traction of the ethereal solution with 5% sodium hydroxide and careful neutralization of the extract of 0–5° gave 5.8 g. (29%) of a yellow solid, melting at 35–37°. The solid changed to an oil again on standing, probably due to some oxidation to the disulfide. The mercaptan was dissolved in dilute sodium hydroxide and treated with an alcoholic solution of iodine until coloration due to iodine was evident. Filtration gave the disulfide of *o*-mercaptodiphenylamine; m.p. 161–162° (lit.,[12] 162°).

Anal. Calcd. for $C_{24}H_{20}N_2S_2$: S, 16.02. Found: S, 15.92, 15.81.

Neutralization of the hydrochloric acid extract gave no insoluble material.

Water dilution of the methanolic extract gave a light yellow solid which melted from 45–50°. Recrystallization from dilute ethanol gave 0.74 g. (4.4%) of diphenylamine melting at 51–52°; a mixed melting point with an authentic specimen showed no depression.

Run II. Run I was repeated, except that the reaction mixture was carbonated rather than hydrolyzed. Following the evaporation of the carbon dioxide the residue was extracted with sodium bicarbonate solution, then with dilute sodium hydroxide. No acid was obtained from the bicarbonate solution. Neutralization of the sodium hydroxide extract gave 6.7 g. (33.5%) of *o*-mercaptodiphenylamine, melting at 35–37°C; a mixed melting point with a sample from Run I was not depressed. No diphenylamine was isolated, but a 37.2% recovery of phenothiazine was obtained.

Run III. Run I was repeated employing anhydrous ether as a solvent rather than dioxane. The only material isolated was 16.0 g. (80.5% recovery) of phenothiazine.

Lithium cleavage of 10-ethylphenothiazine. Run I. 10-Ethylphenothiazine (11.2 g., 0.05 mole) and 0.8 g. (0.115 g. atom) of lithium were refluxed with 100 ml. of purified dioxane for 15 hr. as described above. Color Test I[3] was negative throughout the reaction. The reaction mixture was cooled and carbonated. The resulting mixture was acidified with 5% hydrochloric acid and the layers separated. The ether layer was extracted with an 8% sodium bicarbonate solution. Careful acidification of the cooled extract gave no solid product. The ethereal solution was then extracted with 10% sodium hydroxide solution. Neutralization gave 2.7 g. of a yellow-brown oil (24% if the product was *o*-mercaptodiphenylethylamine). Attempts to prepare the disulfide yielded a tan, gummy material which defied purification. The residual ether solution was evaporated and the residue recrystallized thrice from ethanol to give 3.5 g. (30.7% recovery) of 10-ethylphenothiazine; m.p. and mixed m.p. 100–102°. Neutralization of the original hydrochloric acid layer gave no precipitate.

Run II. Run I was repeated using 0.23 g. atom of lithium rather than 0.115 g. atom. A 33% yield of the mercaptan and a 28.6% recovery of 10-ethylphenothiazine were obtained. Again no diphenylethylamine was obtained.

Attempted lithium cleavage of carbazole. Run I. A mixture of 16.7 g. (0.1 mole) of carbazole and 4.0 g. (0.57 g. atom) of lithium in 200 ml. of purified dioxane was stirred and refluxed for 24 hr. The mixture was cooled and then poured over cracked ice. The resulting white solid (15.5 g., 93% recovery) was found to be carbazole; m.p. 239–243°. A mixed melting point determination with an authentic sample showed no depression.

Run II. Run I was repeated except that only 0.32 g. atom of lithium was employed and that the reaction mixture was carbonated instead of being hydrolyzed. Intermittent Color Test I[3] was negative. The reaction mixture was worked up as described above for the reaction with 10-ethylphenothiazine. The only product isolated was carbazole (88% recovery); m.p. and mixed m.p. 239–242°.

Attempted lithium cleavage of 9-ethylcarbazole. Run I. 9-Ethylcarbazole (19.5 g., 0.1 mole) and 2.0 g. (0.29 g. atom) of lithium were refluxed with 200 ml. of purified dioxane for 14 hr. The mixture was filtered through a glass wool plug into another flask and carefully hydrolyzed with a 1:1 water-dioxane solution. The addition of more water precipitated 16.0 g. (82% recovery) of 9-ethylcarbazole, melting at 63–66°. A mixed melting point determination with an authentic sample showed no depression.

Run II. Run I was repeated using 3.2 g. (0.46 g. atom) of lithium and a reflux time of 24 hr. Hydrolysis of the cooled reaction mixture gave a 95% recovery of 9-ethylcarbazole; m.p. and mixed m.p. 69–70°.

Run III. Run II was repeated except that the reaction mixture was carbonated instead of being hydrolyzed. The only product was 19.0 g. (97% recovery) of 9-ethylcarbazole; m.p. and mixed m.p. 69–70°.

Hydriodic acid cleavage of 10-ethylphenothiazine. To 11.35 g. (0.05 mole) of 10-ethylphenothiazine was added 50 ml. (0.275 mole) of 47% hydriodic acid. The mixture was heated to a moderate reflux and there maintained for 72 hr. with occasional shaking. The odor of hydrogen sulfide was evident throughout the reaction. After cooling, the yellowish solid was filtered off. Recrystallization from dilute ethanol gave 8.5 g. (85.9%) of phenothiazine; m.p. and mixed m.p. 186–187.5°. The original filtrate was extracted with ether and the extract evaporated to give only a very small amount of dark tar. The residual aqueous layer was made alkaline with sodium hydroxide to give 0.2 g. of white solid which did not melt at temperatures up to 365°. The material was insoluble in acetone, but soluble in cold 6*N* hydrochloric acid.

Attempted hydriodic acid cleavage of 9-ethylcarbazole. A mixture of 9.75 g. (0.05 mole) of 9-ethylcarbazole and 50 ml. (0.275 mole) of 47% hydriodic acid was refluxed gently for 72 hr. The only product isolated was 9.7 g. (99% recovery) of 9-ethylcarbazole; m.p. and mixed m.p. 68–70°.

A second experiment gave almost identical results.

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Thermal Rearrangement of Benzoylmeconic Acid

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The chemistry of meconic acid, 3-hydroxy-4-pyrone-2,6-dicarboxylic acid (I), is very obscure and no reactions are recorded in which nuclear substitution of the compound has been effected.

There are reports, however, of the nuclear substitution of its partially decarboxylated derivative, comenic acid. Verkade[1] has described the partial decarboxylation of meconic acid with hydrochloric acid and has proven that the carboxyl lost during the reaction is from the position adjacent to the hydroxyl since the resulting comenic acid reacts with diazobenzene acetate. This indicates the presence in the compound of a methylene group which could only be located in the 2 position. The bromination of meconic acid also results

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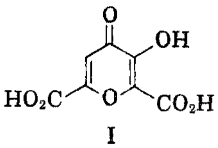
[12] A. I. Kiprianov and I. K. Ushenko, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 2201 (1947) [*Chem. Abstr.*, **42**, 5016 (1948)].

[1] P. E. Verkade, *Rec. trav. chim.*, **43**, 879 (1924).

in partial decarboxylation with the bromine taking the position vacated by the lost carboxyl.[2]



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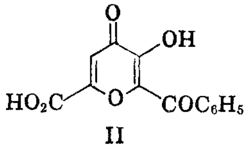

II

The experiments recorded in this report furnish proof that acylation of the pyrone ring can be accomplished from the phenolic ester of meconic acid by thermal rearrangement in which the acyl radical probably takes the position vacated by the carboxyl under the forcing conditions described. The 2-benzoylcomenic acid (II) thus formed is phenolic as indicated by the reaction with ferric chloride, and its ketonic nature is proved by the reaction with 2,4-dinitrophenylhydrazine. The fact that the bis-phenacyl ether ester derivative could be formed from the pyrone acid is additional proof of the postulated structure.

3-Benzoxychelidonic acid (benzoylmeconic acid) has been prepared to ascertain the properties of the substance before decarboxylation and rearrangement.

Confirmatory evidence that the disruptive forces of partial decarboxylation are responsible for the rearrangement is found in the fact that 3-benzoxycomenic acid from comenic acid, when heated at the same temperature over the same time interval, failed to produce the rearrangement.

An examination of the infrared spectrum shows most of the absorption peaks to be in about the expected positions. Only in the case of carbonyl and carboxyl absorption were unexpected values given. The presence of three different kinds of carbonyls, namely, carboxyl, pyrone, and benzoyl, greatly influence the absorption of each other. As a consequence the band with a peak at 1685 cm.$^{-1}$ broadens out to overlap 1725 cm.$^{-1}$ which is the carboxyl absorbing area exhibited by meconic acid.

EXPERIMENTAL[3]

2-Benzoylcomenic acid [II]. Twenty grams of meconic acid and 15 ml. benzoyl chloride were mixed in a 500 ml. flask which was fitted with an air cooled condenser to which was attached a gas trap. The mixture was heated at 145° for 24 hr. in a Fisher High-Temp oil bath. At the end of the reaction period 100 ml. of water was added and the white solid was filtered off. The yield was quantitative. The analytical sample was recrystallized 3 times from absolute ethanol.

The sample thus purified was placed in a vacuum sublimator and any sublimate collected at 160° or below was discarded. The residue was removed from the sublimator and again recrystallized from ethanol. The melting point was determined by the capillary tube method using Dow Corning 550 silicone oil. The compound rapidly discolored above 270° and was completely decomposed at 284°.

A sample of the purified substance gave a red-purple color with a 1 percent solution of ferric chloride.

Anal. Calcd. for $C_{15}H_8O_6$: C, 60.00; H, 3.09. Found: C, 60.38; H, 2.89.

Infrared data. The infrared spectrum was observed with a Perkin-Elmer Infrared Spectrophotometer Model 21 on a Nujol mull/capillary. Two peaks were observed for hydroxyl absorption at 3530 and 3380 cm.$^{-1}$ Other absorption bands observed were C=O at 1685, —C=C— 1642, and benzenoid ring at 1500 cm.$^{-1}$

The 2,4-dinitrophenylhydrazone of II was prepared by permitting 1 g. of II, 1 g. of 2,4-dinitrophenylhydrazine and 20 drops of concentrated hydrochloric acid to reflux for 5 min. with 50 ml. absolute ethanol. The mixture was filtered while hot into 50 ml. of water. A chocolate colored precipitate was obtained which was recrystallized once from absolute ethanol, m.p. 189–194° (dec.).

Anal. Calcd. for $C_{19}H_{12}N_4O_9$: N, 11.33. Found: N, 11.52.

Clemmensen reduction. Five grams of II was refluxed with 100 ml. of 6*N* hydrochloric acid and 20 g. of amalgamated zinc for 6 hr. The mixture was then filtered while hot and allowed to cool. Nearly 4 g. of crystals was obtained. The analytical sample was obtained by fractional sublimation of the material. The first half of the sample obtained by vacuum sublimation was discarded. The residue was then completely sublimed to a white compound, m.p. 119–121°.

An alcoholic solution of the compound gave a purple coloration with a dilute solution of ferric chloride.

Anal. Calcd. for $C_{13}H_{10}O_5$: C, 63.41; H, 4.09. Found: C, 63.19; H, 4.32.

3-Benzoxychelidonic acid. Three grams of meconic acid and 5 ml. benzoyl chloride were refluxed for 2 hr. in 100 ml. of dry benzene.

During the reaction a white insoluble powder was formed which, after the benzene solution had cooled, was filtered off. Recrystallizing the powder from ethanol produced hard chalky white rosettes which appeared to soften above 245°. As the temperature was raised above 260° there developed yellow spots which had decomposed at 269° to brown or black. This compound had no effect upon ferric chloride solutions.

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.27; H, 2.65. Found: C, 55.01; H, 2.49.

Bis-phenacyl derivative. Two grams of II, 1 g. of sodium bicarbonate and 5 ml. of water were allowed to react. To this mixture was then added 2 g. of phenacyl bromide and 90 ml. absolute ethanol. After refluxing the material for 2 hr., it was made just acid with concentrated hydrochloric acid and filtered while hot. Storage in the refrigerator permitted pale yellow needles to separate. Recrystallization of the precipitate from absolute ethanol gave colorless needles, m.p. 119–121°.

Anal. Calcd. for $C_{29}H_{20}O_8$: C, 70.15; H, 4.06. Found: C, 70.02; H, 4.19.

3-Benzoxy comenic acid. Two g. of commercial meconic acid was heated in an open flask overnight at 155° immersed in a Fisher High-Temp oil bath. The resulting chalky white comenic acid was analyzed without further processing.

Anal. Calcd. for $C_6H_4O_5$: C, 46.12; H, 2.58. Found: C, 46.30; H, 2.69.

The comenic acid produced above, with the exception of the few milligrams removed for analysis, was treated with 3 g. of benzoyl chloride and the mixture was heated at 145° for 24 hr. The resulting product was a black viscous mass. The material was very soluble in alcohol and benzene. The compound was taken up in boiling heptane from which white curds precipitated on chilling. The air dried material consisted of white microscopic prisms, m.p. 112–114°.

Anal. Calcd. for $C_{15}H_8O_6$: C, 60.00; H, 3.09. Found: C, 59.79; H, 3.21.

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[2] *Beilstein's Handbuch der organischen Chemie*, 4th Ed., Vol. 18, p. 503.

[3] All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J., and all melting points were determined on a Fisher-Johns melting point assembly, unless indicated otherwise.

Acknowledgment. The author acknowledges with gratitude the assistance given by Dr. J. D. Edwards of the Veteran's Administration Hospital, Houston, Tex., and the Perkin Elmer Corp. for preparing infrared spectrograms. The author wishes to thank the Research Corp. for the financial support without which this study would not have been possible.

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Some Reactions of 2,6-Dimethyl-4-pyrone

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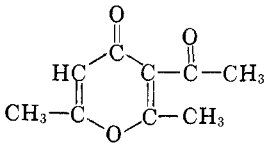

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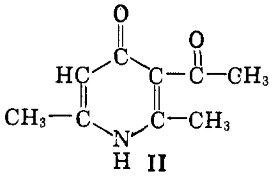

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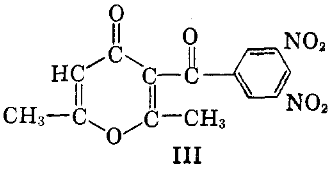

III

A continuing study of the fundamental chemistry of 4-pyrones has led to an examination of the reactivity of 2,6-dimethyl-4-pyrone, which offers the signal advantage of being easily prepared from dehydroacetic acid,[1] but is a pyrone of considerable stability with both of the reactive 2- and 6-positions filled.

Numerous experiments have been attempted to ascertain with what reagents the compound would react and the first of these was found to be mercuric chloride. Since the mercurated pyrone was found to retain its mercury very tenaciously other avenues of nuclear substitution were sought.

The hydroxylation method of Tickle[2] was reviewed with the idea that an improvement of the procedure might offer a means of procuring enough 2,6-dimethyl-3-hydroxy-4-pyrone to serve as source material for further experimentation. However, in the author's hands so little of the compound was obtained that the reactions reported could not be confirmed. Modification of this experiment produced a pyrone-peroxide whose structure has not, as yet, been established. However, the fact that the pyrone undergoes direct mercuration indicates the presence of at least a measure of aromatic character.

In attempts to uncover other aromatic substitutions, a considerable number of methods of acylation were attempted using fuming stannic chloride, polyphosphoric acid, boron trifluoride etherate, and hydroiodic acid as catalysts. All were failures. The Crafts reaction with acetic anhydride was found, however, to effect acetylation in low yield.

2,6-Dimethyl-3-acetyl-4-pyrone (I) has a melting point very near that of 2,6-dimethyl-4-pyrone and cannot be separated from it by solvents; only fractional vacuum sublimation gave reasonable results. The preparation of the lutidone (II) and its 2,4-dinitrophenylhydrazone confirms the structure of I.

Since the previously described experiments have shown that acylation can be accomplished on the pyrone, many methods were tried in an attempt to improve yields and produce a crude compound of relatively high purity. The use of fused zinc chloride as a catalyst at the elevated temperatures furnished by refluxing xylene as a solvent makes possible the easy accomplishment of both objectives as described in the preparation of 2,6-dimethyl-3-(3,5-dinitrobenzoyl)-4-pyrone (III).

EXPERIMENTAL[3]

Mercuration of 2,6-dimethyl-4-pyrone. A mixture of 6.2 g. of 2,6-dimethyl-4-pyrone, 27.1 g. of mercuric chloride and 50 ml. of absolute ethanol was heated under reflux until all the reactants had gone into solution. The mixture was thoroughly chilled and the precipitate was filtered off and air dried. Recrystallization of the crude substance twice from absolute ethanol produced pale yellow needles, m.p. 150–151°. Treatment of this substance with acids, bicarbonates or subliming it failed to remove the mercury.

Anal. Calcd.: for $C_7H_8HgCl_2O_2$: C, 21.25; H, 2.03; Cl, 17.91. Found: C, 20.58; H, 1.82; Cl, 18.22.

Since the analytical results do not agree with the calculated values for the above compound, another run was made and the product recrystallized four times from ethanol. The analysis was C, 20.59; H, 1.69; Cl, 18.15. Obviously, the material was a pure compound with such constancy of composition and no change of melting point, but not of postulated structure.

Peroxide of 2,6-Dimethyl-4-pyrone. To a mixture of 40 ml. of 50% hydrogen peroxide and 30 ml. of water containing ten drops of concentrated sulfuric acid was added 18.6 grams of 2,6-dimethyl-4-pyrone.

The mixture was allowed to stand at room temperature until all the pyrone had dissolved and then gently warmed to 30–40° for 0.5 hr. Storage of the sample in the refrigerator for 24 hr. produced 16.7 g. of white prisms. Five g. of the above sample was heated under reflux with benzene in an all-glass assembly fitted with a Dean-Stark water separator for 90 min. Upon cooling of the benzene solution about 3 g. of heavy spars of the pyrone-peroxide crystallized out, m.p. 95–96.5°, very slow heating.

The peroxide exhibits a peculiar color reaction with dilute solutions of ferric chloride in that a purple color develops after about 10 min., persists for nearly 2 hr. and then gradually fades. Solutions of potassium iodide were slightly discolored by the compound only upon long standing.

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.16. Found: C, 54.06; H, 5.45.

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(1) F. Feist, *Ann.*, **257**, 253 (1890).

(2) T. Tickle, *J. Chem. Soc.*, **81**, 1004 (1902).

(3) All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J. All melting points were determined on a Fisher-Johns melting point assembly.