

methylnaphthoquinone by the same reagent and is similarly initiated by the use of active-hydrogen promoters or by heating. By this method trinitrotoluene has been converted in yields as high as 32% into trinitro-*m*-xylene, which appears to be an end product. Trinitrobenzene affords trinitrotoluene and trinitro-*m*-xylene as reaction products, and the same two substances were obtained from *m*-dinitrobenzene by treatment with lead tetraacetate, followed by nitration. Nitrobenzene is converted in low yield into *o*- and *p*-nitrotoluene, identified as the corresponding nitrobenzoic acids.

Under similar conditions, benzene is converted by lead tetraacetate in acetic acid into benzyl acetate in yields up to 18%. Chlorobenzene behaves similarly and yields a mixture which has been

characterized as containing *p*-chlorobenzyl acetate. Naphthalene is converted into the 1-acetoxy derivative in 26% yield. The reaction does not appear promising as applied to nitro and polynitronaphthalenes.

Analogies to the electrolytic decomposition of metal salts of carboxylic acids in the Kolbe synthesis have led to the discovery of related methods of alkylation consisting in the treatment of the nitro compound in acetic acid solution with acetyl peroxide and the electrolysis of a solution of the nitro compound in acetic acid containing sodium acetate. Trinitrotoluene was converted by both methods into trinitro-*m*-xylene in low yields.

CONVERSE MEMORIAL LABORATORY

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 29, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Alkylation of Para Quinones with Acyl Peroxides

BY LOUIS F. FIESER AND ALBERT E. OXFORD¹

In continuation of previous work in this Laboratory on the alkylating action of esters of tetra-valent lead,^{2,3} a few exploratory experiments were made to see if the reaction of lead tetraacetate with 2-methyl-1,4-naphthoquinone in acetic acid solution to give 2,3-dimethyl-1,4-naphthoquinone can be promoted by the addition of substances other than active-hydrogen reagents and methanol.² It was found that a number of solvents, including some which do not themselves appear to be attacked, not only promote the methylation reaction but also, in the absence of a quinone or other methyl acceptor, exert a presumably catalytic effect and promote the decomposition of lead tetraacetate to carbon dioxide and an inflammable gas.

In experiments conducted with 0.005 mole of methylnaphthoquinone in 14 cc. of acetic acid at 90–100° with excess solid lead tetraacetate present throughout, no reaction occurred in the absence of a promoter, as previously observed,² but a usually vigorous gas evolution ensued, with darkening of the solution and ultimate production of the 2,3-dimethyl compound, on the addition of

1–3 g. of any one of the following substances: methanol,² water, isopropyl alcohol, *t*-butyl alcohol (thirty-minute lag, then gentle effervescence), isopropyl ether, benzene, toluene, cyclohexane (benzene-free), *n*-octane (synthetic). Under the same conditions but in the absence of methylnaphthoquinone, all of these substances except *t*-butyl alcohol brought about a steady if somewhat less vigorous decomposition of lead tetraacetate in the acetic acid solution. The gas evolution was particularly rapid and vigorous in the presence of added benzene, while with toluene as the promoter there was a prolonged induction period followed by a very slow gas evolution. Cyclohexane is a slightly less effective promoter for the decomposition than benzene, and *n*-octane produces, after a brief lag, a still more moderate gas evolution. The cyclohexane employed as a promoter was found to be largely recoverable unchanged after a reaction period of eight hours, in which time a considerable amount of lead tetraacetate had suffered decomposition before the reaction had come to a standstill. Although the action of the hydrocarbon somewhat resembles that of a true catalyst, it is noteworthy that the reaction slows down after a time and that a given quantity of cyclohexane brings about the decomposition of only a limited amount of lead tetraacetate. The

(1) International Fellow of the Rockefeller Foundation on leave of absence from the London School of Hygiene and Tropical Medicine.

(2) Fieser and Chang, *THIS JOURNAL*, **64**, 2043 (1942).

(3) Fieser, Chapp and Dault, *ibid.*, **64**, 2052 (1942).

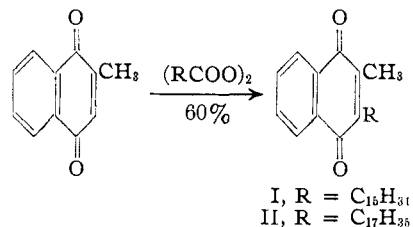
decomposition has been observed to come to a stop with a considerable amount of recoverable cyclohexane still present, and yet to be set in motion again by the addition of a fresh lot of this hydrocarbon. It was found further that the heating of lead tetraacetate with cyclohexane in the absence of acetic acid resulted in no evident decomposition and that methylnaphthoquinone could not be methylated under these conditions. The slowing down of the decomposition in acetic acid-cyclohexane may be due to some extent to the accumulation of lead diacetate, for the addition of this reagent to a mixture of methylnaphthoquinone, acetic acid, toluene and cyclohexane retarded the methylation reaction but did not prevent it.

The gas evolved in the course of the decomposition of lead tetraacetate in the presence or absence of an acceptor contains both carbon dioxide and an inflammable gas not absorbed in alkali. The amount of the neutral gas is often considerable (Table I, Experimental Part) and was found in one experiment conducted in the absence of an acceptor to be approximately 1/2.3 the volume of carbon dioxide, which is close to the ratio to be expected if the gas is pure ethane.

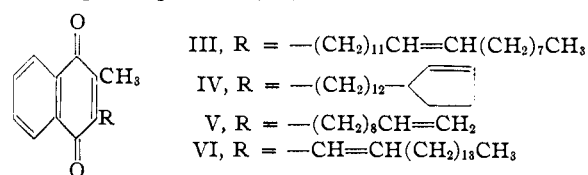
The decomposition therefore appears analogous to the Kolbe reaction. As noted in the second paper of this series,³ the consideration that diacyl peroxide is regarded by some as an intermediate in the electrolysis of potassium acetate, coupled with the possibility that lead tetraacetate may initially dissociate to give this substance and lead acetate, led us to attempt the alkylation of quinones with diacyl peroxides in place of esters of tetravalent lead. This indeed can be accomplished; 2-methyl-1,4-naphthoquinone and diacyl peroxide, for example, afforded 2,3-dimethylnaphthoquinone when warmed together in acetic acid at about 90°. In this and many other instances the reaction proceeds readily and cleanly and under conditions of dilution, solvent and temperature similar to those found favorable for effecting analogous alkylations with the tetravalent lead derivatives. In the reaction with diacyl peroxides, however, no promoter is required, there is no induction period,³ and one equivalent of the reagent gives better results than a 3-4 fold excess.^{2,3} Inferences concerning the mechanisms of the two reactions and the question of a possible correlation between them can best await quantitative studies.

Many instances are on record of the thermal decomposition of diacyl peroxides in the presence of solvents which serve as acceptors of the hydrocarbon residue. This type of reaction has been investigated extensively, particularly as applied to diaroyl peroxides, by the Dutch workers Böeseken, Gelissen and Hermans, *et al.*, and by Wieland and collaborators, as summarized in an excellent review by Hey and Waters.⁴ Recent applications to the peroxides of aliphatic acids are reported by Kharasch, Kane and Brown.⁵ The present observations appear novel in that the reaction is applied to a type of acceptor so favorable for the reaction that the alkylation can be conducted with equivalent amounts of reactants in a solvent essentially inert to the peroxide.

The introduction of higher saturated alkyl radicals is illustrated by the smooth reaction of 2-methyl-1,4-naphthoquinone in ligroin solution with dipalmitoyl and distearoyl peroxide to give the 3-pentadecyl and 3-heptadecyl derivatives I and II. These quinones both melt about 4° lower than 2-methyl-3-octadecyl-1,4-naphthoquinone,



which has been prepared by a much longer synthesis.⁶ As applied to the derivatives of the higher fatty acids, the present method is probably more convenient than the process of alkylation with a mixture of red lead and the fatty acid.² Furthermore, it can be employed for the introduction of at least certain types of unsaturated hydrocarbon residues. Thus the peroxides from erucic, chaulmoogric and undecenoic acids were employed successfully for the synthesis of the quinones III-V. 2-Methyl-3-norchaulmoogryl-1,4-naphthoquinone (IV) is of interest because of



(4) Hey and Waters, *Chem. Rev.*, **21**, 186 (1937).

(5) Kharasch, Kane and Brown, *THIS JOURNAL*, **63**, 526 (1941).

(6) Karrer and Epprecht, *Helv. Chim. Acta*, **23**, 272 (1940); Fernholz, Ansbacher and MacPhillamy, *THIS JOURNAL*, **62**, 430 (1940).

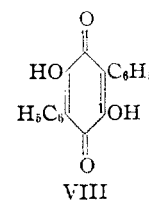
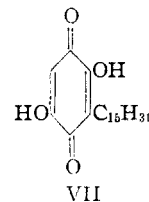
the presence in a structure related to that of the K vitamins of the hydrocarbon residue of an acid employed in the treatment of leprosy. The synthesis has the advantage of convenience and wide scope, since the diacyl peroxides required are obtainable by the action of sodium peroxide on a solution of the acid chloride in petroleum ether, and the examples cited show that a double bond remote from the carboxyl group does not interfere with either the formation or utilization of the peroxides. The α,β -unsaturated 2-heptadecenoic acid likewise afforded a peroxide which on interaction with methylnaphthoquinone gave a product, m. p. 72–73°, having the composition of 2-methyl-3-hexadecenyl(1')-1,4-naphthoquinone (VI). The substance does not give the Dam-Karrer test⁷ with alcoholic alkali and hence the double bond cannot have shifted to the β -position. The quinone is bright yellow, whereas compounds III–V, which are of comparable molecular weight but which do not possess a double bond in the α -position in the side-chain, are very pale yellow, and hence there is some analogy to the relationship between the 3- α -alkenyl (orange) and 3- β -alkenyl (yellow) derivatives of 2-hydroxy-1,4-naphthoquinone.⁸

Paralleling results obtained by the alternate method of alkylation,² it was found that a higher alkyl group present at the 2-position of a 1,4-naphthoquinone, in contrast to a methyl group, impedes the introduction of a second alkyl substituent. Thus, although α -naphthoquinone on treatment with diacetyl peroxide afforded only the 2,3-dimethyl derivative in low yield, the reaction of the quinone with dipalmitoyl peroxide provided a satisfactory method for the synthesis of 2-pentadecyl-1,4-naphthoquinone. The applicability of the diacyl peroxide method in the benzoquinone series was established by the conversion of cumoquinone into duroquinone and into 2,3,5-trimethyl-6-pentadecylquinone by interaction with diacetyl peroxide and with dipalmitoyl peroxide, respectively.

On extending the study to quinones having substituents other than alkyl groups, we were surprised to find that 2-methoxy-1,4-naphthoquinone could be recovered unchanged from the attempted reaction with diacetyl peroxide, whereas 2-hydroxy-1,4-naphthoquinone afforded phthiocol in good yield. Similarly 2,5-dihydroxybenzoquinone

reacted satisfactorily with dipalmitoyl peroxide in acetic acid solution to give the mono substitution product VII, while under the same conditions the dimethyl ether was largely recovered unchanged. 2,5-Dihydroxy-3-pentadecylbenzoquinone (VII) is a higher homolog of the naturally occurring anthelmintic pigment embelin⁹ ($R = C_{11}H_{23}$), to which the same synthesis may be applicable. 2,6-Dimethoxybenzoquinone gave at least a very small amount of the monomethyl derivative, but from the present observations it appears that methoxy quinones are definitely more inert to the products of the thermal decomposition of diacyl peroxides than hydroxy quinones and that the latter are perhaps somewhat more reactive than unsubstituted or alkylated quinones. The one bromoquinone investigated also reacted very readily in an appropriate solvent. Tribromoquinone was converted into tribromotoluquinone in acetic acid solution in about 68% yield but only in poor yield with the use of ligroin. This example of the reaction should offer a particularly favorable case for quantitative study because of the ease with which the high melting and sparingly soluble product can be separated from the reaction mixture. To test the possibility of using bromine to block temporarily nuclear positions and thus expand the scope of the synthetic method, we made a trial of the hydrogenation of tribromotoluquinone in acetic acid in the presence of palladium-barium sulfate and sodium acetate¹⁰ and indeed isolated toluhydroquinone.

Arylation with dibenzoyl peroxide was tried in a few instances with unpromising results. In experiments with methylnaphthoquinone conducted in both acetic acid and ligroin the starting material was consumed but no reaction product could be isolated. 2,5-Dihydroxybenzoquinone, however, afforded in very small yield a substance corresponding in properties to the fungus pigment polyporic acid¹¹ (VIII). Dicinnamoyl peroxide gave only negative results in attempted reaction with methylnaphthoquinone, while with 2,5-dihydroxybenzoquinone it gave only a trace of material forming lustrous plates and ex-



(7) Dam, Geiger, Glavind, P. Karrer, W. Karrer, Rothschild and Salomon, *Helv. Chim. Acta*, **22**, 310 (1939).

(8) Hooker, *This Journal*, **58**, 1163 (1936).

(9) Structure: Asano and Yamaguti, *J. Pharm. Soc. Japan*, **60**, 105 (1940) [*C. A.* **34**, 5069 (1940)].

(10) Compare Fieser and Holmes, *ibid.*, **60**, 2553 (1938).

(11) K \ddot{u} gl, *Ann.*, **447**, 78 (1926).

hibiting brilliant colors in ligroin (purple) and in sulfuric acid (green). The poor results may be due in part to the choice of unsuitable experimental conditions; it may also be significant that dibenzoyl and dicinnamoyl peroxide are notably prone to enter into decompositions leading to esters and diaryls.¹²

Experimental Part¹³

Gas Evolution Attending the Decomposition of Lead Tetraacetate.—In the exploratory experiments summarized in Table I the gases were swept from the reaction vessel to an azotometer with a stream of carbon dioxide and the volume of unabsorbed gas measured.

Another experiment (0.6 g. water, 10 g. lead tetraacetate, 7 cc. acetic acid) was carried out in a stream of dry oxygen and the gases collected over water (total, 92 cc.). The carbon dioxide (46 cc.) was then absorbed in strong caustic potash; the oxygen (26 cc.) was absorbed in alkaline pyrogallol and the residual hydrocarbon gas measured (20 cc.).

TABLE I

PRODUCTION OF HYDROCARBON GAS IN THE DECOMPOSITION OF LEAD TETRAACETATE

Experiments conducted in glacial acetic acid solution (14 cc.) at 80–100° for 1.5 hr. or until visible reaction had ceased.

Quinone (0.005 mole)	Promoter, g.	Lead tetraacetate, g.		Neutral gas, cc.
		Added	Re-covered	
None	Malonic acid, 0.8	14	none	104
None	Malonic acid, 0.15	14	8.3	79
None	Malonic acid, 0.05	10	6.5	71
None	Water, 1.2	20	trace	155
Methylnaphthoquinone	none	6	none	none
Methylnaphthoquinone	Malonic acid, 0.15	14	5.4	81
Methylnaphthoquinone	Water, 1.2	20	trace	141
Trimethylbenzoquinone	none	10	8.2	2
Trimethylbenzoquinone	Malonic acid, 0.05	10	6.3	17.5
Benzoquinone	Water, 1.1	19	trace	109

Preparation of the Peroxides.—The various diacyl peroxides were prepared for the most part by vigorously shaking a solution of the acid chloride (usually made by the phosphorus trichloride method) in petroleum ether (b. p. 20–40°) with a solution of sodium peroxide (large excess) in ice-water in a stoppered flask. The upper layer containing the peroxide was separated from the alkaline liquor or soap solution, dried, and allowed to evaporate. Usually the crude peroxide was found to evolve gas upon heating at 90–100° and to give no acid reaction when a cold solution in methanol was tested with moistened litmus paper. In this event, the crude material was regarded as satisfactory for use without further purification. The peroxides were stored and weighed out in the cold room (5°), where they could be safely scraped from a glass dish with a silver spatula.

(12) Wieland and Rasuwajew, *Ann.*, **480**, 157 (1930).

(13) Microanalyses by Miss Eleanor Werble. The melting points are uncorrected.

The following procedure for the preparation of **dipalmitoyl peroxide** is typical. A solution of 3.3 g. of crude palmitoyl chloride in 10 cc. of petroleum ether was added with ice cooling to a solution of 1 g. of sodium peroxide in a few cc. of ice-water. After the addition of a little ice the flask was corked and shaken well for a minute or two. More solid sodium peroxide (1 g.) was added, together with more ice and petroleum ether, and the corked flask was shaken thoroughly for at least ten minutes with the introduction of small amounts of ice from time to time and with short periods of cooling in a freezing bath. The mixture was then transferred with about 100 cc. of added petroleum ether to a separatory funnel, and after shaking for a few minutes a little ether was added to facilitate separation of the layers. The top layer was separated as far as possible, dried over calcium chloride, filtered into a glass dish and allowed to evaporate spontaneously at room temperature. The residue consisted of 1 g. of colorless crystals, m. p. about 65°, and this was used directly for an alkylation. A sample of the peroxide recrystallized from methanol melted at 67–68°.

The crude **distearoyl peroxide** melted at 63–64° and a sample crystallized from methanol, in which it is not very soluble, melted at the same temperature. The crude peroxides from **erucic** and **2-heptadecenoic acid** melted at 30° and 45°, respectively, and that from **undecenoic acid** was liquid at room temperature and solidified in the cold room. An attempted conversion of **chaulmoogric acid** into the chloride with thionyl chloride gave a resin and it was found better to warm the acid with the calculated amount of phosphorus trichloride on the steam-bath, pour off the top layer from the phosphorous acid, and remove hydrogen chloride by evacuation at the water pump. The residue afforded a peroxide melting at 50–55°. **Dicinnamoyl peroxide** was prepared by the above procedure rather than in acetone solution¹²; 5 g. of acid chloride afforded 3.0 g. of peroxide, m. p. 127–130°.

Diacetyl peroxide was prepared best according to Gambarjan¹⁴ from acetic anhydride in ether. With an initial reaction temperature of –5° instead of –15°, the yield was only 5.5 g. (G., 9 g.), and unless the evaporation was carried out in the cold room about half of the volatile peroxide was lost. The yield was much lower when the solvent ether was replaced by petroleum ether, in which acetic anhydride is only sparingly soluble.

Methylation of 2-Methyl-1,4-naphthoquinone.—In parallel experiments conducted to determine the optimum proportion of the reactants, tubes containing 1-g. samples of the quinone in 14 cc. of acetic acid were charged with 0.4 g. (0.6 equiv.), 0.75 g. (1.1 equiv.), and 1.4 g. (2 equiv.) of diacetyl peroxide, respectively, and heated together in the same bath at 90–95° until effervescence ceased. The solutions were cooled, poured into water and the products crystallized from methanol. The first experiment afforded much unchanged starting material and only 0.1 g. of impure 2,3-dimethyl-1,4-naphthoquinone, m. p. 112–118°, after several crystallizations. The second yielded 0.55 g. of the once crystallized dimethyl derivative, m. p. 118–123°, while the third gave a gummy product yielding only 0.1 g. of dimethylnaphthoquinone, m. p. 118–122°, after recrystallization. The ratio 1:1.1 therefore seems to be

(14) Gambarjan, *Ber.*, **42**, 4010 (1909).

TABLE II
 ALKYLATION OF QUINONES WITH DIACYL PEROXIDES (1.1-1.3 EQUIVALENTS)

-1,4-naphthoquinone	Diacyl peroxide from	Solvent	Product, -1,4-naphthoquinone	Isolation, % yield	Cryst. from	M. p., °C.	Appearance	Analyses, % C and H
2-Methyl	Palmitic acid	Ligroin	2-Methyl-3-pentadecyl (Formula I)	A, 60	Ligroin (70-100°)	95-97	Very pale yel. needles	C ₃₈ H ₅₈ O ₂ : 81.61; 10.02 Found: 81.69; 9.90
2-Methyl	Stearic acid	Ligroin	2-Methyl-3-heptadecyl (Formula II)	A, 60	Ligroin (50-70°)	96	Very pale yel. needles	C ₃₈ H ₅₈ O ₂ : 81.89; 10.31 Found: 81.44; 10.10
2-Methyl	Erucic acid	Ligroin	2-Methyl-3-heneicosenyl(12')- (Formula III)	D, small	Alcohol (six times)	39-81 ^a	Yel. cryst. aggregates	C ₃₂ H ₄₈ O ₂ : 82.69; 10.42 Found: 82.57; 10.37
2-Methyl	Chaulmoogric acid	Ligroin	2-Methyl-3-norchaulmoogryl- (IV)	C, 40	Methanol (1), alcohol (3)	65-68 ^b	Pale yel. needles	C ₂₈ H ₄₂ O ₂ : 82.70; 9.43 Found: 82.47; 9.27
2-Methyl	Undecenoic acid	Ligroin	2-Methyl-3-deceny(9')- (V)	C, 40	Alcohol	68	Coarse, pale yel. needles	C ₂₁ H ₃₂ O ₂ : 81.24; 8.45 Found: 81.29; 8.18
2-Methyl	2-Heptadecenoic acid ^c	Ligroin	2-Methyl-3-hexadeceny(1')- (VI)	D, 25	Alcohol, methanol	72-73	Bright canary yel. microcrystals	C ₂₇ H ₄₂ O ₂ : 82.17; 9.71 Found: 82.33; 9.71
2-Hydroxy	Acetic acid	AcOH	Phthiocol	Add water, 50	Alcohol	167-169	Golden needles	
α -Naphthoquinone	Palmitic acid	Ligroin	2-Pentadecyl-	D, small	Alcohol	71-72	Pale yel. needles	C ₃₅ H ₅₆ O ₂ : 81.45; 9.86 Found: 81.63; 9.91
-1,4-benzoquinone			1,4-benzoquinone					
Trimethyl	Acetic acid	Ligroin	Tetramethyl (Duroquinone)	B, small	Alcohol	108-111		
Trimethyl	Palmitic acid	Ligroin	2,3,5-Trimethyl-6-pentadecyl	C, 25	Alcohol	74	Pale yel. needles	C ₂₁ H ₃₀ O ₂ : 79.93; 11.18 Found: 80.17; 11.04
2,6-Dimethoxy ^d	Acetic acid	AcOH	2-Methyl-3,5-dimethoxy	B, small	CCl ₄	123-124 ^e	Golden needles	C ₉ H ₁₀ O ₄ : 59.31; 5.55 Found: 59.01; 5.61
2,5-Dihydroxy ^f	Benzoic acid	AcOH	3,6-Diphenyl-2,5-dihydroxy (Polyporic acid, VIII)	A, very small	AcOH	Dec. above 280°	Purple-bronze plates	C ₁₈ H ₁₂ O ₂ : 73.95; 4.14 Found: 73.53; 4.32
2,5-Dihydroxy	Palmitic acid	AcOH	3-Pentadecyl-2,5-dihydroxy (VII)	A, small	Ligroin; alcohol; CHCl ₃	136-138	Orange plates ^g	C ₂₁ H ₃₄ O ₄ : 71.94; 9.79 Found: 71.82; 10.10

^a This may be a mixture of the *cis*- and *trans*-forms. The erucic acid used (Eastman Kodak Co.) was not purified but converted directly to the acid chloride by means of thionyl chloride. ^b Softening from 57°. ^c The acid was prepared according to Lauer, Gensler and Miller, *THIS JOURNAL*, **63**, 1153 (1941). ^d Graebe and Hess, *Ann.*, **340**, 237 (1905). ^e Anslow, Ashley and Raistrick, *J. Chem. Soc.*, 441 (1938), report the m. p. 125° (4,6-dimethoxytoluquinone). ^f Knoevenagel and Büchel, *Ber.*, **34**, 3995 (1901). ^g The quinone gives a light violet color in dilute alkali.

the best. The second experiment was duplicated except that half of the peroxide was added at the beginning and the rest when the first effervescence had ceased; the yield was the same (0.60 g., m. p. 115-119°). In another experiment *n*-propyl alcohol was employed successfully as the solvent.

Methylation of Tribromoquinone.—A mixture of 2.4 g. of tribromoquinone¹⁵ (m. p. 147°), 0.85 g. of diacyl peroxide and 24 cc. of acetic acid was warmed gently in a water-bath, when solution soon took place, and the temperature was slowly raised to 90° and kept there for one hour and at 100° for one-half hour longer, when effervescence had ceased. Pale yellow plates of tribromotoluquinone had begun to separate from the hot solution and, after cooling, the copious crystallizate was collected and amounted to 1.3 g., m. p. 230°, dec. The material precipitated from the mother liquor with water afforded after crystallization a further 0.4 g. of product, m. p. 210-220°;

total yield 68%. A sample recrystallized from alcohol melted at 232-235°, dec. (lit., 235-236°).

Anal. Calcd. for C₇H₃O₂Br₃: C, 23.40; H, 0.84. Found: C, 23.85; H, 1.10.

When tribromoquinone (3 g.) was treated with diacyl peroxide (1.1 g.) in purified ligroin¹⁶ (40 cc., b. p. 95-100°) at 95-100° for one and one-half hours, the reaction mixture afforded only a trace of tribromotoluquinone and consisted largely of brown-red gums and a brown sandy product of indefinite melting point which could not be purified.

For **catalytic hydrogenation**, a solution of 0.65 g. of tribromotoluquinone and 0.65 g. of anhydrous sodium acetate was shaken with hydrogen in the presence of 8 g. of palladium-barium sulfate. The reaction stopped after the absorption of 200 cc. of gas in one-half hour. The solution was filtered and evaporated to dryness in vacuum and the residue extracted with ether in the presence of a little

(15) Sarauw, *Ann.*, **209**, 120 (1881); Datta and Bhoomik, *THIS JOURNAL*, **43**, 309 (1921).

(16) The solvent was shaken with a solution of potassium permanganate in dilute sulfuric acid and then with a mixture of concentrated sulfuric and nitric acids.

dilute sulfuric acid. Evaporation of the solvent left a dark gum which when dissolved in benzene and treated with petroleum ether afforded crystalline material, m. p. 120–121° (0.15 g.). Recrystallized from benzene–ligroin, the substance formed colorless plates, m. p. 124° (toluhydroquinone, m. p. 124–125°). The sample was free from bromine.

Anal. Calcd. for C₇H₈O₂: C, 67.69; H, 6.49. Found: C, 67.91; H, 6.56.

Other Alkylations.—The principal results of the synthetic experiments are summarized in Table II. The procedure generally employed for the introduction of higher alkyl and alkenyl groups may be illustrated by the following account of the preparation of 2-methyl-3-pentadecyl-1,4-naphthoquinone. A solution of 1 g. of dipalmitoyl peroxide in 10 cc. of purified ligroin (95–100°) in a boiling tube was treated with 0.25 g. of methyl-naphthoquinone, a chip of porous pot was added, and the mixture was warmed and stirred until the quinone had dissolved. The bath temperature was gradually raised until effervescence set in at 90°, and after one hour the temperature was raised to 100° during thirty minutes and then allowed to fall to 90°, when gas evolution had ceased.

The reaction products were isolated in one of the following ways.

A. Separation as a solid from the cooled solution was followed by recrystallization.

B. When no material crystallized on cooling, other than the fatty acid derived from the peroxide, the solution sometimes was evaporated to dryness and the residue fractionally crystallized (not recommended for quinones with long alkyl side chains).

C. As in B, but the residue was dissolved in alcohol and treated with aqueous sodium hydrosulfite solution accord-

ing to the procedure of Fieser¹⁷; the reduced mixture was shaken with ligroin (b. p. 30–60°), when the substituted hydroquinone usually appeared as a white solid at the interface and could be collected by suction filtration. The solid was dried and oxidized with silver oxide in ethereal solution in the presence of sodium sulfate.

D. As in C, except that after reduction the hydroquinone did not separate from the water–ligroin mixture as a solid but remained in the hydrocarbon layer. In this case the ligroin solution was washed with aqueous alkali-hydrosulfite and extracted with Claisen's alkali, etc., exactly as in a procedure described for the isolation of vitamin K₁ from alfalfa concentrates.¹⁷

Each of the analytical samples of fully substituted quinones gave a negative test with Craven's reagent.¹⁸

Summary

Both the methylation of quinones by lead tetraacetate in acetic acid solution and the decomposition of the tetraacetate to carbon dioxide and hydrocarbon gas in the absence of an acceptor are promoted by a number of hydroxylic and hydrocarbon solvents.

Diacyl peroxides are excellent agents for the alkylation of *p*-benzo- and 1,4-naphthoquinones having a free position in the quinonoid ring, and a number of new or difficultly accessible quinones have been prepared with ease by this method.

(17) Fieser, *THIS JOURNAL*, **61**, 3467 (1939).

(18) Craven, *J. Chem. Soc.*, 1605 (1931).

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 14, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Relative Acid Strengths of Formic, Acetic, and Propionic Acids in Alcohols and Dioxane–Water Mixtures

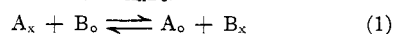
BY MARTIN KILPATRICK AND R. DEAN EANES

The determination, in various alcohols, of the acid strengths of substituted benzoic acids relative to benzoic acid, has shown that the logarithm of the acid strength varies linearly with the reciprocal of the dielectric constant of the medium over the range $D = 78.5$ to $D = 24.2$.¹ On the other hand, in dioxane–water mixtures, the logarithm of the acid strength does not vary linearly with the reciprocal of the dielectric constant. The present paper shows that these conclusions are also valid for certain aliphatic acids.

The acetic and propionic acids, free from homologs, were refluxed with the pure anhydrides and fractionally distilled. Formic acid was treated

with boric anhydride to remove water and distilled under reduced pressure. The purification of methyl and ethyl alcohol, ethylene glycol, and dioxane and the preparation of the solutions have been described in the earlier papers as has the e. m. f. method by which the experiments were carried out.²

Table I gives the ratio of the dissociation constant of formic acid to that of acetic acid in the various solvents containing lithium chloride. The ratio of the dissociation constants is the equilibrium constant, $K_{A_x B_0}$, for the reaction



where A_x is formic acid and B_0 acetate ion.

(2) Elliott and Kilpatrick, *J. Phys. Chem.*, **45**, 454, 466, 472, 485 (1941).

(1) For references see Kilpatrick, *Chem. Rev.*, **30**, 159 (1942).