[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION[1]]

Photosensitized Oxidation of Myrcene

BY R. L. KENNEY AND G. S. FISHER

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Myrcene (I) autoxidizes readily but gives chiefly polymeric products. In contrast to this it was found that in the presence of strong light and a photosensitizer, myrcene added one mole of oxygen per mole rapidly at room temperature to give a very high yield of monomeric hydroperoxides. Ultraviolet spectral data demonstrated that the conjugated system was not appreciably affected until the oxidation was carried beyond one mole of oxygen per mole. The infrared spectrum of the hydroperoxide suggested that both 3-methylene-7-hydroperoxy-7-methyl-1,5-octadiene (II) and 3-methylene-6-hydroperoxy-7-methyl-1,7-octadiene (III) were formed, II in the larger amount, but absorption from the conjugated system complicated the interpretation of the spectrum. This was overcome by oxidizing tetrahydromyrcene (IV) in the same manner. Compounds analogous to both II and III were clearly indicated by the infrared spectrum of the hydroperoxide obtained. The proportion of II was estimated at 25 to 35% on the basis of the intensity of the absorption band at 6.05 μ relative to that of the corresponding bands in carveol and limonene. On the basis of published molar extinction coefficients for *trans*-olefin absorption near 10.3 μ, the proportion of *trans*-III was estimated to be about 50%.

The hydroperoxides from both I and IV can be reduced to the corresponding alcohols by sodium borohydride or sodium sulfite. On catalytic hydrogenation myrcene hydroperoxide absorbed a little less than 3 moles of hydrogen per mole leaving the isolated double bonds of II and III intact.

Published information on the oxidation of myrcene (I) with molecular oxygen seems to be limited to the observations of Karyakin and Nikitin[2] that it does undergo photoöxidation readily to give both OOH and C=O bands in the infrared. It is generally known, however, that myrcene autoxidizes rather readily to give chiefly polymeric products. Schenck, *et al.*,[3] have described the photosensitized oxidation of α- and β-pinene and limonene and observed that this reaction differed markedly from thermal or photo autoxidation. By carrying out the oxidation in dilute alcoholic solution using methylene blue as the sensitizer they reported that in each case a single product, rather than the mixtures, was obtained. On the other hand, in toluene with chlorophyll as the sensitizer conjugated olefins such as 1,3-hexadiene added oxygen as a dienophile to give peroxides.[4]

From the preparative point of view the low concentrations of terpene, high power consumption and slow reaction rates reported by Schenck are undesirable. This report is concerned with one phase of a comprehensive research program undertaken to develop practical methods for the production of substantially pure hydroperoxides from terpenes by photosensitized oxidation.

Myrcene was of particular interest as a substrate for this type of oxidation because it could yield either hydroperoxides at the isolated double bond or peroxide at the diene. Oxidation conditions which had been successful with other terpenes[5] were also used for the photosensitized oxidation of myrcene. As shown in Table I, the reaction proceeded rapidly at 25° and the yield, of hydroperoxides, based on oxygen absorption, was substantially quantitative provided the oxidation was stopped when one mole of oxygen had been absorbed. An additional one-half mole of oxygen was absorbed at a decreasing rate without appreciable increase in hydroperoxide content. The viscosity of the product increased rapidly during this second stage of oxidation. Under the same conditions, but without chlorophyll, no oxygen was absorbed in three hours.

TABLE I

OXYGEN ABSORPTION AND HYDROPEROXIDE FORMATION DURING PHOTOSENSITIZED[a] OXIDATION OF MYRCENE

Run	Time, min.	O_2 absorbed, moles/mole	Hydroperoxide, mole/mole
34[b,c]	28	0.098	0.098
25[b,d]	54	.66	.64
43[e]	140	.76	.71
43	180	.90	.84
39[c,f]	150	1.00	.96
41[c,f]	343	1.47	.96
26[b,d,g]	54	0.85	.82

[a] 3 mg. of commercial chlorophyll (4% in oil) per gram of substrate, illuminated at 25° with 300 watt reflector spot lights. [b] 5-g. sample. [c] 1 lamp. [d] 3 lamps, 6 mg. of chlorophyll/g. [e] 41-g. sample, 4 lamps. [f] 2-g. sample. [g] Tetrahydromyrcene.

These observations pointed to attack at the isolated double bond until it is consumed, followed by attack on the conjugated system. As shown in Table II, ultraviolet absorption spectra of the crude products obtained after various degrees of oxidation confirmed this. Comparison of the infrared spectra of myrcene and its hydroperoxide (Fig. 1 and Table III) shows that as anticipated the absorption bands

TABLE II

MOLECULAR EXTINCTION COEFFICIENTS AT 224 mμ FOR OXIDIZED MYRCENES

O_2 absorbed, moles/mole	Molecular extinction coefficient, ε[a]
0.00	16,400
.098	16,300
.204	15,600
.436	16,100
.590	15,900
1.00	14,400
1.47	4,400

[a] Mol. wt. (log I_0/I)/cl, where mol. wt. = average molecular weight calculated from oxygen absorption, I_0/I = 1% transmission, c = concentration in g./l., l = cell length in cm.

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Presented at the National Meeting of American Chemical Society, Chicago, Ill., September 7-12, 1958.

[2] A. V. Karyakin and V. A. Nikitin, *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **17**, 636 (1953).

[3] G. O. Schenck, H. Eggert and W. Denk, *Ann.*, **584**, 177 (1953).

[4] G. O. Schenck, *Angew. Chem.*, **64**, 12 (1952).

[5] J. C. Braun, R. L. Kenney, T. C. Singleton and G. S. Fisher, unpublished observations.

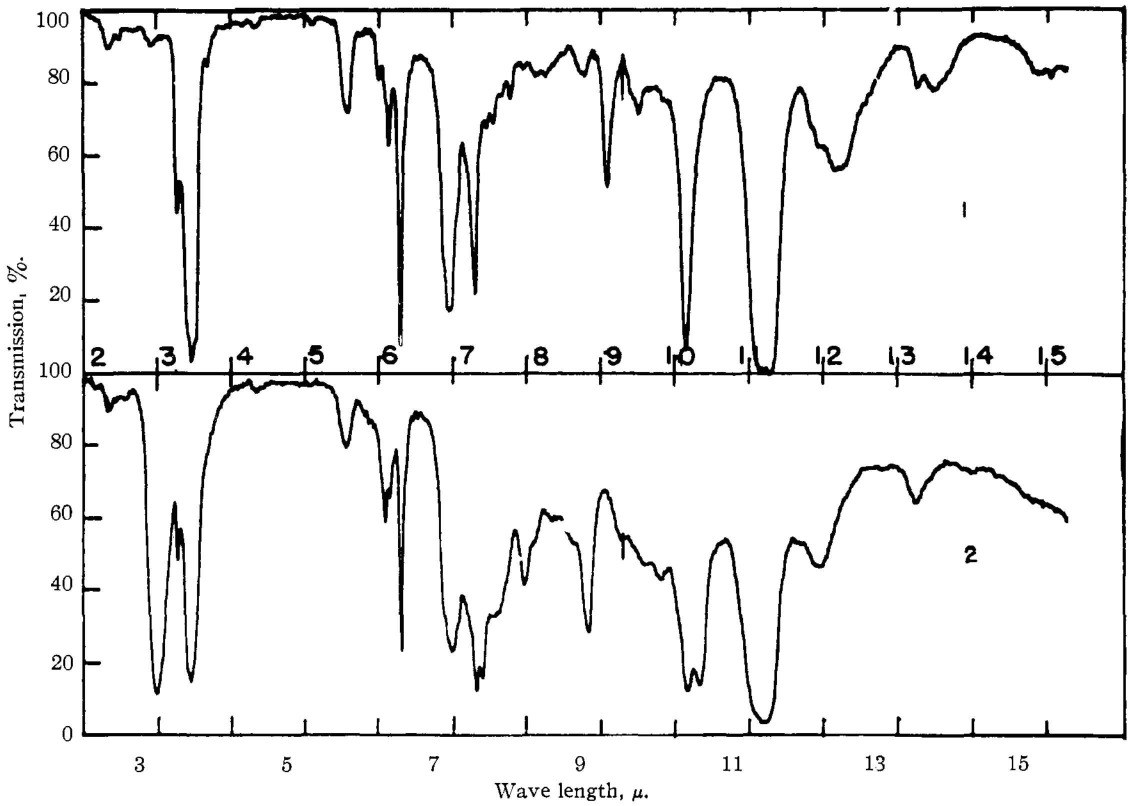


Fig. 1.—Infrared absorption spectrum of 1, myrcene, and 2, myrcene hydroperoxide.

at 3.25, 5.55, 6.12, 10.10 and 11.2 μ[6] are nearly unchanged by the addition of one mole of oxygen but are decreased by further oxidation. Stretching vibration of the trisubstituted double bond gives rise to the weak band observed at 5.97 μ in the spectrum of myrcene and out-of-plane bending of the attached CH bond is responsible for the broad band at about 12.15 μ[7]. However, it is not entirely obvious whether they disappear in the hydroperoxide or are masked by the bands appearing at 6.05 and 11.9 μ.

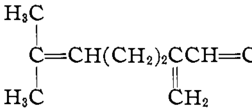
TABLE III

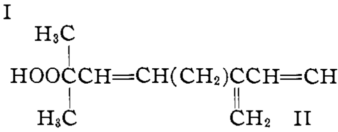
OBSERVED ABSORBANCE[a] OF MYRCENE AND RELATED PRODUCTS AT CHARACTERISTIC WAVE LENGTHS

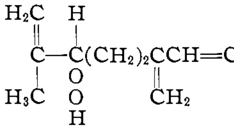
Wave length, μ	Myrcene	Hydroperoxide 48%	96%	"148%"[b]	Alcohol 1[c]	2[d]
10.26	(0.13)[e]	0.37	0.60	0.72	0.53	0.50
10.10	1.0	.98	.85	.72	.88	.00
9.05	0.24	.11	.00	.00	.00	.00
8.8	0.02	.19	.41	.37	.47	.35
6.27	1.02	1.00	.83	.52	.95	(.03)
6.12	0.18	0.18	.17	(.17)	.18	(.14)
6.05	(.09)	.15	.22	.29	.22	.25
5.50	.13	.12	11	.06	.14	.00
3.25[f]	.20	.19	.17	.10	.17	.01
2.95	.00	.42	1.04	1.12	1.10	1.45

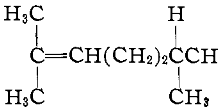
[a] See Experimental section for conditions. All values are baseline-corrected. [b] Myrcene + 1.48 moles of O_2 per mole. [c] Hydroperoxide (96%) reduced with $NaBH_4$. [d] Hydroperoxide 96% hydrogenated catalytically, 2.8 moles H_2 per mole. [e] Values in parentheses are not peaks. [f] Absorbance at 3.25 μ − absorbance at 3.30 μ (minimum) used to avoid interference of OH band.

Obviously two hydroperoxides, 3-methylene-7-hydroperoxy-7-methyl-1,5-octadiene (II) and 3-methylene-6-hydroperoxy-7-methyl-1,7-octadiene (III), could be formed depending on which end of the double bond is attacked and II can exist in either the *cis* or *trans* form. The strong bands which appear at 7.36 and 10.26 μ in the hydroperoxide indicate conclusively that *trans*-II is present in major amounts.[8]


$\overset{H_3C}{\overset{|}{\underset{\underset{H_3C}{|}}{C}}}{=}CH(CH_2)_2\underset{\underset{CH_2}{\|}}{C}CH{=}CH_2$ I


$HOO\overset{H_3C}{\overset{|}{\underset{\underset{H_3C}{|}}{C}}}CH{=}CH(CH_2)\underset{\underset{CH_2}{\|}}{C}CH{=}CH_2$ II


$\overset{H_2C}{\overset{\|}{\underset{\underset{H_3C}{|}}{C}}}{-}\overset{H}{\overset{|}{\underset{\underset{\underset{H}{O}}{\underset{|}{O}}}{\underset{|}{C}}}}(CH_2)_2\underset{\underset{CH_2}{\|}}{C}CH{=}CH_2$ III


$\overset{H_3C}{\overset{|}{\underset{\underset{H_3C}{|}}{C}}}{=}CH(CH_2)_2\overset{H}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH_2CH_3$ IV

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[6] R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954), have assigned bands in myrcene due to vibrations of the $C{=}CH_2$ groups as follows: 3.34 μ CH stretching, 5.51 μ overtone of band at 11.1 μ, 6.22 μ C=C stretching, and 10.08 μ and 11.10 μ out-of-plane bending vibrations of the CH bonds in the $CH{=}CH_2$ group. The doublet at 6.12 and 6.27 μ was not resolved in their spectra, but this splitting with a shift to longer wave length is characteristic of the conjugated system.[7]

[7] L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 19–46.

[8] The band at 7.36 μ in the spectrum of the hydroperoxide is due to the familiar resonance splitting of the CH_3 symmetrical deformation

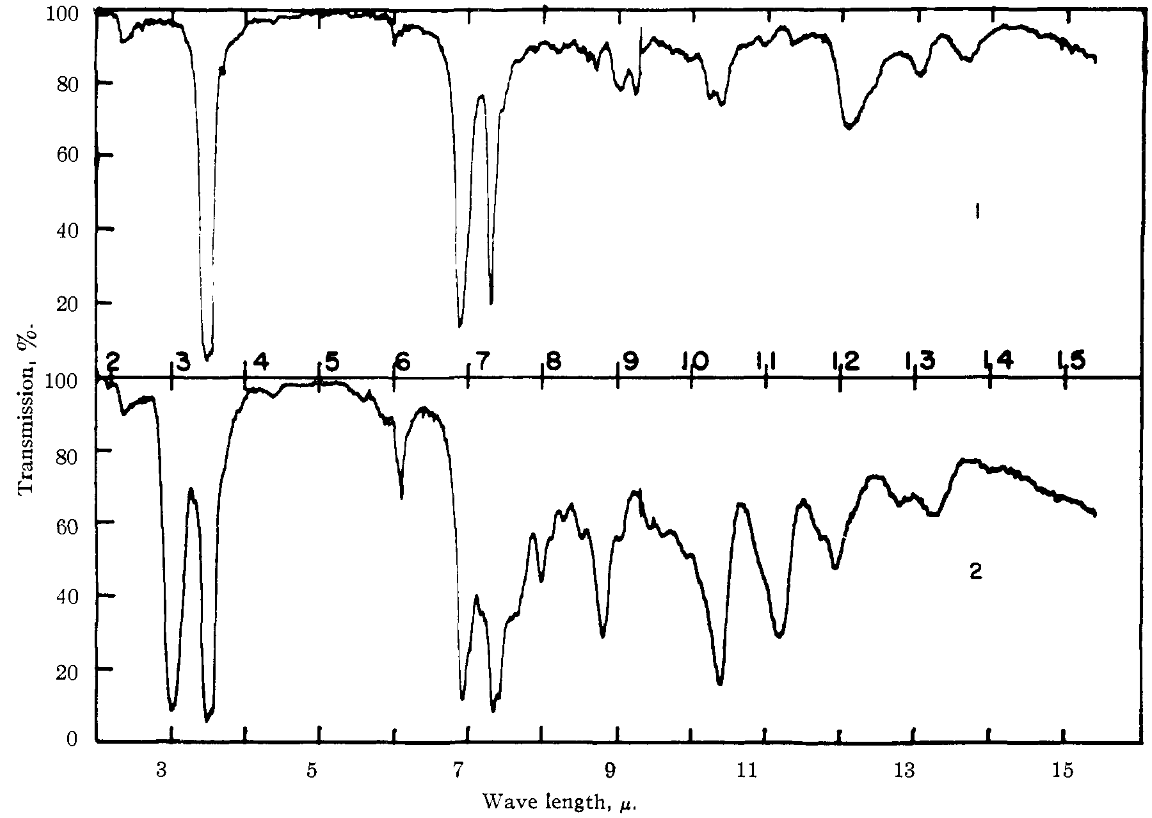

Fig. 2.—Infrared absorption spectrum of 1, tetrahydromyrcene, and 2, tetrahydromyrcene hydroperoxide.

The distinct C=C stretching band at 6.05 μ could be assigned either to *cis*-II or to III. The relative magnitude of the various bands favors the assignment to the isolated terminal double bond in III[7] but the confirmatory CH bands are obscured by the bands in the myrcene spectrum. To eliminate this difficulty tetrahydromyrcene (IV) was prepared and oxidized in the same manner. The oxidation rate and yield of hydroperoxide were comparable to those obtained with myrcene. The infrared spectra (Fig. 2) clearly indicated the formation of hydroperoxides analogous to II and III. Comparison of the absorbance of the hydroperoxides at 6.05 μ with the absorbance obtained for carveol and limonene at this wave length with the same cell and scanning conditions suggests that the products contain 25 to 35% of the terminal double bond compound. Model compounds for compound III were not available, but molecular extinction coefficients of about 130 are reported for the 10.35 μ band in *trans*-4-octene and *trans*-3-hexene[8a] and a range of 92 to 119 is reported[8b] for bands between 10.22 and 10.37 μ in other *trans*-olefins. Use of these values with our data for the hydroperoxides would indicate that *trans*-II makes up about 50% of these products. Although no band was observed in the 14.5 μ region corresponding to *cis*-II, it may be present. The *cis*-olefin absorption in this region is much less reliable than the *trans*-olefin absorption at 10.3 μ.[7]

Reduction of the hydroperoxides with sodium borohydride in water or sodium sulfite in alcohol proceeds smoothly to yield the corresponding unsaturated alcohols. Catalytic hydrogenation of myrcene hydroperoxide using platinum oxide catalyst was incomplete. The conjugated diene system was reduced completely but neither the terminal or *trans*-disubstituted double bond was reduced. Conversion to the alcohols does not have any major effect on the O–H absorption bands at 2.95 and 8.8μ, but does eliminate the O–O band at 11.9 μ.

Both the hydroperoxides and the corresponding alcohols from myrcene will polymerize when stored at room temperature in contact with air. The hydroperoxides should be handled with care. Decomposition of myrcene hydroperoxides is accompanied by rapid polymerization to a resinous product. Heat removal is difficult and the reaction can become explosive.

Experimental

Myrcene (I).—The myrcene used in this work was prepared by careful fractionation of a commercial sample.[9] Ultraviolet spectral analysis using isoöctane as the solvent was used as the criterion of purity[10] and all material used was at least 95% pure.

Tetrahydromyrcene (IV).—Myrcene was hydrogenated neat using platinum oxide as the catalyst. The reaction was followed volumetrically and there was a marked change in rate after two moles of hydrogen had been absorbed. Hydrogenation was stopped at this point and the product was used without further purification.

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band when two methyl groups are attached to the same saturated carbon atom.[7] The strong band at 10.26 μ corresponds to the CH out-of-plane bending vibration of a *trans* disubstituted olefin.[7]

(8a) E. J. Hart and A. W. Meyer, This Journal, **71**, 1980 (1949); (b) H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

(9) Kindly supplied by The Glidden Co.

(10) R. T. O'Connor and L. A. Goldblatt, ref. 6, report λ_{max} 225 mμ, ε 17,000.

Oxidation Conditions.—In general the oxidations were carried out in 50-ml. reactors which were immersed in a running water-bath at 20 to 25°. The reactors were attached to a suitable gas measuring system and the sample (2–5 g.) was stirred vigorously with a magnetic stirrer. Normal variation in stirring rate did not affect the rate of oxidation. The photosensitizer was commercial oil-soluble chlorophyll stated to contain 4% of chlorophyll in oil. In most cases 3 mg. of this product was added per gram of substrate and there was no further addition of catalyst. One or more 300 watt reflector spot lights placed about 10 cm. from the reactor were used as the source of light.

In a typical case, 2.004 g. (0.0147 mole) of myrcene containing 0.006 g. of crude chlorophyll illuminated with one 300 watt light absorbed 0.0147 mole of oxygen in 150 minutes. The product had a peroxide number of 11,400 meq. per kilogram or 96% of theoretical. Ultraviolet and infrared spectral characteristics are given in Tables II and III. Similar products were obtained by removing unreacted myrcene from partially oxidized products by evaporation *in vacuo* at below 35°.

Spectrophotometric Measurements.—The ultraviolet spectra were run in isoöctane solution on a manual Beckman[11] DU spectrophotometer. The infrared, spectra were recorded on a Perkin-Elmer 21[11] double beam spectrophotometer with NaCl optics. All samples were run neat in 0.027-mm. cells. Quantitative curves were made with slit program 927, suppression 8, speed 0.4 micron/min., scale 5 cm./micron and normal gain. The curves given in Figs. 1 and 2 were made with slit program 927, suppression 5, speed 0.7 micron/min., scale 2 cm./micron, slightly less than normal gain to suppress noise and 50% attenuation (1 cm./10% transmission). Paper calibrated in absorbance was used and values were read directly from the curves.

Reduction of Myrcene Hydroperoxide.—A portion (1.00 g.) of the 96% hydroperoxide was hydrogenated in a conventional quantitative hydrogenator at 25° using 25 mg. of platinum oxide as the catalyst. Two moles of hydrogen per mole was absorbed in 2.5 hours, an additional 0.7 mole per mole was absorbed during the next 3 hours and a total of 2.81 moles after 20 hours. The ethyl acetate was removed under vacuum at *ca.* 50° and the product was steam distilled and isolated by ether extraction. The infrared spectral characteristics are given in Table III (alcohol 2).

A sample of myrcene hydroperoxide (26 g. of 80% purity) was reduced by stirring it at room temperature with 1.75 g. of $NaBH_4$ dissolved in 15 ml. of ethanol and 10 ml. of water for about 16 hours. The product (10 g.) was isolated by adding water, extracting with ether and distilling at 0.1 mm. after removal of the ether. This is "alcohol 1" in Table 3. This product, which was water-white, had $n^{20}D$ 1.4857. Distillation through a 6-inch long column packed with protruded nickel at 0.2 mm. gave fractions boiling from 47 to 74° with only slight separation of isomers. With increasing boiling point absorbance at 10.26 μ decreased from 0.70 to 0.50 while absorbance at 6.05 μ increased from 0.16 to 0.28.

Tetrahydromyrcene Hydroperoxide.—Tetrahydromyrcene (2.25 g.) containing 6 mg. of crude chlorophyll per gram was illuminated with three 300 watt lamps and oxidized in the usual way. It absorbed 0.85 mole of oxygen per mole in 54 minutes, at which time the rates decreased rapidly and the reaction was stopped. The product contained 0.82 mole of hydroperoxide per mole. Removal of unoxidized material left a residue having a peroxide number of 12,400 (theory is 11,600 for the monohydroperoxide) and characteristic infrared absorption at 11.1 μ — baseline-corrected absorbance (A) = 0.74, 10.30 μ — A = 0.74, 8.8 μ — A = 0.43, 6.07 μ — A = 0.15, and 2.95 μ — A = 1.23.

Olustee, Fla.

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[11] Trade names are given as experimental detail and do not constitute recommendation of these instruments over any other.

[Contribution from the Department of Chemistry, University of New Hampshire]

Investigation of an Abnormal Organocadmium Reaction[1]

By Paul R. Jones and Stephen L. Congdon

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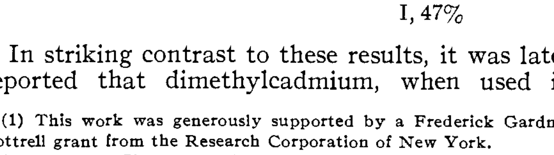
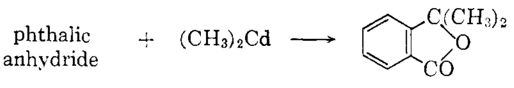
The reaction of the methylcadmium reagent with phthalic anhydride has been investigated with regard to the reaction time and the nature and quantity of the organometallic reagent. The expected product, *o*-acetylbenzoic acid (I), predominates in reactions of relatively short duration, while the formation of 3,3-dimethylphthalide (II) is enhanced with an increase in time or quantity of cadmium compound. I is relatively inert toward the methylcadmium reagent except during a prolonged reflux period. These results are consistent with the conclusion that I exists, under the conditions of this reaction, not as the ring tautomer (3-methyl-3-hydroxyphthalide) but as the open chain ketoacid. Infrared spectra of I in various media serve to corroborate this point of view.

Acid anhydrides, as well as acid chlorides, are generally considered to be convenient starting materials for the preparation of ketones by means of an organocadmium reaction.[2] de Benneville[3] has described the synthesis of a series of *o*-acylbenzoic acids from phthalic anhydride and the appropriate alkyl- or arylcadmium compound, yields ranging from 47 to 67%. Dimethylcadmium, for example, leads to *o*-acetylbenzoic acid (I).



I, 47%

In striking contrast to these results, it was later reported that dimethylcadmium, when used in excess, converted phthalic anhydride to 3,3-dimethylphthalide (II) in 60% yield.[4]



II, 60%

In an attempt to reconcile these two conflicting reports, we have investigated the nature of the products from the interaction of phthalic anhydride and the methylcadmium reagent with variation in the time and the nature and quantity of the cadmium compound. The results, given in Table II (Experimental section), are consistent with several conclusions. Both *o*-acetylbenzoic acid (I) and 3,3-dimethylphthalide (II) are formed even when the reaction time is relatively short; but the amount of II, by comparison with I, is increased

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[1] This work was generously supported by a Frederick Gardner Cottrell grant from the Research Corporation of New York.

[2] J. Cason, *Chem. Revs.*, **40**, 15 (1947).

[3] P. L. de Benneville, *J. Org. Chem.*, **6**, 462 (1941).

[4] C. H. Wang, R. Isensee, A. M. Griffith and B. E. Christensen, This Journal, **69**, 1909 (1947).