On removing most of the adhering oily material on a porous tile, the solid (*ca.* 20 mg.) was repeatedly crystallized from aqueous methanol to give shining white flakes melting at 174-175°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.95; H, 8.46.

JADAVPUR, CALCUTTA 32, INDIA

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

Air Oxidation of Resin Acids. II. The Structure of Palustric Acid and its Photosensitized Oxidation[2]

BY WALTER H. SCHULLER, RICHARD N. MOORE AND RAY V. LAWRENCE

RECEIVED AUGUST 27, 1959

The final proof of structure of palustric acid has been accomplished with the location of the two double bonds in the 7,8-13,14 positions of the substituted perhydrophenanthrene nucleus. This assignment is based on the following observations: (a) the ultraviolet absorption maximum of 266 mμ, (b) the formation of a maleic anhydride adduct, (c) the rapid formation of a transannular peroxide in a photosensitized oxidation, (d) the stability of the transannular peroxide in excess base, (e) the presence of only one vinyl hydrogen atom in the transannular peroxide, (f) the similarity of specific rotations of palustric and dehydroabietic acids, and (g) the presence of only one vinyl hydrogen atom in palustric acid.

In spite of the considerable amount of research which has been carried out on pine gum and gum rosin, only about eight resin acids have been isolated and fully characterized from these sources[3a,4-6] A recent addition to this group was palustric acid, isolated by Lawrence and coworkers[5] from pine gum and gum rosin by means of chromatographic techniques.

The similarity of the carbon skeleton of this new resin acid to the well characterized *l*-abietic, levopimaric and neoabietic acids was revealed by the acid-catalyzed isomerization of palustric acid to *l*-abietic acid; the acid-catalyzed isomerization of levopimaric acid to palustric acid; the heat-catalyzed isomerization of levopimaric acid to palustric acid; and the formation of a maleic anhydride adduct from palustric acid on heating identical to the adduct obtained from *l*-abietic acid and neoabietic acid under similar conditions and from levopimaric acid at room temperature.[5]

The formation of a maleic anhydride adduct was also taken as indicative of the presence of a conjugated diene system in palustric acid. The ultraviolet absorption maximum of 266 mμ (absolute ethanol) found for palustric acid was recognized as being within the range characteristic of homoannular conjugated dienes.[3b] The final proof of structure involving the location of the two double bonds in the molecule, was not possible on the basis of the available information.[5] The isomerization data were interpreted as possibly favoring a 7,8-13,14 assignment of the two double bonds in palustric acid. Using Fieser's extension[3b] to homoannular dienes of Woodward's rule, the ultraviolet absorption maximum was calculated[5] for each of the six possible positions for the location of two conjugated double bonds in ring B (see structure I). Only the value for the structure corresponding to the 5,6-7,8 arrangement (calcd. $\lambda_{\max}$ 268 mμ) closely approximated the experimentally observed maximum of 266 mμ. The calculated values for the two possible positions of a conjugated homoannular diene system in ring C are 273 mμ (9,10-13,14) and 283 mμ (10,11-9,14). However, the extension of Woodward's rule to homoannular dienes[3b] is based upon a very limited number of examples and in its present form may not be as reliable as the parent rule often is in the area of acyclic and heteroannular conjugated diene systems.

In the present work, palustric acid was dissolved in 95% ethanol containing a suitable sensitizing dye and the solution was simultaneously aerated and irradiated with visible light. A rapid reaction was observed to take place, proceeding at essentially the same rate as the photosensitized oxidation of levopimaric acid under the same conditions.[7] The reaction rate was found to be independent of the concentration of the resin acid for all dyes tested, based on the change in optical rotation and on the decrease in the specific extinction coefficient at 266 mμ. In an experiment in which pure oxygen was used and the amount of oxygen absorbed was measured quantitatively, it was found that exactly one mole of oxygen per mole of palustric acid was taken up in the reaction. The crystalline product was characterized as a transannular peroxide on the basis of (a) the lack of any characteristic absorption in the ultraviolet region of 220-320 mμ; (b) the elemental analyses and neutralization equivalent; (c) the initiation of polymerization of the vinyl monomers styrene, acrylic acid and methyl methacrylate on heating in the presence of the photoperoxide; and (d) the absence of an O-H stretching band in the infrared region of 3 μ in the corresponding cyclohexylamine salt and methyl ester. The photosensitized 1,4-addition of oxygen to yield transannular peroxides is limited to homoannular, conjugated dienes and proceeds *via* addition to the terminal carbon atoms in the conjugated diene system, without prior rearrangement of the

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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. Article not copyrighted.

[2] Presented at the Florida Section, Meeting-In-Miniature of the American Chemical Society, May 8, 1959, St. Petersburg, Florida.

[3] (a) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 40-68; (b) pp. 185-188.

[4] J. L. Simonsen and D. H. R. Barton, "The Terpenes," 2nd Ed., Vol. III, University Press, Cambridge, 1952, pp. 374-458.

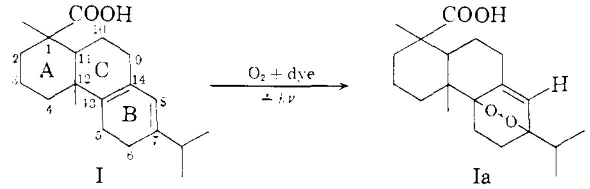
[5] V. M. Loeblich, D. E. Baldwin, and Ray V. Lawrence, THIS JOURNAL, **77**, 2823 (1955).

[6] B. L. Hampton, *J. Org. Chem.*, **21**, 918 (1956).

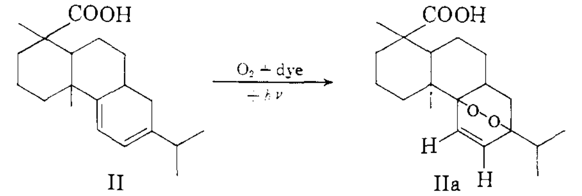
[7] R. N. Moore and Ray V. Lawrence, THIS JOURNAL, **80**, 1438 (1958).

double bonds, in the wide variety of cases reported to date.[7–10]

The transannular peroxide of palustric acid was found to be stable in the presence of excess base, exhibiting no significant change in properties on refluxing for 10 minutes in 95% ethanol in the presence of a 10:1 molar ratio of sodium hydroxide: palustric acid photoperoxide. The stability toward base of dialkyl peroxides in which the peroxide group is attached to two tertiary carbon atoms and the instability toward base of dialkyl peroxides in which the peroxide group is attached to one (or more) secondary carbon atoms has been demonstrated.[10–12] In the resin acid series the base-catalyzed rearrangement of levopimaric acid photoperoxide was shown to yield the expected hydroxy ketone.[10] On the basis of the alkali stability of the transannular peroxide, therefore, the following four of the six possible arrangements of a conjugated diene system located in ring B are eliminated: 5,6–7,8; 5,13–8,14; 5,6–13,14 and 6,7–8,14 (levopimaric acid). Both of the remaining arrangements (I: 7,8–13,14 and II: 6,7–5,13) would be expected to yield base-stable transannular peroxides on photosensitized oxidation.



I Ia



II IIa

The two peroxides Ia and IIa differ, however, in one important respect; namely, in the number of vinyl hydrogen atoms in the molecule. It was concluded from the nuclear magnetic resonance spectrum of palustric acid photoperoxide based on the ratios of the area under the peak in the vinyl hydrogen region to the areas under the peaks in the regions of hydrogen on saturated carbon, and carboxylic acid hydrogen that the transannular peroxide contained only a *single* olefinic hydrogen atom. Thus IIa was ruled out in favor of Ia as being the correct structure for palustric acid photoperoxide.

The possibility that the homoannular conjugated diene system might be located in ring C was ruled out on the basis of the above facts. A 9,10–13,14-diene system would yield an alkali-sensitive transannular peroxide on photosensitized oxidation while the only other possible arrangement, a 9,14–10,11-diene, would yield a base-stable transannular peroxide containing two vinyl hydrogen atoms. No conjugated diene systems can be located in ring A due to the location of quaternary carbon atoms at positions 1 and 12.

The relative similarity of specific rotations of palustric ($[\alpha]_D + 71.8°$) and dehydroabietic ($[\alpha]_D + 62°$) acids, both as 2% solutions in ethanol, also is in accord with the 7,8–13,14-assignment (I) as opposed to the 6,7–5,13-arrangement (II). The transformation of palustric into dehydroabietic acid by means of the loss of a hydrogen atom from each of the two non-asymmetric carbon atoms 5 and 6 in I would not be expected to result in any substantial change in optical rotation. Such a transformation involving the loss of a hydrogen atom from the asymmetric carbon atom 14 in II would be expected to be accompanied by a very significant change in optical rotation.

The nuclear magnetic resonance spectrum of palustric acid itself provided conclusive evidence for formula I as being the correct structure of this new resin acid. Again it was concluded from a comparison of the ratios of the area under the peak for hydrogen on olefinic carbon to the areas under the peaks for hydrogen on saturated carbon and carboxylic acid hydrogen, that there is only *one* vinyl hydrogen present in the molecule. No other arrangement, homoannular or heteroannular, of a conjugated diene system within the appropriately substituted perhydrophenanthrene nucleus, but the 7,8–13,14-assignment results in a structure possessing but a single vinyl hydrogen atom with the exception of the well characterized neoabietic acid.[3a] All other conjugated diene structures that can be written contain two or more olefinic hydrogen atoms.[13]

The isomerization data cited above[5] with respect to palustric acid, plus the subsequent detailed studies concerning the thermal isomerization of levopimaric acid,[14] and neoabietic acid[15] and the acid-catalyzed isomerization of levopimaric acid[16] can be rationalized in the light of the above-defined structure of palustric acid. This is especially so since the thermal isomerizations already have been shown to be acid-catalyzed rearrangements.[14,15] Earlier work on the acid-catalyzed isomerization of levopimaric and neoabietic acids[17] led to the suggestion of a carbonium ion intermediate in which $\Delta^{8(14)}$-dihydroabietic acid with an electron deficient carbon atom at position 7 and $\Delta 7(8)$-dihydroabietic acid with an electron deficient carbon atom at position 14 are the major structures of a resonance hybrid. It is to be noted that levopimaric, palustric, neoabietic and *l*-abietic acids can all yield this same carbonium ion intermediate upon attack of a proton at appropriate locations within the respective molecules. The

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(8) A. B. Tobolsky and R. M. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 26–33.

(9) W. Bergmann and M. J. McLean, *Chem. Revs.*, **28**, 367 (1941).

(10) R. N. Moore and Ray V. Lawrence, THIS JOURNAL, **81**, 458 (1959).

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(13) W. H. Schuller, R. N. Moore and Ray V. Lawrence, *Chemistry & Industry*, 954 (1959).

(14) V. M. Loeblich, D. E. Baldwin, R. T. O'Connor and Ray V. Lawrence, THIS JOURNAL, **77**, 6311 (1955).

(15) V. M. Loeblich and Ray V. Lawrence, *ibid.*, **79**, 1497 (1957).

(16) D. E. Baldwin, V. M. Loeblich and Ray V. Lawrence, *ibid.*, **78**, 2015 (1956).

(17) P. F. Ritchie and L. F. McBurney, *ibid.*, **71**, 3736 (1949); **72**, 1197 (1950).

subsequent, or concurrent loss of a proton from appropriate positions alpha to the electron-deficient carbon atoms can lead to the formation of all four acids in question. A second point of interest is the fact that the sensitivity of these resin acids toward acid would seem to fall in the order *l*-abietic acid, more stable than neoabietic and palustric acids, which in turn are more stable than levopimaric acid.[14–16] The relative similarity of neoabietic and palustric acids in this respect may be due to the fact that the terminal carbon atoms of the conjugated diene system in both cases are disubstituted. The relative instability of a homoannular diene system coupled with the lack of full substitution on carbon atom number 6 would tend to explain the considerable reactivity of levopimaric acid while the heteroannular distribution of the diene system in abietic acid may well be responsible for its stability.[3b]

In the present work, the photosensitized oxidation of palustric acid was carried out with a number of different dyes and the time required for the complete destruction of the conjugated diene system determined. The results are compared in Table I with the results obtained by treating levopimaric acid under essentially identical conditions. Both acids were found to react at about the same rate in each case, within experimental error. Some oxidations with mixed dyes were carried out and the results are included in Table I.

Table I

A Comparison of Various Sensitizers in the Photosensitized Oxidation of Palustric and Levopimaric Acids

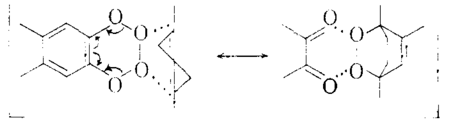
	Time required for complete reacn., hr.	
Sensitizing dye	Palustric acid	Levopimaric acid
Rose bengal	3.1	3.5[a]
Methylene blue	2.8, 3.9, 3.8	4.5,[a] 4.5, 4.1
Erythrosin B	3.7	4.8,[a] 3.2
Chlorophyll (Mg)[b]	4.1	4.4
Eosin YS	7.6	7.7[a]
Thymol blue	No reacn.	No reacn.[a]
Crystal violet	No reacn.	No reacn.[a]
Eosin YS + erythrosin B	4.4	
Eosin YS + erythrosin B + methylene blue	3.3	
Methylene blue + crystal violet + thymol blue	13.9	

[a] Reference 7. [b] The chlorophyll used was a 4% solution in oil supplied by Keystone Chemurgical Corp.

An apparent parallelism between the ease of photochemical 1,4-addition of oxygen (no photosensitizer present) and the 1,4-addition of maleic anhydride to many polynuclear compounds has been pointed out as well as the fact that the bridges formed are located at the same points.[9] Although this parallel would appear to be capable of extension to the photosensitized 1,4-addition of oxygen in some cases (polycyclic,[18] monocyclic[19]) the present work constitutes an exception as indicated by the following comparisons: palustric and levopimaric acids react at about the same rate in the photosensitized reaction (Table I) while with maleic anhydride, levopimaric acid reacts at room temperature and palustric acid only on heating[5]; the transannular peroxides from levopimaric and palustric acids contain 6,14- and 7,13-peroxido bridges, respectively, while both acids yield the same 6,14-maleic anhydride adduct.

During the course of the work it was considered of interest to determine what effect, if any, there would be upon palustric acid when subjected singly and in combinations of two to the three elements necessary for photosensitized oxidation. No change in the ultraviolet absorption spectrum of palustric acid was observed after six hours in each case of aeration in the dark, irradiation with visible light and on addition of methylene blue in the dark, respectively. Similarly, no reaction was observed on aeration plus irradiation, aeration plus methylene blue in the dark and irradiation plus methylene blue. In the last experiment the air was first swept out of the ethanol solution with nitrogen and the system sealed. Irradiation resulted in the bleaching of the dye, but no significant change in the ultraviolet absorption spectrum of palustric acid was observed.

In the photosensitized oxidation of levopimaric acid, it was noted that the structural feature present in the active sensitizing dyes and absent in the inactive dyes was the orthoquinoid group. This observation was confirmed with respect to palustric acid. It is herein suggested that the requisite structural feature may be further restricted to orthoquinoid groups in which one or both of the external atoms are heteroatoms such as S, O or N. Schenck[20,21] has suggested that sensitizing dyes on irradiation are raised to the diradical state whereupon they form a loose complex with oxygen which in turn reacts with the cyclic olefin to yield the transannular peroxide and the dye in the ground state. The evidence for the elevation of certain sensitizing dyes to the diradical state on irradiation is substantial[22] and as oxygen itself is believed to exist as a diradical in the ground state, it is suggested that the structure of the reactive intermediate is a six-membered cyclic peroxide resulting from the coupling of the two diradicals. A possible transition state for the reaction with palustric and levopimaric acids can thus be written as follows wherein the sensitizing dye is a simple quinone.[7]



Crystal violet has been reported[23] to yield a diradical on irradiation. Its inactivity as a sensitizing dye may well be due to the fact that only paraquinoid resonance structures containing an external

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(18) G. D. Laubach, *et al.*, This Journal, **78**, 4743 (1956); **78**, 4746 (1956); **78**, 4756 (1956).

(19) J. L. Simonson, "The Terpenes," 2nd ed., Vol. I, University Press, Cambridge, 1947, pp. 185, 202.

(20) G. O. Schenck, *Naturwissenschaften*, **35**, 28 (1948).

(21) G. O. Schenck, *Z. Elektrochem.*, **55**, 505 (1951).

(22) J. P. Simons, *Quart. Revs.*, **13**, 6 (1959).

(23) G. N. Lewis and M. Kasha, This Journal, **66**, 2100 (1944).

heteroatom (nitrogen) can be written for this dyestuff.

Experimental[24]

Palustric Acid.—The palustric acid employed in these experiments was obtained from commercial gum rosin by the chromatographic procedure of Loeblich, Baldwin and Lawrence.[5]

Apparatus.—The apparatus used was the same as that described by Moore and Lawrence for the photosensitized oxidation of levopimaric acid.[6] The determination of relative dye efficiencies as well as the experiments in which first one and then two of the necessary elements for photosensitized oxidation were omitted, were carried out in the 100-ml. test-tube reactors.

Sensitizers.—All experiments carried out in the 100-ml. test-tube reactors were made at a dye level of 50 mg./l. of active solids (for each dye, in the case of mixed dye systems) and a palustric acid concentration of 0.02 *M* in 95% ethanol as solvent. The reaction rates were determined by following the change in ultraviolet absorption. The time required for complete oxidation of palustric acid was measured as the time required for complete destruction of the ultraviolet absorption maximum at 266 mμ.

Oxygen Absorption.—A photosensitized oxidation of palustric acid was carried out in which the oxygen absorbed was measured quantitatively. A solution comprised of 0.2521 g. of palustric acid and 2 mg. of methylene blue in 25 ml. of 95% ethanol was placed in a 50-ml. erlenmeyer flask fitted to a gas buret. The system was flushed and filled with oxygen. The solution was stirred magnetically while being irradiated with a 15-watt fluorescent light and a 75-watt incandescent bulb. Oxygen absorption was essentially complete in 1.5 hr., but agitation and irradiation were continued for an additional 2 hr. to ensure completeness of reaction. The sample absorbed 20.15 ml. of oxygen at 25.5° and 762.7 mm. pressure which amounts to 0.991 mole oxygen/mole of palustric acid.

7,13-Peroxido-$\Delta^{8(14)}$-dihydroabietic Acid (Ia).—A solution comprised of 8.17 g. of palustric acid and 0.135 g. of eosin YS in sufficient 95% ethanol to give a final volume of 2700 ml. (0.01 *M* in resin acid and 50 mg./l. in dye) was charged to the 40-watt apparatus and irradiated and aerated simultaneously. The reaction was followed by means of the change in optical rotation and by the change in the ultraviolet absorption spectrum. The rate of the reaction was found to be independent of the concentration of resin acid. The reaction was over in 1.5 hr., but aeration and irradiation were continued for an additional 1.5 hr. before termination. The solution of reaction product exhibited no appreciable nor characteristic absorption in the ultraviolet region between 220–320 mμ. The reaction mixture was evaporated to about 15 ml. under reduced pressure (pot temperature to about 30°) and cold water added. The product came down as a thick gum which rapidly solidified to a fluffy solid. It was dried over Drierite to a constant weight of 8.58 g. (94.6%). The crude solid was dissolved in acetone, treated with activated charcoal, filtered, and water added. The product oiled out and solidified upon seeding; weight 7.38 g. Recrystallization from acetone-water gave long needles, yield, 3.23 g., $[\alpha]^{25}\text{D}$ −67.0° (*c* 1.0% in 95% ethanol). This material was dissolved in acetone, passed through a short column of activated charcoal to remove the remaining traces of dye, and water added. Star clusters of needles were obtained; yield 1.71 g. (18%), $[\alpha]^{26}\text{D}$ −73.8° (*c* 1.0% in 95% ethanol). Recrystallization from acetone–water yielded 1.29 g. of monohydrate, $[\alpha]^{27}\text{D}$ −73.9° (*c* 1.0% in 95% ethanol), m.p. 111° with resolidification to remelt at 154° (with decomposition and evolution of gas).

Anal. Calcd. for $C_{20}H_{30}O_4 \cdot H_2O$: C, 68.15; H, 9.15; neut. equiv., 352. Found: C, 68.34; H, 9.12; neut. equiv., 350.

The monohydrate was dried to constant weight at 65° *in vacuo* over phosphorus pentoxide; weight loss calculated for the loss of $1 \cdot H_2O$ 5.11%, found 5.11%. The anhydrous product had a m.p. 154° (with decomposition and evolution of gas), $[\alpha]^{27}\text{D}$ −78.1° (*c* 1.0% in 95% ethanol); no characteristic absorption in the ultraviolet region of 220–320 mμ.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04; neut. equiv., 334. Found: C, 72.05; H, 9.04; neut. equiv., 334.

Methyl 7,13-Peroxido-$\Delta^{8(14)}$-dihydroabietate.—A solution of 5.00 g. of palustric acid (0.06 *M*) and 0.028 g. of rose bengal (100 mg./l.) was prepared in a total volume of 280 ml. of 95% ethanol. It was charged to the 15-watt apparatus and irradiated and aerated until complete oxidation of the resin acid had been accomplished (2 hr.). The reaction mixture was diluted with water and extracted with ether. Evaporation of the ether yielded an oil which was dissolved in acetone and precipitated as the 2-amino-2-methylpropanol salt. The salt was recrystallized three times from acetone to give 2.90 g. (41.3%) of white needles. The amine salt was slurried in 95% ethanol and acidified with acetic acid. The product oiled out but crystallized when slurried in water; m.p. 116° with decomposition and frothing, $[\alpha]^{25}\text{D}$ −70.0° (2% in 95% ethanol). Treatment of 0.50 g. of this material with a slight excess of ethereal diazomethane gave the methyl ester which readily crystallized when the solvent was removed; yield of once-crystallized product 0.33 g. (63%). The ester was recrystallized to the constant m.p. 125–126°, $[\alpha]^{25}\text{D}$ −76.0° (2% in 95% ethanol); yield of pure ester 0.24 g. (46%). The infrared spectrum exhibited no O–H stretching band in the region of 3 μ.

The specific rotation of the methyl ester as calculated from the value for pure Ia is essentially identical to the value found above. This would tend to confirm the purity of both compounds since the ester was prepared from acid which had been regenerated from a purified amine salt of the crude reaction mixture.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.50, 72.59; H, 9.16, 9.29.

Cyclohexylamine Salt of 7,13-Peroxido-$\Delta^{8(14)}$-dihydroabietic Acid.—To 0.125 g. of pure 7,13-peroxido-$\Delta^{8(14)}$-dihydroabietic acid dissolved in 3 ml. of methyl ethyl ketone was added 12 drops of redistilled cyclohexylamine. The solution was chilled, the precipitate collected by centrifugation and washed with *n*-pentane. The salt was recrystallized from methyl ethyl ketone–95% ethanol in the presence of a small excess of cyclohexylamine. The recrystallized salt was washed with *n*-pentane and dried under reduced pressure over Drierite; yield 0.106 g., m.p. 202–204° dec., $[\alpha]^{26}\text{D}$ −59.5° (*c* 0.31% in 95% ethanol); no characteristic absorption in the ultraviolet region of 200–320 mμ; no O–H stretching band in the 3 μ region and no C=O stretching bands in the 5.8 and 8.8 μ regions of the infrared absorption curve. The carboxylate ion stretching band was observed in the infrared region of 6.5 μ.

Anal. Calcd. for $C_{26}H_{43}NO_4$: C, 72.0; H, 10.00; N, 3.23; neut. equiv., 433.6. Found: C, 72.10, 71.97; H, 10.13, 10.12; N, 3.23; neut. equiv. 432.

Initiation of Polymerization of Vinyl Monomers.—All monomers were purified by distillation immediately before use.

Styrene.—Test-tubes containing 15 ml. of styrene and 0.0677 g. (0.5% by weight) of palustric acid photoperoxide and ascaridole, respectively, were stoppered and heated at 100° together with two stoppered test-tubes containing only styrene. After 4 hr., the blanks were fluid while the other solutions were very viscous. After 40 hr., the blanks consisted of soft almost fluid gels while the tubes containing added peroxide yielded hard, transparent glass-like castings.

Acrylic Acid.—Small test-tubes containing 1.0 g. of acrylic acid plus 0.03 g. (3%) of palustric acid photoperoxide and the cyclohexylamine salt of same, respectively, were stoppered and heated at 100° together with several stoppered tubes containing only acrylic acid. After 75 minutes, the first trace of polymer appeared in the blanks. The run containing the photoperoxide was a hard, clear glass at this point; yield 81% of polymer after residual monomer was removed by drying under reduced pressure over potassium hydroxide pellets. The run containing the photoperoxide salt yielded 39% of a transparent, tough solid in this time.

Methyl Methacrylate.—The same procedure was followed as above. After 2 hr. the blanks exhibited a trace of polymer. At this point an excess of methanol was added to the blanks which were still fluid, and to the run containing added palustric acid photoperoxide which was sirupy. The matted precipitates were collected and dried; yield of polymer from blank 0.5%; yield from run containing added peroxide 12.5%.

Stability of Palustric Acid Photoperoxide in Excess Base.—A solution comprised of 1.6920 g. of palustric acid and 14

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[24] All melting points are uncorrected.

mg. of rose bengal in sufficient 95% ethanol to give a total volume of 280 ml. (0.02 *M* in palustric acid and 50 mg./l. in dye) was aerated and irradiated simultaneously in the 15-watt apparatus for 83 minutes (temp. 27–45°). At this point the photosensitized oxidation was essentially complete as indicated by a very small value of α at 266 mμ and $[\alpha]^{27}\mathrm{D}$ $-41.4°$. Aeration and irradiation were continued for an additional 20 minutes to ensure completeness of reaction. Essentially no change in α nor $[\alpha]\mathrm{D}$ was observed. No characteristic absorption was exhibited in the ultraviolet region of 220–320 mμ. To exactly one-half of the solution was added 1.12 g. of sodium hydroxide, dissolved by shaking (0.2 *M* in sodium hydroxide; 10:1 ratio of palustric acid sodium hydroxide); the alkaline solution was then refluxed for 10 minutes. Essentially no change was found in the ultraviolet absorption spectrum of the solution between 220–320 mμ and the optical rotation remained essentially unchanged at $[\alpha]^{27}\mathrm{D}$ -41.9. The solution was evaporated under reduced pressure to 40 ml., water (50 ml.) added, drying continued to a volume of 40 ml., water (20 ml.) added, and the solution reduced to a final volume of 50 ml. Glacial acetic acid (2.4 ml.) was added and the acidic solution extracted with ether. The ethereal extracts were combined, taken to dryness under reduced pressure, and dried over potassium hydroxide and Drierite *in vacuo;* yield 0.79 g. (84%). This was dissolved in acetone, 0.40 ml. of freshly distilled cyclohexylamine added, and the precipitate which formed collected by filtration, washed with pentane and dried; yield 1.01 g. (99% from acid), $[\alpha]^{27}\mathrm{D}$ $-24.5°$ (*c* 1.0% in 95% ethanol).

The other half of the original solution of palustric acid photoperoxide was concentrated under reduced pressure and water added. The oil which formed solidified and was collected by filtration and dried; yield 0.79 g. (84%). This was dissolved in acetone, 0.40 ml. freshly distilled cyclohexylamine added, the precipitate collected by filtration, and dried; yield 0.96 g. (94% from acid), $[\alpha]^{27}\mathrm{D}$ $-25.0°$ (*c* 1.0% in 95% ethanol).

The infrared absorption spectra of both salts and the ultraviolet absorption spectra between 220–320 mμ of both salts were found to be essentially identical. The infrared spectra exhibited no O–H stretching band in the 3 μ region and no C=O stretching bands in the 5.8 and 8.8 μ regions. The carboxylate ion stretching band was observed at 6.5 μ.

Nuclear Magnetic Resonance Absorption Spectra.—The nuclear magnetic resonance absorption spectra were run in a Varian high-resolution spectrometer, operating at 56.4 m.c. Both compounds were run as saturated solutions in carbon tetrachloride. The chemical shifts obtained, expressed as frequency shifts from benzene as an internal standard in parts per million of the operating frequency, are: palustric acid: olefinic hydrogen, +2.0; carboxylic hydrogen, −4.8; hydrogen on saturated carbons, +4.8 to +6.4 with strongest peaks at +5.2 and +6.1. 7,13-Peroxido-$\Delta^{8(14)}$-dihydroabietic acid: olefinic hydrogen, +1.86; carboxylic hydrogen, −1.82; hydrogens on saturated carbons, +4.2 to +6.4, with strongest peak at 6.21.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Reaction of Phenyl Radicals with Carbon Monoxide; Some Observations on the Induced Decomposition of Benzoyl Peroxide[1]

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The reaction of phenyl radicals with carbon monoxide has been demonstrated by decomposing benzoyl peroxide under CO pressure in benzene, cyclohexane and carbon tetrachloride solution. In every case, yields of products arising from phenyl radical attack on solvent are reduced and benzoic anhydride is produced by what is believed to be an induced decomposition of peroxide by benzoyl radicals. Benzoic anhydride is similarly formed when benzoyl peroxide is decomposed in benzaldehyde under N_2. In the CO reaction in CCl_4, benzoyl chloride is also an important product. As a result of this and previous work, it is concluded that in decompositions of benzoyl peroxide giving rise to substituted benzoic acids these products are the result of induced decomposition involving *simultaneous* radical attack on the aromatic ring and scission of the O–O bond, giving a benzoyloxy radical and a metastable intermediate which rearranges to the acid. This intermediate is suggested as an α-lactone of 1-hydroxycyclohexadienecarboxylic acid. Experiments with ring-deuterated benzoyl peroxide indicate that radical attack and migration of a ring hydrogen are not concerted processes.

The loss of carbon monoxide from acyl free radicals is a well established process in the gas phase

$$\mathrm{R{-}\dot{C}O} \rightleftarrows \mathrm{R\cdot + CO} \qquad (1)$$

thermal and photochemical decomposition of aldehydes and ketones,[3] and also occurs in the liquid phase, notably in the radical chain decarbonylation of aldehydes.[4] In the case of the acetyl radical, Cramer[5] has reviewed thermochemical data and concluded that $\Delta H = 15 \pm 3$ kcal., $E_a = 16 \pm 3$ kcal. for reaction 1 proceeding to the right in the gas phase. Although (1) becomes less endothermic when R · is a highly resonance-stabilized radical,[6] it is evident that the reverse reaction, addition of CO to a hydrocarbon radical, should be a relatively exothermic, low activation energy process. A clear-cut case of such addition is provided by the copolymerization of carbon monoxide and ethylene,[7] and additional examples involving more complex

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[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954.

[4] Work through 1956 on this and related reactions discussed here is reviewed by: C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 273–285.

[5] R. Cramer, THIS JOURNAL, **79**, 6215 (1957).

[6] Thus, the decarbonylation of trimethylacetaldehyde occurs readily at room temperature; *cf.* J. B. Conant, C. N. Webb and W. C. Mendum, *ibid.*, **51**, 1246 (1929).

[7] M. M. Brubaker, D. D. Coffman and H. H. Hoehn, *ibid.*, **74**, 1509 (1952).