crystallized from methanol to yield the pure quinazolinone **3f**: mp 198–200°; ir (Nujol mull) 3260 (NH), 1752 and 1738 (ester CO), and 1638 cm^{-1} (amide CO); nmr (DMSO-d_6) δ 7.93 (s, 1, NH, exchanges with D_2O), 7.58–7.26 (m, 7, ArH), 6.85 (d, 1, J_o = 8.5 Hz, ArH_8), 3.64 (s, 3, OCH_3), 3.19 (s, 3, OCH_3), and 3.13 ppm (s, 2, CH_2CO).

Anal. Calcd for $C_{19}H_{17}ClN_2O_5$: C, 58.69; H, 4.41; N, 7.20. Found: C, 58.94; H, 4.20; N, 7.19.

2-Carbomethoxy-2-carbomethoxymethyl-6-chloro-2,3-dihydro-1-methyl-4(1*H*)-quinazolinone (3g).—Pyrolysis of **1g** provided an 88% yield of **3g**, which was recrystallized from benzene, mp 180–182°.

Anal. Calcd for $C_{14}H_{15}ClN_2O_5$: C, 51.46; H, 4.63; N, 8.57. Found: C, 51.64; H, 4.55; N, 8.67.

2-Carbomethoxy-2-carbomethoxymethyl-6-chloro-2,3-dihydro-3-methyl-4(1*H*)-quinazolinone (3h).—A 94% yield of **3h** was obtained from **1h**. Recrystallization from 1:1:1 MeOH–benzene–cyclohexane provided the analytical sample, mp 147.5–149°.

Anal. Calcd for $C_{14}H_{15}ClN_2O_5$: C, 51.46; H, 4.62; N, 8.57. Found: C, 51.53; H, 4.47; N, 8.67.

2-Carbomethoxy-2-carbomethoxymethyl-6-methoxy-7-chloro-2,3-dihydro-4(1*H*)-quinazolinone (3i).—**3i** was obtained by pyrolysis of **1i**. Four recrystallizations from MeOH gave the purified product (36%),[10] mp 169.5–171.5°.

Anal. Calcd for $C_{14}H_{15}ClN_2O_6$: C, 49.06; H, 4.41; N, 8.17. Found: C, 49.36; H, 4.58; N, 8.07.

2-Carbomethoxy-2-carbomethoxymethyl-6-fluoro-2,3-dihydro-4(1*H*)-quinazolinone (3j).—This compound was prepared in 36%[10] yield from **1j**, mp 178–180° (after recrystallization from MeOH).

Anal. Calcd for $C_{13}H_{13}FN_2O_5$: C, 52.70: H, 4.42; N, 9.45. Found: C, 52.92; H, 4.48; N, 9.42.

2-Carbomethoxy-2-carbomethoxymethyl-2,3-dihydro-1-methyl-4(1*H*)-quinazolinone (3d).—**3d** was prepared by dissolving 3.0 g (0.01 mol) of **1d** in 50 ml of xylene containing 0.1 g of NaOMe and heating to reflux for 3.5 hr. Chilling precipitated 1.32 g of unreacted **1d**. Dilution of the filtrate with petroleum ether (bp 30–60°) gave 1.18 g of product. Two recrystallizations from MeOH yielded 1.02 g (34% conversion) of pure **3d**,[10] mp 118–120°.

Anal. Calcd for $C_{14}H_{16}N_2O_5$: C, 57.52; H, 5.51; N, 9.58. Found: C, 57.73; H, 5.41; N, 9.53.

Registry No.—**1d**, 34804-41-6; **1e**, 34804-42-7; **1f**, 34804-43-8; **1g**, 34804-44-9; **1h**, 34804-45-0; **3a**, 17244-35-8; **3b**, 17244-36-9; **3c**, 17244-40-5; **3d**, 34804-49-4; **3e**, 34804-50-7; **3f**, 34804-51-8; **3g**, 34803-90-2; **3h**, 34803-91-3; **3i**, 34803-92-4; **3j**, 34803-93-5.

Acknowledgment.—We gratefully acknowledge the financial support of the doctoral research of Thomas F. Lemke by Atlas Chemical Industries.

(10) The low yields of these compounds are partially a result of the increased solubility in the recrystallization solvents. No attempt was made to optimize the yields.

Synthesis of Trimethylhydroquinone from Aliphatic Precursors

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Condensation of a properly substituted α,β-unsaturated aldehyde or ketone with an appropriate aliphatic ketone leads to a trimethyl-2-cyclohexen-1-one structure. These molecules are readily aromatized to the corresponding phenols in high purity with Pd/C under mild conditions. A novel indirect electrolytic oxidation involving Fremy's radical[2] yielded trimethyl-*p*-benzoquinone (**9**) which in turn was reduced to trimethylhydroquinone (**1**). The latter is an important intermediate in the synthesis of vitamin E.

Various methyl-substituted phenols and particularly trimethylphenols are prepared from phenol *via* methylation processes. Although these processes can be controlled so that a particular mono- or polymethylated phenol can be obtained as the major product, mixtures are invariably obtained. Such mixtures require separation by methods which can be tedious especially if phenols of high purity are required.

We now wish to describe a general method for obtaining a number of specifically substituted trimethylphenols in pure form. Since only standard laboratory techniques are involved, the overall scheme should lend itself to the preparation of a variety of ^{14}C ring- and/or chain-labeled phenols, *p*-quinones, and the hydroquinones derived thereform.

Our main objective was to find a practical synthesis for 2,3,5- and/or 2,3,6-trimethylphenol based on readily available aliphatic starting materials. Both of these phenols represent important intermediates in the production of trimethylhydroquinone and thus of vitamin E.

The basic concept comprised the construction of a suitably substituted trimethylcyclohexenone carbon skeleton which, in a second step, could be aromatized to the corresponding trimethylphenol (Scheme I).[3]

Chapurlat and Dreux[4] described the condensation of 3-penten-2-one with 2-butanone to yield 3,5,6-trimethyl-2-cyclohexen-1-one (**2**). We found that the same product was obtained from the more readily accessible 4-chloro-2-pentanone[5] and 2-butanone. A different substitution pattern was obtained in the cyclohexenone ring when methyl vinyl ketone was condensed with 3-pentanone under strongly alkaline conditions. The uv absorption at λ_{max}^{EtOH} 239 nm was compatible with the 2,3,6-trimethyl-2-cyclohexen-1-one[6] structure, **4**.

The reaction we studied most carefully was the condensation of crotonaldehyde with 3-pentanone in the presence of KOH.[7] Under optimal conditions a 77% yield (uv analysis) of **6** as a mixture of cis and trans isomers (nmr) was obtained.

(1) To whom correspondence should be addressed.

(2) P. A. Wehrli and F. Pigott, *Inorg. Chem.*, **9**, 2614 (1970).

(3) No stereochemistry is indicated in **2**, **6**, and **7**.

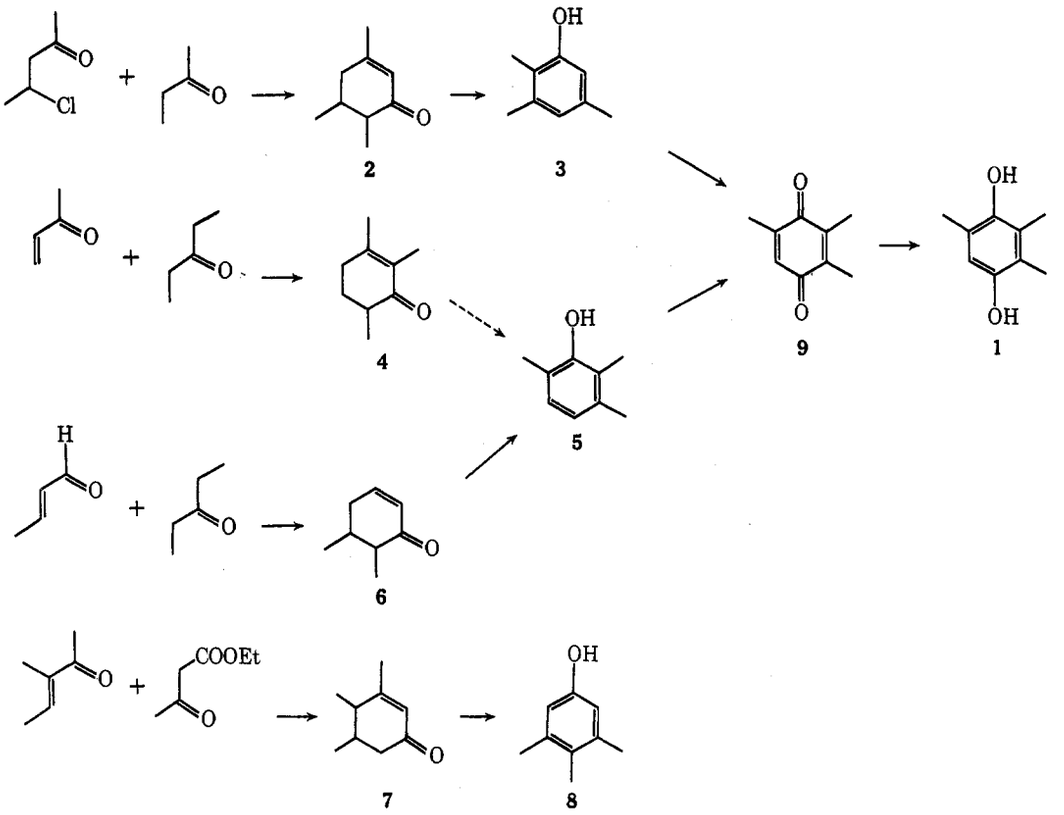
(4) R. Chapurlat and J. Dreux, *C. R. Acad. Sci.*, **253**, 2361 (1961): bp for **2**, 85–86° (4.5 mm).

(5) A. Wohl and R. Maag, *Chem. Ber.*, **43**, 3280 (1910); 4-chloro-2-pentanone is undoubtedly an intermediate in their preparation of 3-penten-2-one.

(6) T. Ichikawa, H. Owatari, and T. Kato, *Bull. Chem. Soc. Jap.*, **41**, 1228 (1968): bp for **4**, 92–96° (16 mm); bp for **6**, 92–100° (24 mm).

(7) After this work was completed, we became aware of a Dutch Patent abstract (6,903,484, Sept 10, 1969): bp for **6**, 74–76° (12 mm).

SCHEME I



The condensation of 3-methyl-3-penten-2-one with ethyl acetoacetate took the expected course with the formation of the hitherto unknown 3,4,5-trimethyl-2-cyclohexen-1-one (**7**). Structure **7** was confirmed by transformation to phenol **8**.

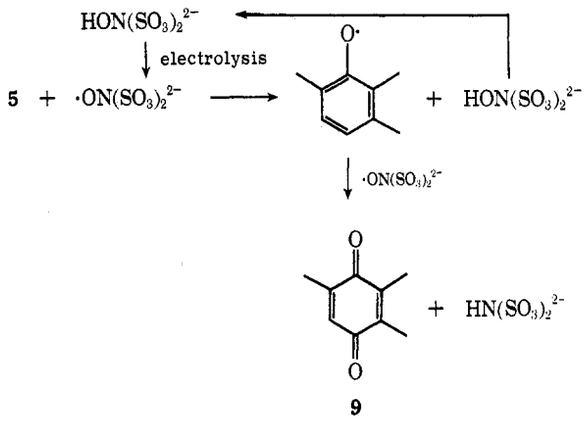
Surprisingly smooth aromatizations of cyclohexenones **2**, **6**, and **7** were achieved by refluxing the compounds in the presence of palladium on charcoal. Only the conversion **6** → **5** was studied in detail. The resulting trimethylphenols were identified with authentic samples by comparison.

Phenols **3** and **5** were converted to the same trimethyl-*p*-benzoquinone **9** by application of a novel indirect electrolytic oxidation. Thus, an aqueous solution of hydroxylamine disulfonate was electrolyzed[2] in the presence of a heptane solution of **3** or **5** to give the *p*-quinone in quantitative yield from **5** and in somewhat lower yield from **3**. Use of the two-phase system protects the *p*-quinone from undergoing side reactions. Furthermore, by carrying out the preparation of Fremy's radical in the presence of the phenol, only 1 mol of hydroxylamine disulfonate is required to achieve the overall oxidation of a phenol to a quinone (Scheme II).[8]

As indicated in Scheme II, the first step in the Teuber reaction[9] is catalytic with respect to Fremy's radical under electrolysis conditions. A molar quantity of the reagent, however, is consumed in the second step.

Reduction of *p*-quinone **9** by standard methods gave the desired trimethylhydroquinone **1** in a high state of purity.

SCHEME II



Experimental Section[10]

3,5,6-Trimethyl-2-cyclohexen-1-one (**2**).—4-Chloro-2-pentanone (30 g, 0.25 mol) and 108 g (1.5 mol) of 2-butanone were stirred at room temperature and 20 g (0.25 mol) of pyridine was added over a period of 2 min. The temperature rose from 25° to 34°. The reaction mixture was stirred at room temperature for 15 min and then a small amount of a heavy liquid phase which had precipitated was removed with a pipette; 5 *M* sodium methoxide (100 ml, 0.5 mol) in methanol was added. The temperature rose to 52° and the reaction mixture was refluxed for 1 hr, cooled, and filtered from 11.5 g of sodium chloride. It was then partitioned between ether and saturated sodium chloride solution. The ether phase was washed once with dilute hydrochloric acid, followed by three washes with saturated

(8) H. J. Teuber and W. Rau, *Chem. Ber.*, **86**, 1036 (1953).
(9) H. J. Teuber and K. H. Dietz, *Angew. Chem.*, **77**, 913 (1965).

(10) Infrared and uv spectra were recorded on a Perkin-Elmer Model 21 and on a Cary Model 14 spectrophotometer respectively. Nmr spectra were carried out on a Varian A-60 apparatus and are reported in parts per million. Melting points were determined in capillaries on a Thomas-Hoover apparatus and are not corrected. The equipment used for the electrolytic oxidation is described in ref 2.

sodium chloride solution (until the aqueous wash was no longer acidic to pH paper). The ether phase was dried over anhydrous sodium sulfate and concentrated *in vacuo*. Distillation of the residue gave 10.0 g (29%) of a slightly yellow liquid boiling at 93–106° (18–19 mm). The analytical sample distilled at 106–107° (18 mm): ir ($CHCl_3$) 1670 (s), 1390 cm^{-1} (m); $\lambda_{max}^{i\text{-PrOH}}$ 233 nm (ϵ 14,000); nmr ($CDCl_3$) δ 1.0–1.35 (m, 6 H), 2.0–2.7 (m, 7 H), 6.0 (s, broad, 1 H), spectrum indicates mixture of diastereoisomers.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.98; H, 10.21.

2,3,6-Trimethyl-2-cyclohexen-1-one (**4**).—To a solution of 34.4 g (0.4 mol) of 3-pentanone and 10 ml of methanol was added 12 g (0.1 mol) of potassium *tert*-butoxide. The temperature rose to 34°. With a dropping funnel there was added slowly 14.0 g (0.2 mol) of methyl vinyl ketone with vigorous stirring. The temperature rose to 50°. The reaction was stirred for 10 min longer. The dark brown mixture was partitioned between ether and saturated sodium chloride solution. The organic phase was washed with saturated sodium chloride solution until neutral. After drying over anhydrous sodium sulfate, evaporation of the solvent, and distillation of the residue there was obtained a fraction weighing 1.5 g and boiling at 93–95° (19 mm). A redistilled sample was characterized: ir ($CHCl_3$) 1660 (s) and 1640 cm^{-1} (s); $\lambda_{max}^{i\text{-PrOH}}$ 239 nm (ϵ 12,100); nmr ($CDCl_3$) δ 1.15 (d, 3 H), 1.7 (s, broad, 3 H), 1.9 (s, broad, 3 H), 2.0–2.6 (m, 5 H); mass spectrum M^+ *m/e* 138, base peak at *m/e* 96.

2,5,6-Trimethyl-2-cyclohexen-1-one (**6**).—A 1.2-l., three-necked flat-bottomed flask, equipped with a mechanical paddle stirrer, thermometer, and addition funnel with the glass delivery tube pulled out at the end, was charged with 64.5 g (1 mol) of 85% potassium hydroxide pellets and 75 g of methanol. The mixture was stirred until the potassium hydroxide was largely dissolved. To the warm mixture was added 430 g (5 mol) of 3-pentanone and the mixture was stirred for a few minutes at 40°. With vigorous stirring so that there was a very deep whirlpool effect, 70.0 g (1 mol) of crotonaldehyde was added dropwise at a rate so the addition would be complete in *ca.* 40 min. After the rate was set (judged visually) the delivery tip was submerged into the swirling reaction mixture so that the addition took place below the surface, thus ensuring most rapid distribution of the crotonaldehyde. The temperature was maintained at 40–45° throughout the addition. The reaction mixture turned dark and the potassium hydroxide pellets were completely dissolved on completion of the addition of the crotonaldehyde. The mixture was stirred for 10 min, cooled in an ice bath, and acidified with concentrated hydrochloric acid while cold. The point of neutralization was readily recognized when the color of the reaction mixture changed from dark brown to light yellow at slightly acidic pH. After extracting three times with diethyl ketone, washing the organic layer with saturated sodium chloride solution, and evaporating the solvent on a rotary evaporator, there remained a clear golden liquid residue weighing 167 g (yield, estimated by uv, 77%). Distillation *in vacuo* through a 30-mm Vigreux column yielded a colorless main fraction, 97 g, bp 74–81° (12 mm)[6,7] (70% based on crotonaldehyde). An analogously prepared sample was analyzed: ir ($CHCl_3$) 1655 cm^{-1} (s); $\lambda_{max}^{i\text{-PrOH}}$ 232 nm (ϵ 8980); nmr ($CDCl_3$) δ 0.95–1.12 (m, 6 H), 1.75 (s, broad, 3 H), 1.8–2.5 (m, 4 H), 6.62 (broad, 1 H); mass spectrum M^+ 138, base peak at *m/e* 82.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.92; H, 10.19.

3,4,5-Trimethyl-2-cyclohexen-1-one (**7**).—Ethyl acetoacetate (13.0 g, 0.1 mol), 3-methyl-3-penten-2-one (9.8 g, 0.1 mol), and a 25% solution of sodium methoxide in methanol (22 ml, 0.1 mol) were refluxed for 18 hr. Precipitation occurred within 1 hr and there was a considerable amount of bumping. The reaction mixture was cooled, treated with water and concentrated hydrochloric acid (gas evolution occurred), and extracted with ether. The ether layer was dried over anhydrous sodium sulfate and concentrated *in vacuo* to afford 15.0 g of residue, $\lambda_{max}^{i\text{-PrOH}}$ 233 nm. The residue was treated with 75 ml of a 10% sodium hydroxide solution and stirred for 5 hr to ensure complete saponification and decarboxylation. It was then extracted with ether and concentrated to afford 10.0 g of a residue. Distillation at 18–20 mm gave 6.4 g (46.5%) of product boiling at 107–111°.

Combined material from two similar reactions was redistilled, bp 109–110° (1.8 mm) (colorless oil) for analysis: ir ($CHCl_3$) 1663 cm^{-1} (s); $\lambda_{max}^{i\text{-PrOH}}$ 233 nm (ϵ 14,480); nmr ($CDCl_3$) δ 0.93–1.33 (m, 6 H), 1.96–2.16 (m, 3 H), 2.16–2.46 (m, 4 H), 5.9–6.03 (s, 1 H); mass spectrum M^+ at *m/e* 138 (fragmentation compatible).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.20; H, 9.96.

2,3,5-Trimethylphenol (**3**).—3,5,6-Trimethyl-2-cyclohexen-1-one (**2**) (1.0 g) was refluxed vigorously and stirred with 100 mg of 10% palladium on charcoal. After *ca.* 4 hr, the evolution of hydrogen stopped. Reflux was continued for 6 hr. The reaction mixture was cooled, diluted with 2 ml of heptane, and filtered through a medium sintered glass funnel. After washing thoroughly with hot heptane, the filtrate was evaporated to *ca.* 5 ml and cooled for 18 hr at 0°. The crystals were filtered, washed with heptane, and air dried to give 500 mg (50%) of 2,3,5-trimethylphenol, mp 90.1–91.1°. The ir spectrum of this material was superimposable with that of an authentic sample.[11]

2,3,6-Trimethylphenol (**5**).—2,5,6-Trimethyl-2-cyclohexen-1-one (**6**) (138 g, 1.0 mol) was weighed into a 1-l. three-necked flask and 7.0 g of 10% palladium on charcoal was added. The flask was equipped with a heating mantle, magnetic stirrer, thermometer, and an efficient water-cooled condenser. The top of the condenser was connected by Tygon tubing to a cooling trap (Dry Ice–acetone) and from there to another 1-l. three-necked flask (safety container), the outlet of which led to a gas measuring device. Before heating, the whole apparatus was flushed carefully with nitrogen. At the onset of reflux collection of hydrogen was started. The first liter was produced very rapidly (*ca.* 5 min). Then a marked slowdown in the evolution of hydrogen occurred for about 30 min. At the end of this induction period, hydrogen started to come off at increasing speeds. The maximum observed under these conditions was 1 l. in 15 min. While very vigorous reflux was maintained throughout the reaction, the evolution of hydrogen generally stopped after 7 to 8 hr, by which time 17–18 l. of hydrogen had been collected in the measuring device. The contents of the flask were cooled to about 100° and flushed with a slow stream of nitrogen. Heptane (100 ml) was introduced through the condenser and the still hot reaction mixture was filtered over a medium sintered glass funnel. Equipment and charcoal were washed with three 50-ml portions of hot heptane. Vpc analysis of the filtrate indicated a 2,3,6-trimethylphenol content of 92–93% on an area comparison (100°, isothermal, 2% silicon–rubber, 1 in. per minute). The colorless filtrate was crystallized for 18 hr at 0°. It was then filtered and washed with three 25-ml portions of cold heptane. After air drying for 4 hr, at room temperature, there resulted a crop of 98.3 g (72%) of pure **5** with a melting point of 63.5–64° (Mettler automatic melting point apparatus).[12]

The mother liquor was extracted directly with six 25-ml portions of 4 *N* sodium hydroxide and the individual portions were combined and acidified with concentrated hydrochloric acid with cooling. Extraction with heptane at *ca.* 40° followed by drying the organic layers over magnesium sulfate and evaporation afforded a solidified residue of 21 g (total yield, 88%). The melting point of this material was 60°.

3,4,5-Trimethylphenol (**8**).—3,4,5-Trimethyl-2-cyclohexen-1-one (**7**) (1 g) and 5% palladium on charcoal (0.1 g) were heated and stirred at 180–190°. After 10 min the foaming had ceased. Heating was continued for a total of 1.75 hr, when the uv spectrum showed it to be a mixture of phenol and starting material. Heating was continued for 1 hr longer at 208–218°. At the end of this time, it was cooled, diluted with ether, filtered, and concentrated on the steam bath. The residue was treated with 40% sodium hydroxide solution and the resulting precipitate was filtered and redissolved in fresh water. The aqueous phase was washed with ether and acidified with 6 *N* hydrochloric acid. An oil precipitated which solidified on standing. It was collected and air dried, yield 170 mg. The ir spectrum of this material was superimposable with that of an authentic sample of 3,4,5-trimethylphenol.

Trimethyl-*p*-benzoquinone (**9**). **A. From 2,3,6-Trimethylphenol** (**5**).—In the following sequence, 15.0 g (0.217 mol) of sodium nitrite, 250 g of ice, and 41.6 g (0.4 mol) of sodium bisulfite were weighed into an ice-cooled 1-l. resin flask. With manual stirring, 22.5 ml (23.6 g, 0.4 mol) of acetic acid was added. Most of the ice dissolved and the temperature dropped to −3°. The clear solution was kept at this temperature and stirred mechan-

(11) Obtained from Aldrich Chemical Co.

(12) W. C. Sears and L. J. Kitchen, *J. Amer. Chem. Soc.*, **71**, 4110 (1949), report mp 61.8–62.8°.

ically for 1.5 hr. At the end of this period 250 ml of a saturated solution of sodium carbonate was added. To this resulting solution of sodium hydroxylamine disulfonate 20.0 g (0.147 mol) of 2,3,6-trimethylphenol (mp 63.4°) and 100 ml of heptane were added. A stainless steel anode[10] (*ca.* 10 mesh/cm²) was immersed into the heterogeneous two-phase system. The cathode, in the form of a stainless steel coil, was placed into a porous pot (Soxhlet type extraction thimble), filled with water plus 2 ml of the electrolyte, and immersed to about $^3/_4$ of its length into the two-phase reaction mixture. The cold two-phase system was now stirred mechanically and electrolyzed for 5 hr at 7–8V/3A at 0–5°. The trimethylphenol dissolved slowly and the color of the hexane layer changed to yellow, then to orange, and again to lemon yellow at the end. The course of the reaction was conveniently followed by tlc (aluminum oxide plates, chloroform, phosphomolybdic acid spray). Only trace amounts of phenol could be detected at the end of the electrolysis. The water layer had a violet color and some inorganic material crystallized. The whole mixture was transferred into a 1-l. separatory funnel. The yellow heptane layer was separated and washed two times with 50 ml of 4 *N* sodium hydroxide and then with saturated sodium chloride solution until the washes were neutral. The water layers were washed twice with heptane. The heptane extracts were combined, dried over magnesium sulfate, filtered, and evaporated to dryness (rotary evaporator, 40° bath temperature). The residue, a lemon oil, crystallized under cold running water. The last traces of solvent were subsequently removed under high vacuum. This procedure gave 20.8 g (94%) of crystalline, yellow trimethylbenzoquinone (**9**), mp 29.6–31°[13] (Mettler automatic melting point apparatus) and tlc examination of this material revealed only one spot.

B. From 2,3,5-Trimethylphenol (3).—Using the same procedure described in A, **9** was obtained in 73% yield, mp 27.8°.

Trimethylhydroquinone (1).—Reduction of a sample of **9** with sodium hydrosulfite and crystallization from water yielded pure **1**, mp 170–173°.[13] Ir and uv spectra of this material were superimposable with those of an authentic sample.[11]

Registry No.—**1**, 700-13-0; **2**, 16782-79-9; **3**, 697-82-5; **4**, 20030-29-9; **5**, 2416-94-6; **6**, 20030-30-2; **7**, 34638-67-0; **9**, 935-92-2.

Acknowledgments.—Thanks are due to the staff of our Physical Chemistry Department directed by Dr. P. Bommer. In particular we are indebted to Dr. H. Wyss for ir, Dr. V. Toome for uv, Dr. T. Williams for nmr, Dr. W. Benz for mass spectra, and Dr. F. Scheidl for microanalyses.

(13) R. Nietzki and J. Schneider, *Chem. Ber.*, **27**, 1426 (1894), report mp 32° for **9** and 169° for **1**.

Notes

On the Electrophilic Substitutions and Additions to the Pyrrolidine Enamine of 1-Acetyl-3-oxopiperidine

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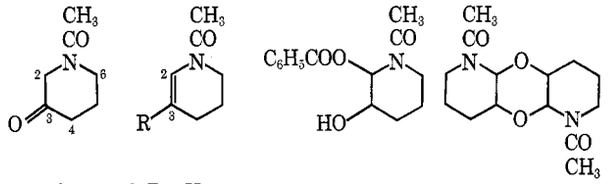
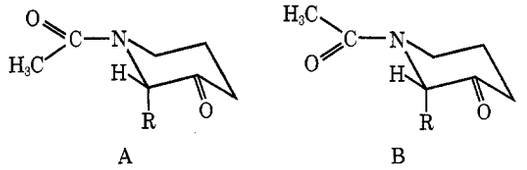
Enamine chemistry has been investigated extensively[1] since Stork's excellent application of enamines for electrophilic substitution reactions.[2] However, only a few examples have been reported of substitutions or additions to enamines of ketones bearing a methylene group flanked by a carbonyl group and a nitrogen atom.[3] In connection with research on synthesis of veratramine,[4] we have examined some reactions of the pyrrolidine enamine of 1-acetyl-3-oxopiperidine (**1**).

The starting ketone **1** was prepared as follows. Treatment of 1-acetyl-1,4,5,6-tetrahydropyridine[5] (**2**) with perbenzoic acid afforded the hydroxy derivative **3** in 50% yield, which on pyrolysis produced **1** in 72% yield along with a dimeric by-product **4**. In accordance with the structure, compound **1** exhibited a peak at *m/e* 141 (M^+) and absorption maxima at 1726 and 1642 cm^{-1} in the mass and ir spectra, respectively. The nmr spectrum of **1** was simplified by rapid ring inversion and, conversely, complicated by the presence of two conformers A and B (R = H) caused by slow rotation of the acetyl group around the C–N bond,[6] as



1 **2**, R = H **3** **4**

5, R = NC_4H_8



A B

(1) For recent reviews, see (a) G. H. Alt in "Enamines," A. G. Cook, Ed., Marcel Dekker, New York, N. Y., 1969, p 115; (b) K. Bláha and O. Červinka in "Advances in Heterocyclic Chemistry," Vol. 6, A. R. Katritzky and A. J. Boulton, Ed., Academic Press, New York, N. Y., 1966, p 147; (c) J. Szmuszkovicz in "Advances in Organic Chemistry," Vol. 4, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience, New York, N. Y., 1963, p 1.

(2) G. Stork, R. Terrel, and J. Szmuszkovica, *J. Amer. Chem. Soc.*, **76**, 2029 (1954); G. Stork and H. K. Landesman, *ibid.*, **78**, 5128, 5129 (1956).

(3) *E.g.*, S. Danishefsky and R. Cavanaugh, *J. Org. Chem.*, **33**, 2959 (1968).

(4) (a) T. Masamune, M. Takasugi, A. Murai, and K. Kobayashi, *J. Amer. Chem. Soc.*, **89**, 4521 (1967); (b) T. Masamune, M. Takasugi, and A. Murai, *Tetrahedron*, **27**, 3369 (1971).

(5) C. Schöpf, A. Komzak, F. Braun, and E. Jacobi, *Justus Liebigs Ann. Chem.*, **559**, 1 (1948); T. Masamune and M. Takasugi, *Yuki Kagobutsu Goseiho*, **18**, 1 (1968).

(6) For recent papers concerning the slow rotation of the C–N bond, see W. E. Stewart and T. H. Siddal, *Chem. Rev.*, **70**, 517 (1970); B. U. Schlottmann, *Tetrahedron Lett.*, 1221 (1971); C. R. Narayanan and B. M. Sawant, *ibid.*, 1321 (1971).