8 g. of caproic acid at 200–210°. Its potassium salt was obtained readily by the action of potassium hydroxide solution. Evaporation of the water, extraction of the potassium caproate in hot alcohol, cooling, filtering and washing with ether gave the salt in a pure state.

Anal. Calcd. for $C_8H_{11}CO_2K$: K, 25.03. Found: K, 25.06.

The non-volatile product in the original reaction flask was extracted while still molten with 100 cc. of petroleum ether. Whatever crystals formed on cooling this solution by ice were removed, after which the hydrocarbon was distilled off, leaving 8–9 g. of an oil. When distilled, besides a tarry residue, there was about 3 g. of an oil which was collected at 213–216° (5 mm.). Its molecular weight and analysis designated it to be *n*-butylketene trimer.

Anal. Subs. 0.2247: CO_2 , 0.6045; H_2O , 0.2058. Calcd. for $(C_4H_9CH=CH=O)_3$: C, 73.41; H, 10.28. Found: C, 73.34; H, 10.24.

Mol. wt. Subs. 0.2201, 0.3154; benzene, 21.975 g.; f. p. lowering, 0.159, 0.223°. Calcd. for $C_{18}H_{30}O_3$: mol. wt., 294. Found: mol. wt., 322, 329.

This polymer was neutral, insoluble in dilute acids and soluble in concentrated sulfuric acid. It did not react with aniline or with bromine. Reaction evidently was possible with alkali, for on long standing with dilute sodium hydroxide solution the oil dissolved.

It was established that only 6 g. out of 50 of caproylphthalimide was recoverable after twenty minutes of heating at 145–150°.

Iso-butyrylphthalimide.—Thirty grams of the pure *iso*-butyrylphthalimide, which had been recrystallized from ethyl acetate and dried *in vacuo* over sulfuric acid for several days, was heated for thirty minutes in an atmosphere of nitrogen. Decomposition began at 225°. The products of the reaction were passed into a flask which contained ice-cold absolute ether and the unabsorbed gases conducted into aniline. A white solid which remained in the side arm of the reaction flask was scraped into the ether at the end of the heating.

This ether solution was bright yellow in color due to dimethylketene.²¹ In one experiment this color did not disappear completely on standing for three days but in another it disappeared in twenty-four hours due to polymerization to the colorless dimer. Evaporation of the ether left a residue of 2.5 g. of dimethylketene dimer (tetramethylcyclobutanedione) which possessed the characteristic camphor-like odor and which melted at 111–114°. From the aniline, 0.9 g. of *iso*-butyranilide was isolated. The dimethylketene which is thus indicated from *iso*-butyrylphthalimide is 30% of the theoretical.

Diphenylacetylphthalimide.—After remaining for two weeks in a vacuum desiccator over sulfuric acid, 20 g. of diphenylacetylphthalimide was pyrolyzed in a nitrogen atmosphere for twenty minutes. Decomposition was between 300–325°. There was

²¹ For the isolation of pure dimethylketene, the ether trap would be replaced by an empty receiver kept at a sufficiently low temperature for liquefaction, a temperature of –78° favoring non-polymerization.

no distillate. The material in the flask was extracted thrice with 50-cc. portions of hot petroleum ether. About 9 g. of phthalimide resisted solution. After removal of the petroleum ether, 10 g. of a dark red oil remained from which 1.2 g. of diphenylketene distilled at 146–150° (14 mm.) and 6 g. between 150–240°. The latter was a red oil which slowly hardened to a glass. This was shown to contain phthalimide and a dimer of diphenyl ketene.

The diphenylketene was characterized by its vigorous reaction with aniline, giving diphenylacetanilide, m. p. 180°, by its yellow color and sharp, aromatic odor, and by its change into a colorless peroxide on standing in the air.

The 6 g. of higher boiling distillate was worked up by dissolving it in 25 cc. of hot alcohol. Phthalimide, m. p. 225–226°, separated on cooling to room temperature. It was filtered off and the filtrate cooled to 0°. A dark red, semi-crystalline mass separated which was filtered by suction and pressed out on a clay plate. Under these conditions, it gradually became almost clear white. When dry, the melting point was 188–190°, which is the melting point given by Staudinger²² for a dimer of diphenylketene. About 1.7 g. of this substance was obtained.

Repetition of the experiment gave 0.9 g. of diphenylketene and 2.1 g. of the dimer.

Summary

Both acetylphthalimide and N-acetylcarbazole undergo decomposition at refluxing temperatures into cyclobutanedione, the dimer of ketene. *Iso*-butyrylphthalimide and diphenylacetylphthalimide undergo a similar pyrolysis into dimethylketene and diphenylketene. These reactions are suitable for synthetic work.

Propionylphthalimide, propionylcarbazole, *n*-butyrylphthalimide, and caproylphthalimide gave reaction products which pointed to the ketenes as intermediate products but these monoalkylketenes could not be isolated as such. Acetyldiphenylamine and diacetamide were also investigated. All of these acylphthalimides except acetylphthalimide are new compounds. The trimer of butylketene was identified as a product of the pyrolysis of caproylphthalimide.

EVANSTON, ILLINOIS

²² Staudinger, *Ber.*, **38**, 1735 (1905); *Ann.*, **356**, 51 (1907).