amount of benzoyl peroxide were mixed and the solution allowed to reflux for four hours as its temperature increased from 75 to 190°. The material was then distilled, and the 71 g. of distillate collected up to 190° at 50 mm. was fractionally redistilled in vacuum. Thirty-eight grams (42% yield) of low melting solid was obtained, b.p. 125–130° (15 mm.). The product appears to be largely a mixture of the monochlorides.

Anal. Calcd. for $C_8H_{12}ClBr$: mmoles of halogen per g. 8.95; for $C_8H_{11}Cl_2Br$: 11.63. Found: 9.17, 9.32.

Reaction of Monochloro-2-bromobicyclo[2,2,2]octane with Potassium *t*-Amyloxide.—One hundred grams of *t*-amyl alcohol in which 11 g. (0.29 mole) of potassium had been dissolved and 22.2 g. (0.1 mole) of monochloro-2-bromobicyclo[2,2,2]octane was refluxed in a 200-ml. flask attached to a gas collection apparatus. After 40 hours about 400 ml. of gas, shown by its infrared spectrum to be ethylene, had been evolved. A titration at this time showed that 0.164 mole of base had been used up. The reaction mixture was shaken with water and the organic layer separated, dried and fractionally distilled. When the *t*-amyl alcohol had been removed the pot temperature rose above 170° without the distillation of any additional material.

Bicyclo[2,2,2]-2,5-octadiene.—Twenty grams (0.51 mole) of potassium and 250 ml. of aniline were placed in a three-necked flask equipped with a vapor-tight stirrer, thermometer, dropping funnel and Claisen distilling head leading through a condenser, receiver and drying tube to a gas collection apparatus. The system was swept with nitrogen and the aniline heated to reflux to dissolve the potassium. Then 38 g. (0.17 mole) of monochloro-2-bromobicyclo[2,2,2]-octane in about 20 ml. of aniline was added slowly to the gently refluxing solution. Some material distilled during the addition of the chlorobromide, and when the addition was complete distillation was continued until the distillate temperature reached 170°. The distillate was washed with cold hydrochloric acid to remove the aniline and then dried over Drierite and fractionally distilled. At about 30° (155 mm.), 4 g. (30% yield) of benzene was collected and at 59–61° (155 mm.), 1.5 g. (8% yield) of product was obtained. One liter of gas (24% yield), shown by its infrared spectrum to be ethylene containing a little acetylene, also was produced in the reaction.

The product of this and other similar preparations was found to have the properties: b.p. 126–127° (atm.), $n^{23.5}D$ 1.4912, d^{32}_4 0.9171.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.54; H, 9.54.

Reactions of Bicyclo[2,2,2]-2,5-octadiene (II).—Bromine was added to II until the red color was no longer discharged, and the resultant oil was cooled in Dry Ice until it crystallized. The crystals were washed with ethanol, recrystallized from ether–ethanol and then from hexane to yield white crystals, m.p. 103–103.5°.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.56; H, 2.37; Br, 75.07. Found: C, 22.79, 22.75; H, 2.49, 2.52; Br, 74.71, 74.76.

When II was refluxed alone, in decalin or in aniline in which potassium had been dissolved for a time (30 minutes) longer than that which had been used in its synthesis, little, if any, gas was formed. However, when about 0.2 g. of II was refluxed under nitrogen so that the vapor came in contact with a wire coil heated to a dull red color, about 25 ml. of gas, shown by its infrared spectrum to be ethylene containing a little acetylene, was produced. The first few drops of distillate from the remaining liquid was shown, also by its infrared spectrum, to contain benzene.

Compound II was found to require 2.0 ± 0.2 moles of hydrogen for complete reduction. The white crystalline product had an infrared spectrum identical to the bicyclo-[2,2,2]octane prepared by reduction of bicyclo[2,2,2]-2-octene.[30]

Infrared Spectra.—The infrared spectra were determined using a Perkin–Elmer instrument, model 21. Samples were run in a 0.1-mm. cell and those run in solution were compensated with pure solvent in the same size cell.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Seven-membered Ring Compounds. IX. Benzosuberoneglyoxylates

BY C. L. ANDERSON,[1] W. J. HORTON, F. E. WALKER[1] AND M. R. WEILER

RECEIVED JULY 6, 1954

Additional examples of enol lactone formation in the condensation of dimethyl oxalate with 1,2,3-trimethoxy-, 1-methyl- and 2,3-dimethylbenzosuberone in contrast to the normal condensation with 1,4-dimethoxy- and 1,4-dimethylbenzosuberone confirm the importance previously assigned to the substituent in position 4.

The sodium methoxide-catalyzed condensation of dimethyl oxalate with benzosuberone was previously reported[2] to yield the expected methyl glyoxylate (Ia) in the case of 2,3,4-trimethoxybenzosuberone (IIa) whereas 2,3-dimethoxy-, 8-methyl- and benzosuberone itself under the same conditions gave enol lactones similar to III.

In the present work, five additional substituted benzosuberones have been prepared and condensed with methyl oxalate. Those benzosuberones with a methoxyl or a methyl group in the 4-position formed methyl glyoxylates whereas those with hydrogen in the 4-position formed enol lactones.

The desired benzosuberones were obtained by a series of steps starting with acylation of 1,4-dimethoxy-, 1,2,3-trimethoxy-, 1,2-dimethyl- and 1,4 - dimethylbenzenes, respectively, with γ-carbethoxybutyryl chloride.[3] The aroylbutyric acids obtained were reduced to the corresponding valeric acids and these on treatment with polyphosphoric acid gave the benzosuberones IIb, IId, IIe and IIf. 1-Methylbenzosuberone was prepared from *o*-tolualdehyde by a published method.[4]

The known 1,4-dimethylbenzosuberone[5] (IIf) was of particular interest in that heretofore enol lactone formation in the glyoxylation reaction had been blocked only by methoxyl groups. Caution concerning the structure of this 1,4-dimethylbenzosuberone is indicated due to the reported cases of migration of groups in hot polyphosphoric acid cyclizations.[6] 1,4-Dimethylbenzosuberone gave a glyoxylate which was an oil. Since the known methyl benzosuberoneglyoxylates all melt below 120° with one reported as an oil[2] whereas the enol lactones are higher melting solids, all being above 112°, the product in this case is formulated as If. The py-

---

[1] Taken in part from the Master's Dissertation and the Doctoral Dissertation of C. L. Anderson and F. E. Walker, respectively.

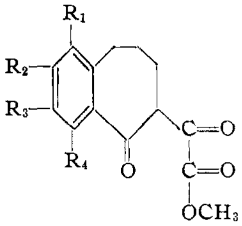
[2] W. J. Horton, C. E. Hummel and H. W. Johnson, THIS JOURNAL, **75**, 944 (1953).

[3] D. Papa, E. Schwenk and H. Hankin, *ibid.*, **69**, 3021 (1947).

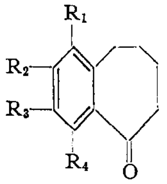
[4] P. D. Gardner, W. J. Horton, G. Thompson and R. R. Twelves, *ibid.*, **74**, 5527 (1952).

[5] R. G. Kadesch, *ibid.*, **66**, 1212 (1944).

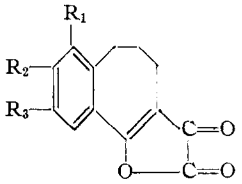
[6] W. L. Mosby, *ibid.*, **74**, 2564 (1952); *J. Org. Chem.*, **18**, 485 (1953).



Ia, $R_2, R_3, R_4 = OCH_3$; $R_1 = H$
Ib, $R_1, R_4 = OCH_3$; $R_2, R_3 = H$
Ic, $R_1, R_2, R_3 = OCH_3$; $R_4 = H$
Id, $R_1 = CH_3$; $R_2, R_3, R_4 = H$
Ie, $R_2, R_3 = CH_3$; $R_1, R_4 = H$
If, $R_1, R_4 = CH_3$; $R_2, R_3 = H$



IIa, $R_2, R_3, R_4 = OCH_3$; $R_1 = H$
IIb, $R_1, R_4 = OCH_3$; $R_2, R_3 = H$
IIc, $R_1, R_3, R_4 = OCH_3$; $R_2 = H$
IId, $R_1, R_2, R_3 = OCH_3$; $R_4 = H$
IIe, $R_2, R_3 = CH_3$; $R_1, R_4 = H$
IIf, $R_1, R_4 = CH_3$; $R_2, R_3 = H$
IIg, $R_1 = CH_3$; $R_2, R_3, R_4 = H$



IIIa, $R_1, R_2, R_3 = H$
IIIb, $R_1, R_2, R_3 = OCH_3$
IIIc, $R_1 = CH_3$; $R_2, R_3 = H$
IIId, $R_2, R_3 = CH_3$; $R_1 = H$

rolysis of this glyoxylation product is in accord with this methyl glyoxylate structure since gas evolution proceeded smoothly and an oil, apparently a β-keto ester, was produced. An attempt to obtain analytical data on the pyrolysis product was thwarted by slight decomposition of the compound to 1,4-dimethylbenzosuberone on distillation. This pyrolysis behavior is unlike that found in the case of the enol lactone of benzosuberone-6-glyoxylic acid (IIIa) which formed tar unless methanol[2] or benzyl alcohol[7] was used.

It seems likely on the basis of the above work that the glyoxylation of 4-substituted benzosuberones is governed by the size of the group in the 4-position and that groups other than methoxy or methyl will be found to prevent enol lactone formation.

The assistance of grants from the Utah Chapter of Sigma Xi, the University Research Fund, and the National Science Foundation are gratefully acknowledged.

Experimental[8]

γ-2,5-Dimethoxybenzoylbutyric Acid.—The acylation of 1,4-dimethoxybenzene with γ-carbethoxybutyryl chloride was carried out as described[3] with the addition of an equimolar portion of dimethyl sulfate prior to the saponification. The product (80%) melted at 78–98.5°; reported[9] m.p. 98–100°.

Acylation in polyphosphoric acid[10] at 71° for 2.5 hours followed by saponification gave γ-2,5-dimethoxybenzoylbutyric acid (28%), m.p. 96–100.5°.

δ-2,5-Dimethoxyphenylvaleric Acid.—A solution of 3.47 g. of the above aroylbutyric acid in methanolic hydrogen chloride (from 5 cc. of acetyl chloride and 60 cc. of anhydrous methanol) was refluxed for 24 hours. After distillation of the methanol 3.04 g. of pale tan crystals, m.p. 46–50°, were obtained from benzene–petroleum ether (60–70°). The crude ester was evaporatively distilled onto a seeded cold finger at 100–120° (bath temperature) and 0.1 mm. and after two crystallizations from petroleum ether (30–60°) the short thick prisms melted at 48–50°.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.85. Found: C, 62.79; H, 6.85.

The methyl ester (2.49 g., 9.37 mmoles) in 50 cc. of acetic acid was reduced with 0.5 g. of palladium–carbon at 70° under 30 lb. hydrogen pressure.[11] The product after removal of the solvent and catalyst was saponified yielding 1.6 g. (6.72 mmoles, 71.8%) of grayish crystals, m.p. 34–41.5°.

The Clemmensen reduction[12] of 12.6 g. (0.496 mole) of γ-2,5-dimethoxybenzoylbutyric acid, m.p. 71–91°, with remethylation using 4.7 cc. (0.05 mole) of dimethyl sulfate gave 5.8 g. (0.024 mole, 49%), b.p. 141–160° (0.15 mm.). By moistening with petroleum ether (60–90°) and seeding, 3.83 g. of colorless crystals, m.p. 42–46°, was obtained. After purification with petroleum ether the product melted at 47–48.5°.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.27; H, 7.67.

The **amide** formed fine colorless needles from cyclohexane m.p. 69.5–70.5°.

Anal. Calcd. for $C_{13}H_{19}O_3N$: C, 65.80; H, 8.07. Found: C, 65.47; H, 7.87.

1,4-Dimethoxybenzosuberone (IIb).—A mixture containing 4.4 g. (0.018 mole) of the above valeric acid in 120 g. of polyphosphoric acid (360 g. of phosphorus pentoxide in 230 cc. of 85% phosphoric acid) was held at 60° for 1 hour. It was then treated as described.[13] The neutral oil (2.24 g., 0.0102 moles; 55%) solidified to oily crystals at −20°. After sublimation at 220–240° (bath temperature) (28 mm.) and crystallization from cyclohexane, colorless groups of blunt needles, m.p. 57–59°, were obtained. Cyclization at 95° for 2 hours gave only polymer.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.63; H, 7.37.

The **oxime** sublimed at 105° (0.1 mm.) and melted at 165–169.5°.

Anal. Calcd. for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.29. Found: C, 66.12; H, 7.22.

Methyl 1,4-Dimethoxybenzosuberone-6-glyoxylate (Ib).—The reaction of 1.25 g. (5.68 mmoles) of the above suberone as described[2] gave a light orange solid insoluble in the reaction mixture. On acidification of the ice-cold aqueous solution of this material 1.42 g. (4.64 mmoles, 81.7%), m.p. 99–106°, was obtained. Extensive recrystallization from benzene gave long bright yellow prisms, m.p. 118.5–119.5°, giving an instantaneous brownish red ferric chloride test. The compound could be crystallized without change from methanol.

Anal. Calcd. for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.83; H, 5.93.

1,2,3-Trimethoxybenzosuber-5-ene-5-ol-6-glyoxylic Acid Lactone (IIIb).—1,2,3-Trimethoxybenzosuberone[14] (4.0 g., 0.016 mole), b.p. 134–136° (0.22 mm.), condensed with dimethyl oxalate[2] gave a precipitate in the reaction mixture on standing for 35 hours. The product dissolved slowly in cold 2% sodium hydroxide and reappeared on acidification as a canary yellow solid changing to orange on air drying, 3.59 g. (0.0118 moles, 73.7%), m.p. 73–82°. It gave an immediate wine red ferric chloride test and dissolved in aqueous sodium bicarbonate with gas evolution. The material in benzene was evaporated to dryness and heated 1 hour on the water-bath. From cyclohexane orange crystals, m.p. 105–110°, were obtained with a 48% recovery.

---

[7] W. J. Horton, H. W. Johnson and J. L. Zollinger, THIS JOURNAL, **76**, 4587 (1954).

[8] Melting points are uncorrected.

[9] G. D. Shah and K. S. Norgund, *J. Univ. of Bombay, Sect. A*, **15**, No. 21, 19 (1947); *C. A.*, **42**, 1911g (1948).

[10] We are greatly indebted to Dr. P. D. Gardner for communications prior to publication of his procedure for intermolecular acylation in polyphosphoric acid: P. D. Gardner, THIS JOURNAL, **76**, 4550 (1954).

[11] E. C. Horning and D. B. Reisner, *ibid.*, **71**, 1036 (1949).

[12] E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 166.

[13] R. C. Gilmore and W. J. Horton, THIS JOURNAL, **73**, 1411 (1951).

[14] J. Koo, *ibid.*, **75**, 1891 (1953).

Further purification using cyclohexane gave IIIb, red orange crystals, m.p. 112–114.5°.

Anal. Calcd. for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.42; H, 5.58.

In a similar run using 2.65 g. (0.0102 mole) of the suberone the deep yellow crystals obtained from the reaction mixture were not heated on the steam-bath for 1 hour. The material (2.50 g., 7.77 mmoles, 76%), m.p. 55.5–60°, resisted purification with benzene–cyclohexane and was extracted from a benzene solution with 2% sodium hydroxide. Acidification of the aqueous solution with cooling gave **1,2,3-trimethoxybenzosuberone-6-glyoxylic acid**, m.p. 64.5–66°, which produced an immediate dark amber color with ferric chloride.

Anal. Calcd. for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63. Found: C, 59.53; H, 5.95.

The compound changed to an orange oil if held at room temperature and reduced pressure for several hours.

Methyl 1,2,3-Trimethoxybenzosuberone-6-glyoxylate (Ic).—When 20.0 g. (0.062 mole) of the above glyoxylic acid in 20 cc. of methanol was brought to the boiling point, the acid dissolved. On cooling, 18.4 g. (0.0548 mole, 89%) was obtained. From methanol containing a small amount of water yellow crystals, m.p. 84.5–85.5°, giving an immediate red brown ferric chloride test were obtained.

Anal. Calcd. for $C_{17}H_{20}O_7$: C, 60.70; H, 5.99. Found: C, 60.72; H, 5.93.

Ethyl γ-2,4,5-Trimethoxybenzoylbutyrate.—Acylation[10] of 1,2,4-trimethoxybenzene[15] (0.025 mole) with 0.035 mole of γ-carbethoxybutyric acid and 58 g. of phosphorus pentoxide–phosphoric acid for 2.5 hours at 45° gave a light apple green solid (7.71 g.). After treatment with 5% sodium bicarbonate 4.85 g. (0.015 mole, 62.6%) of slightly grey crystals, m.p. 71–76°, was obtained. After six crystallizations from benzene–cyclohexane the short thick prisms melted at 75.5–82° and did not depress the melting point of material recovered from an unsuccessful permanganate oxidation of this same compound. The recovered material from aqueous acetone and from dilute methanol formed colorless broad prismatic plates, m.p. 80–82°.

Anal. Calcd. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.75; H, 7.30.

From the bicarbonate solution above, 1.32 g. (4.68 mmoles, 18.7%) of **γ-2,4,5-trimethoxybenzoylbutyric acid**, m.p. 135–157°, was obtained. Crystallization from methanol–benzene (carbon) gave colorless crystals, m.p. 157.5–163.5°. This acid, m.p. 161.5–163°, was also obtained by alkaline saponification of the ethyl ester. After four crystallizations from methanol–acetone it formed long thin rods, m.p. 162–164°. The compound was negative to ferric chloride.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.55; H, 6.42.

The **methyl ester** prepared with methanolic hydrogen chloride in 87% yield melted at 92–94°. From benzene–petroleum ether (60–70°) long thick rods, m.p. 90.5–92.5°, were formed.

Anal. Calcd. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 61.28; H, 6.74.

The methyl ester (5.04 g., 0.017 mole) was reduced with palladium–carbon under 30 lb. pressure as described above. The product after alkaline saponification crystallized on cooling overnight. The acidic product was reprecipitated from 5% sodium bicarbonate by acidification as nearly colorless crystals (4.41 g., 0.0165 mole, 97%), m.p. 61–64° and m.p. 63–67°, crystallized from water. It crystallized from petroleum ether (60–70°)–acetone but melted at room temperature and 0.4 mm. pressure. The tests with ferric chloride and dinitrophenylhydrazine were negative.

This supposed δ-2,4,5-trimethoxyphenylvaleric acid (probably a hydroxy acid) resisted cyclization by phosphorus pentoxide–phosphoric acid when heated on the water-bath for 30 minutes. After 2 hours the product obtained could not be crystallized and gave a green color with ferric chloride.

1-Methylbenzosuberone (IIg).—Freshly distilled *o*-tolualdehyde[16] (3.0 g., 0.025 mole), 9.3 cc. of ethylidenemalonic ester in 35 cc. of absolute ethanol and 10 g. of potassium hydroxide gave by the procedure described,[4] with crystallization from methanol–benzene, 4.9 g. (0.021 mole, 85%) of bright yellow **2-methylcinnamylidenemalonic acid** decomposing at 197°. After four crystallizations from methanol–benzene the decomposition point was unchanged.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.24; H, 5.22.

By catalytic reduction[4] **γ-2-methylphenylpropylmalonic acid**, m.p. 110–119.5°, was obtained in quantitative yield. Crystallization from methanol gave colorless crystals, m.p. 120–123°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.19; H, 6.76.

The decarboxylation of 4.7 g. (0.020 mole) of the malonic acid was complete after 20 minutes at 180° (20 mm.). The material boiling at 179° (12 mm.) (2.9 g., 75%) was recrystallized four times from methanol–benzene, m.p. 58.5–59.5°.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.91; H, 8.25.

The product from the decarboxylation of 5.0 g. (0.021 mole) as above without distillation was combined with 162 g. of polyphosphoric acid and held at 130–140° for 4 hours. After dilution with ice and water and standing at 5° overnight, the brown solid obtained was warmed with aqueous sodium bicarbonate and then weighed 3.25 g. (0.0186 mole, 89%), m.p. 55–59°. It was distilled (b.p. 88–94° (0.27–0.13 mm.) and crystallized four times from cyclohexane to give colorless crystals, m.p. 57–58°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.00; H, 8.22.

The **oxime**, crystallized from cyclohexane, melted at 129.5–130.5°.

Anal. Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99. Found: C, 75.51; H, 7.84.

1-Methylbenzosuber-5-ene-5-ol-6-glyoxylic Acid Lactone (IIIc).—Reaction of 2.32 g. (0.0133 mole) of 1-methylbenzosuberone (IIg) with dimethyl oxalate as described[2] gave a cherry red benzene solution containing only a small amount of solid. The orange colored product weighed 1.33 g. (5.8 mmoles, 44.5%), melted at 157–162.5° dec. and gave a slowly developing dark red color with alcoholic ferric chloride. Purification from ethyl acetate gave diamond shaped prisms, m.p. 161–163° dec.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.44; H, 5.22.

Methyl 1-Methylbenzosuberone-6-glyoxylate (Id).—A solution of 0.34 g. (1.49 mmoles) of the lactone IIIc in 5 cc. of methanol warmed briefly and stored at −20° overnight, gave after washing with petroleum ether (60–70°), 0.37 g. (1.42 mmoles, 96%) of Id, m.p. 59–63°. Repeated crystallization from petroleum ether (60–70°) gave long thin nearly colorless prisms, m.p. 58–62°. These gave an instantaneous dark red color with ferric chloride.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.11; H, 6.31.

2,3-Dimethylbenzosuberone (IIe).—From 35 g. (0.33 mole) of *o*-xylene and 22.3 g. (0.125 mole) of γ-carbethoxybutyryl chloride as above,[3] 13.4 g. (0.061 mole, 49%) of **γ-3,4-dimethylbenzoylbutyric acid** was obtained. After three crystallizations from dilute ethanol and one each from cyclohexane and from benzene, the colorless long microscopic prisms melted at 117–118°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.84; H, 7.07.

Reduction[12] of the above gave **δ-3,4-dimethylphenylvaleric acid**, m.p. 42–63°, in quantitative yield. A portion was sublimed at 120–130° (bath temperature) and 0.27 mm. and crystallized from petroleum ether (60–90°) whereupon long colorless prisms, m.p. 65–66°, were obtained.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.66; H, 8.42.

The crude reduced acid (8.0 g., 0.039 mole) in 60 g. of polyphosphoric acid at 95° for 2 hours gave 4.2 g. of IIe (0.022 mole, 56%), b.p. 181.4–184° (20 mm.), m.p. 38–50°. After two crystallizations from cyclohexane–petroleum ether (60–90°) clumps of colorless prisms, m.p. 49–50.5°, were obtained.

---

[15] W. Baker, E. H. T. Jukes and C. A. Subrahmanyam, *J. Chem. Soc.*, 1684 (1934).

[16] M. Sommelet, *Compt. rend.*, **157**, 852 (1913).

Anal. Calcd. for $C_{18}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.10; H, 8.55.

The **oxime**, sublimed at 105° (0.1 mm.), formed short thick prisms, m.p. 146–150° (inserted at 140°).

Anal. Calcd. for $C_{13}H_{17}ON$: C, 76.81; H, 8.43. Found: C, 77.06; H, 8.45.

2,3-Dimethylbenzosuber-5-ene-5-ol-6-glyoxylic Acid Lactone (IIId).—As before,[2] 2.82 g. (0.015 mole) of the suberone IIe was treated with dimethyl oxalate. In contrast to the previous case,[2] pale yellow silky crystals began to separate in the reaction mixture after 10 minutes. The usual treatment[2] gave 1.3 g. (5.37 mmoles, 36%) of golden yellow broad prisms from ethyl acetate, m.p. 168–168.5° dec., becoming orange at 146°. The compound was insoluble in 5% sodium bicarbonate and gave a slowly developing red brown color with ferric chloride. After four crystallizations from ethyl acetate the yellow long thin prisms melted at 167.5–168 5° dec., turning orange at *ca.* 140°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.27; H, 5.82.

Methyl 2,3-Dimethylbenzosuberone-6-glyoxylate (Ie).—The solution of 0.500 g. (2.06 mmoles) of IIId in 3 cc. of methanol was complete after warming for 5 minutes. After 10 minutes the solution was concentrated and cooled to −20°. The methanol washed product weighed 0.54 g. (1.97 mmoles, 96%), melted at 94–94.5° and gave an immediate dark red ferric chloride test. Four crystallizations from methanol gave nearly colorless short thick prisms, m.p. 94–96°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.06; H, 6.58.

1,4-Dimethylbenzosuberone[5] (IIf).—The acylation of *p*-xylene as described[3] gave γ-2,5-dimethylbenzoylbutyric acid, b.p. 165–170° (0.23 mm.). From petroleum ether (60–90°) material, m.p. 54–68° (72%), was obtained; reported[5] m.p. 72–73°. Reduction[12] gave δ-2,5-dimethylphenylvaleric acid[5] (87.7%) which was cyclized by polyphosphoric acid at 95° for 35 minutes to yield (67%) 1,4-dimethylbenzosuberone, b.p. 110–112° (1.2 mm.); reported[5] b.p. 121–131° (1 mm.).

Methyl 1,4-Dimethylbenzosuberone-6-glyoxylate (If).—The described treatment[2] with 6.3 g. (0.033 mole) of IIf and dimethyl oxalate gave a precipitate in the benzene solution. After 20 hours at room temperature the dark red solution contained only a few crystals. The usual treatment produced an orange red oil (9.0 g., 0.033 mole, 98%) unchanged by heating 1 hour on the steam-bath at 0.6–0.25 mm. It gave an immediate wine red color with ferric chloride.

On heating the orange red oil at 180° decarbonylation occurred and the residue then distilled as a colorless oil, b.p. 109–121° (0.35 mm.). Redistillation gave a faintly yellow middle portion b.p. 110–114° (0.15 mm.) which gave a deep purple color with alcoholic ferric chloride. Repeated distillation with analysis of the center cut gave consistently high results for **methyl 1,4-dimethylbenzosuberone-6-carboxylate** indicating partial decomposition to the suberone.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 77.23; H, 7.79.

SALT LAKE CITY 1, UTAH

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Aromatic Nitro Compounds with Polynuclear Hydrocarbons at Elevated Temperatures

BY CHARLES D. HURD AND LESLIE H. JUEL

RECEIVED JULY 19, 1954

Anthracene and 1-nitronaphthalene react at about 300° to give as the principal product 7,12-dihydro-7,12-*o*-benzenobenz[a]anthracene. Its structure is established by independent synthesis. The mechanism by which it is formed is thought to involve a diene synthesis, followed by elimination of the elements of nitrous acid, the latter undergoing reduction to nitric oxide. Several derivatives of the hydrocarbon have been prepared which include a mononitro derivative, an acetyl derivative, and adducts with picric acid, *sym*-trinitrobenzene and 2,4,7-trinitrofluorene. Naphthacene has been condensed with 1-nitronaphthalene to give 7,14-dihydro-7,14-*o*-benzenobenz[a]naphthacene, the reaction being analogous to that between anthracene and 1-nitronaphthalene. Anthracene and 2-methylanthracene were condensed with 1,4-dihydronaphthalene, and the resulting adducts were dehydrogenated to yield 5,12-dihydro-5,12-*o*-benzenonaphthacene and its 2-methyl derivative, respectively. A new synthesis of 1,2-dihydronaphthalene has been developed involving the reduction of 1-naphthol to 1,2,3,4-tetrahydro-1-naphthol in alkaline media and in the presence of nickel catalyst followed by dehydrogenation of the secondary alcohol in the presence of hydrochloric acid.

This investigation grew out of an observation made at Great Lakes Carbon Corporation and communicated to us by Charles L. Thomas, namely, that the softening point and viscosity of coal tar pitch or pitch fractions could be raised by heating a mixture of the pitch and 1-nitronaphthalene to about 175° for an extended period of time, whereas admixture at lower temperatures merely caused lowering of melting point and viscosity. The high temperature effect pointed to a chemical reaction.

As a starting point for the elucidation of this problem we selected anthracene as a component in coal tar which might be expected to undergo this type of thermal reaction with 1-nitronaphthalene and, indeed, such a reaction was observed on heating the mixture at about 300° for 10–15 hours. The principal product was a white, crystalline hydrocarbon, $C_{24}H_{16}$, melting at 209°. It underwent Friedel–Crafts acetylation to yield a ketone $C_{24}H_{15}COCH_3$, nitration to yield $C_{24}H_{15}NO_2$, and oxidation by chromic anhydride in acetic acid to produce both anthraquinone and carbon dioxide. Picric acid, *sym*-trinitrobenzene and 2,4,7-trinitrofluorenone all formed adducts with this hydrocarbon, the first two on a 1:1 basis and the last 2:1. Hydrogen at 265° and 100 atm., in the presence of a copper-on-alumina catalyst promoted cleavage into naphthalene and dihydroanthracene, although yields were small. A boiling chloroform solution of the hydrocarbon was not changed by bromine and iron, conditions which are known to cause nuclear bromination of toluene.

Of the three most plausible structures (I, II, III), 9-α-naphthylanthracene (I) seemed unlikely because of the evolution of carbon dioxide on oxidation and the non-bromination. To decide between 5,12-dihydro-5,12-*o*-benzenonaphthacene (II) and 7,12-dihydro-7,12-*o*-benzenobenz[a]anthracene (III), their syntheses were planned. The lower analog, 9,10-dihydro-9,10-*o*-benzenoanthracene