gradually increased from 0 to 30%) gave a colorless oil (668 mg.). A portion of this oil (128 mg.) was chromatographed from petroleum ether onto aluminum oxide (18 g., Merck) and eluted in the same fashion in order to obtain as pure a sample as possible. The ultraviolet absorption spectrum of a solution of this oil in isoöctane had a maximum at 240 mμ (*K* 12,500, assuming it to be α-benzylpropiophenone).

The oil (51 mg.) was converted into a 2,4-dinitrophenylhydrazone which, crystallized once from ethanol and once from methanol–ether followed by two washings with petroleum ether (b.p. 30–60°), consisted of yellow-orange needles melting at 132.5–134°.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$ (α-benzylpropiophenone 2,4-dinitrophenylhydrazone): C, 65.33; H, 4.99; N, 13.86. Found: C, 65.54; H, 4.99; N, 13.52.

An authentic specimen of α-benzylpropiophenone 2,4-dinitrophenylhydrazone was prepared. It melted at 132.5–135°.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: N, 13.86. Found: N, 13.53.

This derivative is new. A mixed melting point between it and the 2,4-dinitrophenylhydrazone of the oil obtained *via* the degradation of A was not depressed.

Doeuvre Analysis of A and 1-Phenyl-2-benzyl-2,3-dimethyl-3-buten-1-one (III).—A modification of the method of Doeuvre[15] as improved by Karrer and Kebrle[16] was employed. Ethyl acetate was washed with six portions of water, dried (calcium chloride) and distilled once from phosphorus pentoxide through a 20-cm. Vigreux column. The product boiled over a range of one degree. A standard solution of formaldehyde containing 4.92 × 10^{-2} formaldehyde/cc.[17,18] was used in preparing solutions needed to obtain the plot of optical density (*D*) *vs.* mg. CH_2O per 100 cc.[15] Table I summarizes the data obtained from the Doeuvre analyses. Eugenol 3,5-dinitrobenzoate (m.p. 131–131.5°) was prepared and used as the "known" compound containing one terminal carbon–carbon double bond.

TABLE I

RESULTS OF THE DOEUVRE ANALYSES

Compound	Wt., mg., taken	D^a	Weight formaldehyde, mg. Theory[b]	Obsd.	Cor.[c]	CH_2O, %
Eugenol 3,5-dinitrobenzoate	5.91	0.646	0.50	0.73	0.59	119
III	4.35	.677	.49	.74	.60	130
Solid A	4.70	.150	.50	.31	.17	34
Ethyl acetate	(7 cc.)	.045	(.00)	.14	..	..

[a] Optical density determined at 595 mμ using a Beckman model B spectrophotometer. [b] Theoretical amount of formaldehyde which would be obtained if the compound contained one terminal double bond. [c] Observed (mg.) minus the ethyl acetate blank.

Action of 2,4-Dinitrophenylhydrazine upon A.—The usual procedure for the preparation of a 2,4-dinitrophenylhydrazone was used; the mixture became cloudy within 4 minutes after mixing the reagents and a precipitate formed slowly (under the same conditions III did not form a derivative). The mixture was allowed to remain at room temperature overnight. The precipitate (20 mg.) was removed by centrifugation. When this yellow solid was crystallized from hot methanol, however, it became amorphous, melting at 196–235°. More solid was obtained from the filtrate by addition of water. The latter solid was chromatographed at once from benzene onto activated silica gel (12 g.). Using petroleum ether (b.p. 30–60°)–ether mixtures (in which the concentration of ether was gradually increased from 10–20%) as the eluent, the derivative (300 mg. from 250 mg. A) was obtained in the first 1.25 liters. A portion was crystallized once from benzene–petroleum ether (b.p. 28–38°) and twice from ethanol–benzene, then washed with petroleum ether (b.p. 28–38°) and dried *in vacuo* at 56° for 2 hr. It formed bright yellow microcrystals melting at 172.5–174.5° dec.

Anal. Calcd. for $C_{25}H_{24}N_4O_5$ (mono-2,4-dinitrophenylhydrazone of A, $C_{19}H_{20}O_2$): C, 65.21; H, 5.25. Found: C, 65.86; H, 5.88.

The ultraviolet spectrum of this derivative in 95% U.S.P. ethanol showed maxima at 259 mμ (*K* 9,300) and 349 mμ (*K* 15,200). Minima occurred at 244 mμ (*K* 8,250) and 292 mμ (*K* 2,290).

Action of Silver Oxide upon A.—Tollens reagent was prepared in the usual way. In the first experiment a mixture of A (50 mg.) and pyridine (1 cc.) was warmed on the steam-bath while Tollens reagent (3 cc.) was added. The mixture became black at once; some white solid (undissolved A) remained in the mixture. When the mixture was boiled, a silver mirror appeared. In the second experiment, the mixture was allowed to remain at room temperature. A mirror appeared after 4 to 6 hr.

MINNEAPOLIS 14, MINNESOTA

---

[15] J. Doeuvre, *Bull. soc. chim.*, 612 (1936).

[16] P. Karrer and J. Kebrle, *Helv. Chim. Acta*, **35**, 862 (1952).

[17] I. M. Kolthoff and H. Menzel, "Volumetric Analysis," Vol. II (trans. by N. H. Furman), John Wiley and Sons, Inc., New York, N. Y., 1929, p. 444.

[18] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Rev. Ed., Macmillan, New York, N. Y., 1948.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Organic Peracid Oxidation of Some Enol Esters Involving Rearrangement[1]

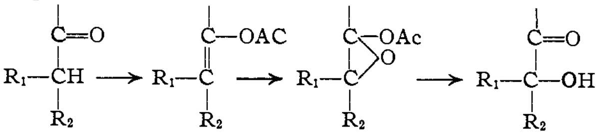
BY PETE D. GARDNER

RECEIVED JANUARY 12, 1956

The reaction of peracetic acid with 5-acetoxybenzosuber-5-ene (VI) was found to give 6-acetoxybenzosuber-5-one (IV) and the cleavage product, γ-(2-carboxyphenyl)-butyric acid (XII), whereas the use of perbenzoic acid resulted in the formation of only IV. The behavior of 3,4-dihydro-1-naphthyl acetate (V) with perbenzoic acid was the same, the corresponding ketol ester II being the only isolated oxidation product. The same transformation was brought about by perbenzoic acid in the coversion of 4-methoxy-α-acetoxystilbene (VII) to ketol ester IX. Initial experiments with an enol lactone XI are described and mechanisms are proposed to account for all of the above observations.

In the course of a program, having as its goal the development of superior methods of formation of unsaturated cyclic ketones, certain ketols and their esters became attractive as possible intermediates. Synthetic procedures were sought which would make available both of the two isomers of a given ketol, *i.e.*, RCOCH(OH)Ar and ArCOCH(OH)R.

It has been demonstrated in the steroid field that enol esters may be converted to ketols by the sequence[2]

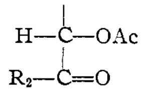


---

[1] The author is indebted to Research Corporation for the financial support of this work.

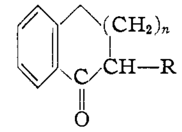
[2] T. Kritchevsky and T. F. Gallagher, *J. Biol. Chem.*, **179**, 507 (1949).

Moreover, it would seem possible to convert the oxide intermediate (R_1 = H), in aprotic media, to the isomeric ketol ester

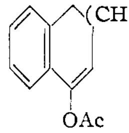


It is known, for example, that Δ^7-9,11-oxido-steroids may be converted to either Δ^8 -7-one or Δ^8 -11-one compounds depending on the choice of acid catalyst and reaction medium used in the isomerization.[3]

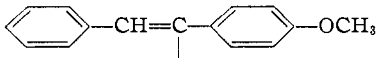
The model compound chosen to evaluate the proposed sequence was benzosuberone (III)[4] as the enol acetate, 5-acetoxybenzosuber-5-ene (VI). When VI was allowed to react with peracetic acid in acetic acid (containing water and hydrogen peroxide), three products were obtained: benzosuberone (III), γ-(2-carboxyphenyl)-butyric acid (XII) and 6-acetoxybenzosuber-5-one (IV). The recovery of benzosuberone is not surprising in that VI decomposes slowly on storage unless atmospheric moisture is excluded. Indeed, the most notable reaction of this class of compounds is hydrolysis to the corresponding carbonyl compound. The formation of the dicarboxylic acid XII *via* ring rupture is probably best accounted for in terms of intermediate XIII resulting from attack of either peracetic acid or hydrogen peroxide. Carbanion migration of this type (C → O) finds precedence in other rearrangements,[6,7] and the final oxidation step (XIV → XII) is consistent with reported hydrogen peroxide chemistry.[8] That XII is formed directly from VI and is not an artifact resulting from oxidation of benzosuberone (III) or the 6-acetoxy compound IV[9] was demonstrated by submitting III and IV to the peracetic acid treatment under the same conditions originally used. In neither experiment was acidic material formed, the starting materials being isolated in 90 and 92% recovery, respectively.



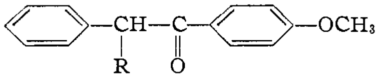
I, n = 1, R = H
II, n = 1, R = OAc
III, n = 2, R = H
IV, n = 2, R = OAc



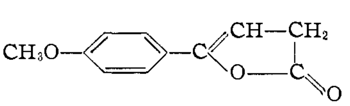
V, n = 1
VI, n = 2



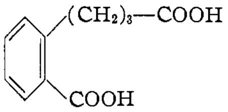
VII



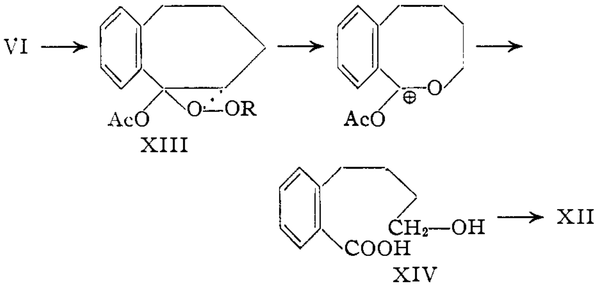
VIII, R = H
IX, R = OAc
X, R = OH



XI



XII

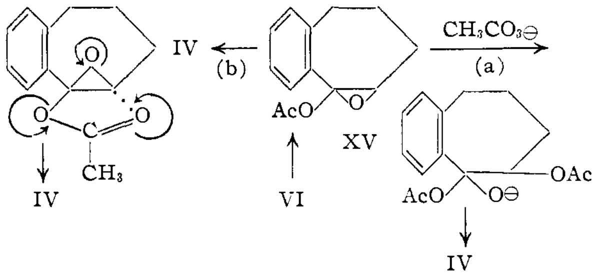


XIII

XIV

Of the various mechanisms by which IV might be formed, two are most reasonable: (a) formation of the epoxy ester XV and subsequent attack by acetic acid, analogous to the behavior of epoxy ethers[11] and (b) spontaneous rearrangement of the epoxide XV. The question was resolved by repeating the oxidation with perbenzoic acid, thus obviating the possibility of route (a) being followed. The only products isolated were starting ketone III and ketol acetate IV indicating (b) to be the path followed. The formation of the epoxy ester XV is not required for the sequence; an intermediate ion resulting from attack of OH^+ (actual or incipient)[12] on VI would seem equally plausible.

The same behavior was exhibited by the 6-membered homolog, α-tetralone (I). Thus, 3,4-dihydro-1-naphthyl acetate (V) was converted to 1-keto-2-acetoxy-1,2,3,4-tetrahydronaphthalene (II) upon treatment with perbenzoic acid.



The fact that simple enol esters may be converted to isolable epoxy ester, whereas subsequent transformations occur in the compounds studied here, suggests that the difference is a result of the combined electron-withdrawing power of the phenyl and acetoxyl groups. Consequently, a more nearly

---

[3] E. Schoenewaldt, L. Turnbull, E. M. Chamberlin, D. Reinhold, A. E. Erickson, W. V. Ruyle, J. M. Chemerda and M. Tishler, This Journal, **74**, 2696 (1952).

[4] This substance was prepared from δ-phenylvaleric acid by the method of Horton and Walker.[5] In addition to the reported product, there was obtained a high-boiling compound shown to be the product of intermolecular condensation, δ-[4-(δ-phenylvaleroyl)]-phenylvaleric acid [$C_6H_5-(CH_2)_4-CO-C_6H_4-(CH_2)_4-COOH$].

[5] W. J. Horton and F. E. Walker, This Journal, **74**, 758 (1952).

[6] D. Y. Curtin and A. Bradley, *ibid.*, **76**, 5777 (1954).

[7] W. von E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953).

[8] E. G. E. Hawkins, *Quart. Revs.*, **4**, 251 (1950).

[9] A ketol has been reported[10] to undergo cleavage by reaction with peracetic acid for a longer period of time but at a lower temperature than that used here. The process is envisioned as an attack by OH^+ at the carbon atom of a carbonyl function. It should be noted that the same over-all transformation could occur by straightforward addition of peracetic acid or hydrogen peroxide to the carbonyl group and subsequent C → O carbanion migration.

[10] J. Meinwald and C. C. Cornwall, This Journal, **77**, 5991 (1955).

[11] C. L. Stevens and J. Tazuma, *ibid.*, **76**, 715 (1954), and references contained therein.

[12] D. Swern in R. Adams, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 386.

balanced olefin, 4-methoxy-α-acetoxystilbene (VII), was prepared and submitted to oxidation with perbenzoic acid. The ketol ester, 4-methoxybenzoin acetate (IX), was the only product isolated. The 4-methoxydesoxybenzoin (VIII) required for the preparation of VII was synthesized by a polyphosphoric acid condensation between phenylacetic acid and anisole.

Two examples of this rearrangement have been reported in the steroid series.[13,14] In both instances, epoxy esters were isolated and characterized but were found to isomerize to ketol acetates upon chromatography on silica gel. The same transformation occurred when the epoxy esters were heated above their melting points. Mechanism (a) suggested above is that proposed by these investigators. That isomerization was not thermally induced in compounds examined in the present study was demonstrated in the case of 4-methoxy-α-acetoxystilbene (VII) which, in one run, was oxidized and processed at temperatures below 30°. The product IX separated upon seeding with material previously obtained.

From these data it would appear that the driving force of the reaction is the energy of resonance stabilization associated with the benzoyl grouping of atoms. The fact that perbenzoic acid gave, in every case, the ketol acetate as the only isolable oxidation product contrasted with the anomalous behavior of peracetic acid (in the one instance in which it was used) suggests that hydrogen peroxide was the effective oxidant in the latter case.

For the purpose of comparison, an authentic sample of ketol ester IV was prepared by acetoxylation of the parent ketone III using lead tetraacetate.[15,16] Although this reaction has not heretofore been considered a general preparative method for ketol esters, we have found it entirely satisfactory for a number of different ketones.[17] An attempt to prepare IX by this method, however, was unsuccessful.

Experiments have been initiated to determine if the formation of the ketol ester is possible *only* by intramolecular displacement as shown in (b). Thus, the lactone of 4-hydroxy-4-(*p*-methoxyphenyl)-3-butenoic acid (XI), in which the relative positions of the double bond and carbonyl group are such that a neighboring group effect is not possible, has been prepared and submitted to oxidation with both of the peracids used above. In both cases, reaction proceeded at a much greater rate than that observed previously, and the products were entirely acidic in nature. The separation of these from benzoic acid proved futile and, although easily separated from the peracetic acid reaction mixture, the product was a mixture of acids which has not yet been resolved. The only substance obtained in pure form from this mixture was the hydrolysis product, γ-(4-methoxyphenyl)-butyric acid. This phase of the study will be the subject of a subsequent report.

Experimental[18]

Characterization of the Acidic By-product from the Benzosuberone Preparation.—Conventional processing[5] of the reaction mixture from 356 g. of δ-phenylvaleric acid and 2.5 kg. of polyphosphoric acid gave, in addition to benzosuberone (61%), 30 g. of dark, acidic liquid, b.p. 205–300° (20 mm.). This acid solidified on standing and was purified by two crystallizations from ethyl acetate–petroleum ether (50–60°) to give 16.5 g. (4.9%) of δ-[4-(δ-phenylvaleroyl)]-phenylvaleric acid, m.p. 94–96°.

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.07; H, 7.75. Found: C, 77.75; H, 7.84.

Permanganate oxidation of a sample of this material gave a 91% yield of terephthalic acid, compared with authentic material as the methyl ester, m.p. 74°.

The semicarbazone of the above keto acid, prepared in ethanolic pyridine, melted at 147–148° after several recrystallizations from ethyl acetate–cyclohexane and from ethyl acetate.

Anal. Calcd. for $C_{23}H_{29}O_3N_3$: C, 69.85; H, 7.39. Found: C, 69.82; H, 7.43.

The 2,4-dinitrophenylhydrazone was formed as an orange, waxy solid. It melted at 103–105° after extensive crystallization from chloroform–methanol.

Anal. Calcd. for $C_{28}H_{30}O_6N_4$: C, 64.85; H, 5.83. Found: C, 65.04; H, 6.15.

5-Acetoxybenzosuber-5-ene (VI).—A mixture of 113 g. (0.705 mole) of benzosuberone, 2 g. of toluenesulfonic acid monohydrate and 300 ml. of acetic anhydride was distilled very slowly through an insulated 24-in. Vigreux column. This collection of 250 ml. of distillate required 5.5 hr., and during this time the head-temperature did not exceed 129° (740 mm.). The residue in the pot was then stirred with water at 30° for 1 hr. and extracted several times with ether. After washing with water, 10% aqueous sodium hydrogen carbonate and water, the ethereal solution was dried (sodium sulfate) and distilled. The fraction boiling at 124–127° (0.75 mm.) solidified on standing and was further purified by recrystallization from petroleum ether (50–60°) to give 110 g. (77.2%) of material, m.p. 57–60°. Further purification by crystallization or evaporative distillation did not change the m.p.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.19; H, 7.04.

Oxidation of VI. (a) Peracetic Acid.—A solution of peracetic acid was prepared by the equilibration of a mixture of 50 g. of 30% hydrogen peroxide, 200 g. of acetic acid and 3.0 g. of sulfuric acid at 25° for 20 hr. The catalyst was then neutralized by the addition of 11.0 g. of sodium acetate trihydrate. To 230 ml. of this solution (found by titration[19] to contain 0.230 mole of peracetic acid) at 25° was added 20.2 g. (0.100 mole) of VI. After 13 hr. at 30°, titration with thiosulfate solution indicated that 76% of total active oxygen had been consumed. The solution was diluted with water and extracted twice with ether. After several washings with water, 10% sodium hydrogen carbonate and water, the ethereal solution was distilled to give 6.1 g. (38%) of benzosuberone, b.p. 95–96° (0.35 mm.), and 5.2 g. of a mixture boiling over the range 98–110° (0.35 mm.). This mixture deposited 2.11 g. of 6-acetoxybenzosuber-5-one (IV) on standing at 0°. Crystallization from ethyl acetate–petroleum ether (50–60°) gave 1.90 g. (8.7%) of material melting at 79–81°. A sample repeatedly crystallized and finally sublimed at 70° and 0.1 mm. melted at 80–81°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.83; H, 6.51.

Conversion to the **dinitrophenylhydrazone** in ethanol was accompanied by alcoholysis of the ester function. The product melted with decomposition at 237–240° after purification from chloroform–methanol.

Anal. Calcd. for $C_{17}H_{16}O_5N_4$: C, 57.30; H, 4.53; N, 15.7. Found: C, 57.55; H, 4.25; N, 15.6.

The basic wash from the original reaction mixture was

---

[13] A. H. Soloway, W. J. Considine, D. K. Fukushima and T. F. Gallagher, This Journal, **76**, 2941 (1954).

[14] N. S. Leeds, D. K. Fukushima and T. F. Gallagher, *ibid.*, **76**, 2943 (1954).

[15] F. Sondheimer, G. Rosenkranz, O. Mancera and C. Djerassi, *ibid.*, **75**, 2601 (1953).

[16] R. Criegee in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 8.

[17] P. D. Gardner and D. E. Steen, unpublished data.

[18] Melting points are corrected.

[19] Reference 12, p. 392.

acidified and extracted several times with ether. Isolation in the usual manner afforded 5.28 g. (25.4%) of γ-2-carboxyphenyl)-butyric acid, m.p. 126–130°. Repeated crystallization from ethyl acetate–heptane raised the m.p. to 138.5–139° (lit.[20] 139–140°), neut. equiv. 104.2.

(b) **Perbenzoic Acid.**—A solution of 50.5 g. (0.250 mole) of VI in 100 ml. of benzene was treated at 30° with 505 ml. of a chloroform solution of perbenzoic acid containing 0.275 mole of active oxygen. The mixture was cooled as necessary to maintain a temperature of 30° and held at that temperature for 8.5 hr. The solution was washed in succession with dilute sodium hydrogen sulfite solution, 10% sodium hydroxide solution and twice with water. Distillation of solvent on a steam-bath *in vacuo* and further distillation of the residue yielded 42.6 g. of yellow liquid, b.p. 128–130° (0.4–0.5 mm.), which solidified on seeding with material obtained above. Two recrystallizations from ethyl acetate–petroleum ether (50–60°) gave 26.4 g. (48.5%) of ketol ester IV; m.p., alone and when mixed with material previously obtained, 80–81°.

6-Acetoxybenzosuber-5-one from Lead Tetraacetate Oxidation of Benzosuberone.—Lead tetraacetate was prepared and used *in situ* by the portionwise addition (1 hr.) of 688 g. (0.350 mole) of red lead oxide to a solution of 44.0 g. (0.275 mole) of benzosuberone in 500 ml. of acetic acid and 100 ml. of acetic anhydride. The entire reaction was conducted with mechanical stirring and while maintaining a temperature of 77°. After a total of 3.5 hr., 2 l. of water and 700 ml. of ether were added and the mixture filtered with suction to remove lead dioxide. The aqueous layer was extracted with two additional portions of ether and the combined ethereal solution was dried with anhydrous sodium sulfate. Following distillation of solvent from the mixture, the product was distilled through a 12-in. heated Vigreux column to give 13.1 g. (29.8%) of recovered benzosuberone, b.p. 104–109° (0.75 mm.), and 27.2 g. (45.3%) of IV, m.p. 79–80°. No depression of m.p. was observed with a mixture of this material with IV previously obtained.

Attempted Oxidations of III and IV.—A 5.0 g. sample of III was mixed with 60 ml. of solution containing 0.060 mole of peracetic acid for 20 hr. Isolation in the usual manner gave 4.5 g. (90%) of recovered III. A similar experiment using 5.0 g. of IV and 60 ml. of the peracid solution gave 4.6 g. (92%) of recovered IV.

3,4-Dihydro-1-naphthyl Acetate (V).—A solution of 100 g. (0.685 mole) of α-tetralone,[21] 300 ml. of acetic anhydride and 2.0 g. of toluenesulfonic acid monohydrate was slowly distilled as described above for VI, 250 ml. of distillate being collected over a 2-hr. period. Isolation as described above followed by distillation gave 101 g. of material boiling over the range 75–84°. Partial solidification occurred on standing and the whole was recrystallized from petroleum ether (50–60°) with seeding. A second crystallization gave 64.1 g. (49.7%) of V, m.p. 58–59°. The sample for analysis was repeatedly recrystallized and finally sublimed at 60° (0.2 mm.), m.p. 58–59.5°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.86; H, 6.48.

Perbenzoic Acid Oxidation of V.—To 187 ml. of a chloroform solution containing 0.141 mole of perbenzoic acid, by titration, was added 23.8 g. (0.127 mole) of V. The reaction mixture was cooled as necessary to maintain a temperature of 25°. After 2 hr. the solution was processed as in the case of VI and the crude product distilled. There was obtained 5.60 g. (23.5%) of recovered α-tetralone, b.p. 75–77° (0.5 mm.), and, following a 2.1-g. intermediate fraction, 9.11 g. of crude 1-keto-2-acetoxy-1,2,3,4-tetrahydronaphthalene (II), b.p. 120–130° (0.5 mm.). The remainder of the reaction mixture consisted of a viscous pot-residue. The distillate, consisting mostly of II, solidified and was recrystallized to give 7.50 g. (29.1%) of solid, m.p. 74–75°. A sample purified by further recrystallization and sublimation melted at 74.5–75° (lit.[22] 74.5–75°).

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.93. Found: C, 70.44; H, 5.85.

The orange **dinitrophenylhydrazone** derivative, formed in ethanol, proved to be that of the ketol rather than the ester. It melted at 190–191° dec. after several crystallizations from chloroform–methanol.

Anal. Calcd. for $C_{16}H_{14}O_5N_4$: C, 56.14; H, 4.12. Found: C, 56.04; H, 4.38.

4-Methoxydesoxybenzoin (VIII).—A mixture comprised of 14.0 g. (0.103 mole) of phenylacetic acid, 11.1 g. (0.103 mole) of anisole and 300 g. of polyphosphoric acid[23] was stirred at 100° for 45 min. Upon decomposition of the complex in ice and water, solid material separated and was collected by suction filtration. One recrystallization from methanol afforded 17.8 g. (76.5%) of nearly colorless prisms, m.p. 74–75°. The m.p. of a sample mixed with authentic material was not depressed.

This substance was converted to 4-methoxy-α-acetoxystilbene (VIII) by a reported procedure.[24]

Oxidation of 4-Methoxy-α-acetoxystilbene (VII) with Perbenzoic Acid.—The procedure employed here was the same as that used in previous cases. Thus, 13.4 g. (0.05 mole) of VII, 0.0678 mole of perbenzoic acid and 132 ml. of chloroform were allowed to react at 30° for 5 hr. Processing in the usual manner gave 14.1 g. of nearly colorless liquid which did not crystallize on standing for 1 month at 0°. When seeded with authentic 4-methoxybenzoin acetate (IX) at 0° and triturated with petroleum ether (50–60°), partial solidification occurred. Recrystallization from ethanol-water gave 7.10 g. (50%) of IX, m.p. 78–79° (lit.[25] 85°). Another experiment, modified only in that the entire isolation was conducted at temperatures not exceeding 30°, gave 47% of IX. Acid hydrolysis of a sample of this material with aqueous sulfuric acid in dioxane gave 4-methoxybenzoin, m.p. 106.5–107° (lit.[25] 106°).

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.85. Found: C, 74.36; H, 5.82.

AUSTIN, TEXAS

---

[20] W. Hückel and E. Goth, *Ber.*, **57**, 1285 (1924).

[21] W. E. Truce and C. E. Olson, THIS JOURNAL, **74**, 4721 (1952).

[22] F. Straus, O. Bernoully and P. Mautner, *Ann.*, **444**, 165 (1925).

[23] Kindly supplied by Victor Chemical Works, Chicago, Ill.

[24] R. P. Barnes, S. R. Cooper, V. J. Tulane and H. Delaney, *J. Org. Chem.*, **8**, 153 (1943).

[25] R. P. Barnes and V. J. Tulane, THIS JOURNAL, **63**, 867 (1941).