

which was obtained from the sodium addition compound in 24% yield, crystallized from acetone-xylene in colorless plates; m. p. 227.5–230° with evolution of gas. Since the acid was difficult to purify, it was converted to its methyl ester for analysis. The ester crystallized from acetone ethanol in clusters of colorless prisms; m. p. 158–164°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4. Found: C, 84.3; H, 5.4.

9,10-Dicarboxy-9,10-dihydro-1,2,5,6-dibenzanthracene (IV), obtained from the dilithium addition compound of 1,2,5,6-dibenzanthracene in 59% yield, crystallized from acetone-benzene in clusters of colorless prisms; m. p. 262–264° with gas evolution. The acid is very soluble in acetone but only slightly soluble in benzene. It was analyzed in the form of its dimethyl ester, which crystallized from acetone-ethanol in stout, colorless needles; m. p. 255–257°.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.8; H, 5.1. Found: C, 78.1; H, 5.0.

The reaction between the disodium compound of 1,2,5,6-dibenzanthracene and carbon dioxide did not always proceed in the same manner. Usually a 60–70% yield of an acid was obtained which crystallized from benzene in colorless needles; m. p. 242–255° with decomposition. Since the acid was difficult to purify, it was converted to its methyl ester, which crystallized from benzene-methanol in broad, colorless needles; m. p. 174–175°. Although the ester was not obtained quite pure, analysis showed that the acid was 9-carboxy-9,10-dihydro-1,2,5,6-dibenzanthracene (V).

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4. Found: C, 84.1; H, 5.3.

In some runs the disodium compound yielded the same dicarboxylic acid that was obtained from the dilithium addition compound. In one run there was obtained a 79% yield of an acid, m. p. 255–258°, whose methyl ester

crystallized in broad, colorless needles which melted at 100–101°. Unfortunately, this product was all used up in certain tests and we were unable to secure any more of it in subsequent experiments.

6,12b-Dicarboxy-6,12b-dihydro-3-methylcholanthrene (VI), was obtained in 42% yield from the dilithium addition compound of 3-methylcholanthrene.² From hot benzene the dicarboxylic acid separated in brownish-yellow crystals; m. p. 242–246°. Considerable losses were experienced in the process of recrystallization, for the acid appeared to be unstable. Its dimethyl ester crystallized from acetone-methanol in clusters of short, brownish prisms; m. p. 205–208°.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 77.7; H, 5.7. Found: C, 77.1; H, 5.9.

The acid isolated in 59% yield from the disodium addition product crystallized in pale yellow needles; its methyl ester formed pale yellow cubes from acetone-methanol; m. p. 178–179°. Analysis of the latter showed that the acid was a monocarboxy-6,12b-dihydro-3-methylcholanthrene, but whether the carboxyl group was in the 6- or 12b-position was left undecided.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 84.1; H, 6.1. Found: C, 83.9; H, 5.5.

Summary

The reaction between a number of polycyclic hydrocarbons with sodium and with lithium has been investigated. From the intensely colored alkali metal addition compounds of the hydrocarbons the dihydro derivatives were obtained by treatment with methanol. With carbon dioxide the addition compounds yielded salts of carboxylic acids.

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The Hydroxylation of Unsaturated Substances. III. The Use of Vanadium Pentoxide and Chromium Trioxide as Catalysts of Hydroxylation

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The catalytic hydroxylation of unsaturated substances has been under way in this Laboratory for some time. Of particular usefulness has been the method recently described¹ and extended to embrace a great number of substances.² In this method hydrogen peroxide in anhydrous tertiary butyl or tertiary amyl alcohols and in the presence of osmium tetroxide adds onto carbon-carbon double bonds to form glycols. Although the mechanism of this reaction has not been en-

tirely elucidated, evidence has been accumulated to indicate that it proceeds through the formation of perosmic acid which probably dissociates into hydroxyl radicals and osmium tetroxide. In this way the catalyst seems to act, like ultraviolet light,³ as though it dissociates the hydrogen peroxide into hydroxyl radicals which subsequently add onto double bonds or cause other oxidations.

Like osmium there are a number of metals belonging to the IV, V and VI sub-groups of the Periodic System which are known to form very

(1) Milas and Sussman, *THIS JOURNAL*, **58**, 1302 (1936).

(2) Milas and Sussman, *ibid.*, **59**, 2545 (1937); also unpublished results.

(3) Milas, Kurz and Anslow, Jr., *ibid.*, **59**, 543 (1937).

unstable peracids rather than peroxides.⁴ These metals include Ti, Zr, Th, V, Nb, Ta, Cr, Mo, W and U. A study of the behavior of the oxides of these metals on hydroxylation has been undertaken during the past year and some preliminary results are now available with vanadium pentoxide and chromium trioxide. Table I summarizes some of the results obtained.

TABLE I
SUMMARY OF RESULTS

Substance	Main product	Yield, %	
		With V ₂ O ₅	With CrO ₃
Trimethyl-ethylene	Trimethyl-ethylene glycol	36.4	37.3
Diethyl fumarate	Diethyl racemate	57	..
Anethole	Anisaldehyde	55	13.7
Isoeugenol	Vanillin	66	58.3
Isosafrole	Piperonal	67.5	14.0
Benzene	Phenol	30	12.2

In addition to the substances mentioned in the foregoing table, cyclohexene yielded a small amount of *cis*-cyclohexanediol-1,2, an unidentified aldehyde and considerable quantities of adipic acid. Cresols were obtained from toluene and naphthols from naphthalene. These reactions and their mechanism are being actively investigated at present and will be reported elsewhere.

Experimental

The Catalysts. (1) **Vanadium Pentoxide.**—This catalyst may be obtained from the Vanadium Corporation of America or it may be prepared in accordance with the method described elsewhere.⁵ Vanadium pentoxide is almost entirely insoluble in tertiary butyl or tertiary amyl alcohol but, when the latter contains hydrogen peroxide, it goes promptly into solution to form blood red pervanadic acid.⁶ The reaction mixture, as a rule, remains blood red until the end of the reaction when either the vanadium pentoxide precipitates out as a dark brown solid, or remains in solution as blue or green lower oxide. In every case the catalyst may be rejuvenated easily by the addition of more peroxide reagent.

(2) **Chromium Trioxide.**—Unlike vanadium pentoxide, this catalyst is soluble in both tertiary butyl and tertiary amyl alcohols yielding brownish-red solutions. However, when hydrogen peroxide is present these solutions are deep blue. This color is due to the formation of the unstable perchromic acid.⁷ The catalytic reactions with chromium trioxide are, as a rule, more vigorous but less efficient in the production of the desired product than reactions with other catalysts. At the end of each reaction

the blue color disappears and goes over into a transitory purple color and finally a bluish-green precipitate comes down which has the properties of chromic oxide. When the reaction has reached this stage, the catalyst cannot be rejuvenated by the addition of peroxide reagent.

Trimethylethylene Glycol from Trimethylethylene.—Fourteen grams of trimethylethylene (b. p. 38.3–38.4°) was mixed with an equimolecular quantity of the peroxide reagent¹ and to the mixture was added 0.03 g. of vanadium pentoxide. The catalyst dissolved in a few minutes and the solution warmed up considerably. It was then cooled under running water for twenty-four hours when the reaction appeared complete. The mixture was filtered and the filtrate fractionally distilled through a Davis column to remove the solvent and the unused trimethylethylene (5 g.). When the residue was fractionated under reduced pressure, a fraction (5 g.) was obtained which boiled at 80–83° (13 mm.). The b. p. of trimethylethylene glycol is given in the literature as 80–82° (13 mm.)⁸ and 85–87° (15 mm.)⁹ The yield of this glycol, calculated on the basis of the trimethylethylene used, amounted to 37.3%. Another experiment, repeated in exactly the same way as the above, yielded 36.4% of trimethylethylene glycol.

The experiment was again repeated using the same quantities of trimethylethylene and the peroxide reagent but, instead of vanadium pentoxide, 0.02 g. of pure chromium trioxide was used. The solution warmed up and had to be cooled under running water. At the end of twenty-four hours the reaction was over and the catalyst had precipitated out as a bluish-green solid. When the mixture was fractionated, 8 g. of unused trimethylethylene and 1.5 g. of the glycol were obtained in addition to some acetic acid.

Racemic Acid from Diethyl Racemate.—To 17.2 g. of diethyl fumarate (Eastman Kodak Company) were added 66 cc. of the peroxide reagent and 0.02 g. of vanadium pentoxide. After the catalyst went into solution, the mixture warmed up considerably and had to be cooled under running water. At the end of twenty-four hours the solution had turned greenish-blue and the reaction was complete. The solvent was then removed under reduced pressure and the ester saponified in 10% alcoholic potash. When the alcohol was distilled and the residue acidified with dilute hydrochloric acid, 3 g. of unreacted fumaric acid was recovered. The filtrate yielded 11 g. of calcium racemate precipitated in ammoniacal solution.¹ This corresponds to a yield of 57% of the diethyl fumarate used.

Anisaldehyde from Anethole.—To 5 g. of anethole (Eastman Kodak Company) were added 45 cc. of the peroxide reagent and 0.02 g. of vanadium pentoxide. The catalyst went slowly into solution, which heated up almost to the b. p. of the solvent. The reaction was over in about two hours when the mixture became deep red and the peroxide had completely disappeared. Considerable amounts of acetaldehyde vapor came off during the reaction. The solvent was then removed under reduced pressure and the residue dissolved in glacial acetic acid. Aliquot parts of this were analyzed for anisaldehyde by precipitating the latter as the *p*-nitrophenylhydrazone in accordance

(4) Riesenfeld, *Ber.*, **41**, 3536 (1908); Machu, "Wasserstoffperoxyd und die Perverbindungen." Verlag von Julius Springer, Wien, 1937, p. 240.

(5) Milas, *THIS JOURNAL*, **49**, 2005 (1927).

(6) Meyer and Pawletta, *Z. angew. Chem.*, **39**, 1284 (1926); Rumpf, *Compt. rend.*, **200**, 317 (1935).

(7) Moissan, *ibid.*, **97**, 96 (1883); Bancroft and Murphy, *J. Phys. Chem.*, **39**, 377 (1935).

(8) Ciamician and Silber, *Ber.*, **44**, 1283 (1911).

(9) Böeseken, *Rec. trav. chim.*, **45**, 555 (1926).

with the method described elsewhere.¹⁰ The yield of anisaldehyde amounted to 55%. A small amount of the *p*-nitrophenylhydrazone was recrystallized twice from glacial acetic acid; m. p. 159–160°. Ciusa and Vecchiotti¹¹ give 160° as the m. p. of this phenylhydrazone. In addition to anisaldehyde some anisic acid was isolated from the reaction, and a small amount of a deep red solid which is presumably an addition product of vanadium pentoxide with anisaldehyde.¹²

Another experiment was performed in which the catalyst was 0.02 g. of chromium trioxide. The solution heated up within a short time to almost the b. p. of the solvent. After about one hour the reaction was over when the mixture became deep brown and a small amount of the chromic oxide separated out. As before, the mixture was analyzed for anisaldehyde and found to have only 13.7% of it.

Piperonal from Isosafrole.—Five grams of isosafrole (Eastman Kodak Company) was mixed with 45 cc. of the peroxide reagent and to the mixture was added 0.02 g. of vanadium pentoxide. As the catalyst dissolved, the mixture heated up as before to almost the b. p. of the solvent. The reaction was over in about two hours when the mixture was still blood red due perhaps to the presence of the addition complex between vanadium pentoxide and piperonal.¹² The yield (67.4%) of piperonal, in this case, was also estimated by precipitating its *p*-nitrophenylhydrazone.¹⁰ This *p*-nitrophenylhydrazone was recrystallized twice from 95% ethyl alcohol, m. p. 202–203°. An authentic sample prepared and purified in the same way had a m. p. of 203–203.5°; mixed m. p. showed no depression.

In another experiment in which 0.02 g. of chromium trioxide was used as the catalyst, the yield of piperonal was only 14%.

Vanillin from Isoeugenol.—Five grams of isoeugenol (Eastman Kodak Company) was mixed with 45 cc. of the peroxide reagent and 0.02 g. of vanadium pentoxide. As in the case of the experiments with the other two essential oils, the catalyst went into solution, which heated up but not as much as in the two previous cases. The reaction was complete in about twelve hours when the mixture had become more intensely red.¹² An analysis for the presence of vanillin by precipitating the *p*-nitrophenylhydrazone¹⁰ gave a yield of 66% of vanillin.

The above experiment was then repeated using 0.02 g. of chromium trioxide as the catalyst. When the product was worked up, a yield of 58.3% of vanillin was obtained.

(10) Milas, *THIS JOURNAL*, **52**, 744 (1930).

(11) Ciusa and Vecchiotti, *Gazz. chim. ital.*, **42**, I, 532 (1912).

(12) Tunmann and Rosenthaler, *Pflanzenmikrochemie*, 334 (1931).

Phenol from Benzene.—Fifteen and six-tenths grams of benzene (thiophene-free) was mixed with an equimolecular quantity of the peroxide reagent and 0.04 g. of vanadium pentoxide. The catalyst went slowly into solution which, after a few hours, acquired a blood red color. At the end of twenty-four hours, the reaction was complete, the red color had disappeared and the catalyst separated out as a dark green precipitate. The mixture was then filtered, the filtrate fractionated to remove the solvent and unused benzene (13 g.), the residue dissolved in water, and the amount of phenol estimated by precipitating the insoluble tribromophenol. Two and nine-tenths grams of tribromophenol was obtained corresponding to 30% yield of phenol calculated on the basis of the amount of benzene used. A sample of tribromophenol was recrystallized from dilute alcohol, m. p. 93°, and showed no depression upon mixing with an authentic sample of tribromophenol.

When the foregoing experiment was repeated using 0.04 g. of chromium trioxide as the catalyst, only 12.1% of phenol was obtained in spite of the fact that a larger amount (4.1 g.) of benzene was utilized. In addition to phenol, the residue from this experiment contained a dark solid which failed to dissolve in water, but was soluble in dilute alkali showing that it was probably a polyphenol. This was separated before the estimation of phenol was made in the sample.

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Summary

1. Hydrogen peroxide in anhydrous tertiary butyl alcohol and in the presence of vanadium pentoxide or chromium trioxide effects the oxidation (hydroxylation) of a number of unsaturated substances.

2. Trimethylethylene glycol was obtained from trimethylethylene; diethyl racemate from diethyl fumarate; anisaldehyde and anisic acid from anethole; piperonal from isosafrole; vanillin from isoeugenol; and phenol from benzene.

3. In all of the cases described, the catalytic reactions seem to proceed through the intermediate formation of the unstable peracids of the catalysts used; *e. g.*, pervanadic and perchromic acids.

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