of lead tetraacetate (calculated on the basis of an assay with iodide and thiosulfate). The mixture usually was heated under reflux for 3 hours, and then cooled and poured into water. The aqueous solution was extracted with ether, and the extracts washed with water and aqueous sodium or potassium carbonate. It was found that the use of 5% aqueous sodium hydroxide as a wash in some cases caused hydrolysis of the acetate esters in the products. The ether extracts were evaporated to dryness and the pure product usually obtained by recrystallization from ethanol.

Reaction of Sodium Hydroxide with 2,4,6-Trimethyl-*o*-quinolbenzenesulfonimide Acetate.—A suspension of 0.5 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate in 20 ml. of 15% aqueous sodium hydroxide was heated under reflux for 3 hours and allowed to cool and stand overnight. A small amount of solid was removed by filtration and discarded. The filtrate upon acidification with concentrated hydrochloric acid yielded 0.25 g. (57.3%) of pale yellow solid. Recrystallization from dilute ethanol gave pure product, m.p. 180–181.5°.

Anal. Calcd. for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.86; H, 5.93; N, 5.02.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

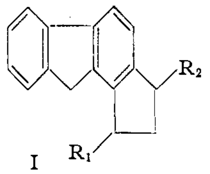
1,2-Cyclopentenofluorene. Part II[1]

BY ERNST D. BERGMANN AND RAPHAEL IKAN

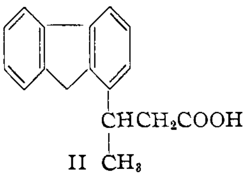
RECEIVED MARCH 10, 1958

For comparsion with the dehydrogenation products of cevine and jervine, 1′-methyl- and 1′,3′-dimethyl-1,2-cyclopentenofluorene, 1,2-cyclohexenofluorene and 1,2-dimethylfluorene have been synthesized. All these substances have very similar spectra. It is not impossible that the dehydrogenation products in question are 1,2-benzofluorene derivatives.

In order to test the current hypothesis that the dehydrogenation of cevine and jervine leads to derivatives of 1,2-cyclopentenofluorene, thus involving the transformation of a six- to a five membered ring, the parent substance (I, $R_1 = R_2 = H$) and its 3′-methyl derivative (I, $R_1 = H$; $R_2 = CH_3$) had been synthesized.[1] The two hydrocarbons resembled in their spectrum closely the above dehydrogenation products, but were not identical with them. In the present communication, the 1′-methyl derivative (I, $R_1 = CH_3$; $R_2 = H$) and the 1′,3′-dimethyl compound (I, $R_1 = R_2 = CH_3$) have been prepared. From the chloride of fluorene-1-carboxylic acid and dimethylcadmium, 1-acetylfluorene has been obtained. Its condensation with ethyl cyanoacetate, followed by hydrolysis, partial decarboxylation and catalytic hydrogenation led to β-(1-fluorenyl)-butyric acid (II); an alternative method consists in the reaction of 1-acetylfluorene with ethyl bromoacetate and zinc, followed by dehydration and catalytic reduction. Cyclization of II gave 3′-keto-1′-methyl-1,2-cyclopentenofluorene (III) which by reduction gave (I, $R_1 = CH_3$, $R_2 = H$) and by reaction with methylmagnesium iodide and subsequent hydrogenation yielded (I, $R_1 = R_2 = CH_3$). The melting points of these two hydrocarbons (71 and 82°, respectively) were not identical with that of any of the compounds isolated from the dehydrogenation products of cevine and jervine.[1] The absorption spectra were very similar to those reported for these dehydrogenation products; this was in accordance with the observations made in our previous communication.[1]



I



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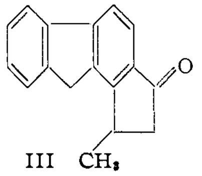
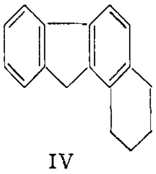
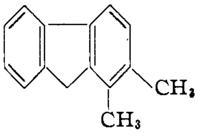


III



IV



V

Winkler and Reichstein[2] have suggested that the ultraviolet absorption spectra cannot be expected to differentiate between 1,2-cyclopentenofluorene and other 1,2-alkyl derivatives of fluorene. In order to substantiate this suggestion, 1,2-cyclohexenofluorene (IV) and 1,2-dimethylfluorene (V) have been synthesized; obviously, a compound like IV would not be formed in the dehydrogenation of a polycyclic natural product.

The previously described[1] β-(1-fluorenyl)-propionic acid was converted by an Arndt–Eistert reaction into γ-(1-fluorenyl)-butyric acid (VI) and the latter cyclized to 4′-keto-1,2-cyclohexenofluorene (VII). Reduction by the method of Huang-Minlon gave IV as a well-crystallized substance. For the synthesis of the liquid 1,2-dimethylfluorene (V) a method was applied which recently has been developed in our laboratories[3]: 2,3-dimethylbenzoic acid was prepared from *o*-xylene by a 4-step synthesis (over-all yield, 21%) and its chloride condensed with cyclohexene. (2,3-Dimethylbenzoyl)-cyclohexene (VIII) was then isomerized by means of a mixture of phosphoric and formic acid[4] to 5,5a,6,7,8,8a-hexahydro-2,3-dimethylfluorenone (IX) and the latter dehydrogenated to 2,3-dimethylfluorenone. Reduction by the method of Huang-Minlon gave V.

In Table I, the spectra of the compounds prepared in this study are compared with that of the dehydrogenation product $C_{24}H_{30}$ obtained by Craig

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[1] Part I, E. D. Bergmann and R. Ikan, THIS JOURNAL, **78**, 2921 (1956). In this paper, the melting point of 1,2,3,4-tetrahydrofluorene-1-carboxylic acid had been omitted; it is 168°.

[2] R. E. Winkler and T. Reichstein, *Helv. Chim. Acta*, **37**, 721 (1954); *cf.* F. Korte, *Ber.*, **88**, 1527 (1957).

[3] E. D. Bergmann, *Bull. Res. Council Israel*, **6A**, 150 (1955–1956).

[4] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 2208 (1953).

TABLE I

ULTRAVIOLET SPECTRA (mμ log ε)) IN ETHYL ALCOHOL

$C_{24}H_{30}$	I, R_1 = R_2 = H	I, R_1 = H, R_2 = CH_3	I, R_1 = CH_3, R_2 = H	I, R_1 = R_2 = CH_3	IV	V	X[a]
270(4.40)	270(4.62)	270(4.30)	269(4.40)	270(4.38)	270(4.46)	265(4.45)	263(4.86)
287(4.20)	282(4.46)	284(4.16)	284(4.23)	284(4.22)	280(4.20)	284(4.11)	285(4.10)
295(3.85)	292(4.10)	291(3.78)	293(3.82)	293(3.70)	291(3.78)	293(3.40) (inflection)	296(4.20)
300(3.70)	303(3.96)	303(3.62)	305(3.66)	304(3.64)	303(3.79)	303(3.75) (inflection)	306(4.18)
308(3.65)	319(2.38)	310(3.20)					316(4.14)

[a] In addition, peaks have been reported at 254 mμ (4.67), 327 mμ (3.36) and 345 mμ (3.09).

and Jacobs[5] from cevine (see also Figs. 1 and 2).

It is suggested that the compounds in question are not derivatives of 1,2-cyclopentenofluorene (I, R_1 = R_2 = H), but of 1,2-benzofluorene (X). It is obviously more likely that this system is formed in a dehydrogenation reaction than I. The spectrum of X[6] therefore has been included in Table I, and experiments on the synthesis of methylated 1,2-benzofluorenes are now in progress.

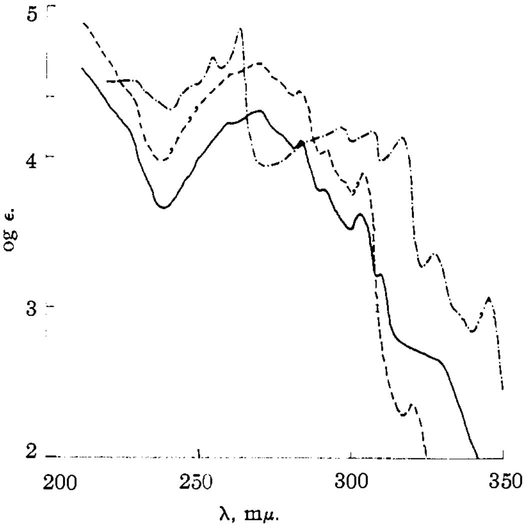


Fig. 1.—Ultraviolet spectra of 1,2-cyclopentenofluorene (I, R_1 = R_2 = H), ---------; 3′-methyl-1,2-cyclopentenofluorene (I, R_1 = H, R_2 = CH_3), ———; and 1,2-benzofluorene (X), ---.---.; all in 95% ethanol.

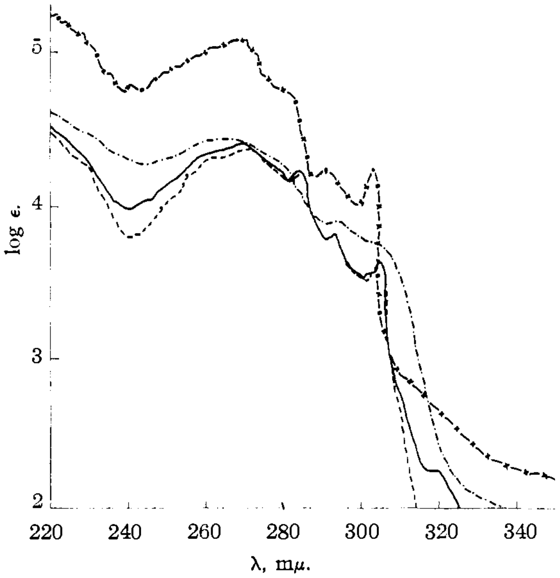
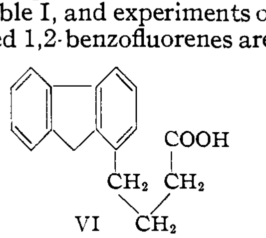
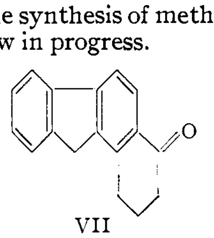


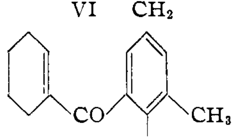
Fig. 2.—Ultraviolet spectra of 1′-methyl-1,2-cyclopentenofluorene (I, R_1 = CH_3, R_2 = H), ———; 1′,3′-dimethyl-1,2-cyclopentenofluorene (I, R_1 = R_2 = CH_3), ---------; 1,2-dimethylfluorene (V), -.-.-.; and 1,2-cyclohexenofluorene (IV), -x-x-x; all in 95% ethanol.



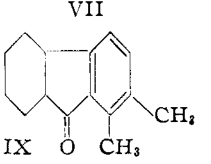
VI



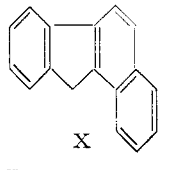
VII



VIII



IX



X

Experimental

1-Acetylfluorene.—At 0°, 1.63 g. of cadmium chloride was added to a Grignard solution prepared from 0.4 g. of magnesium and 2.4 g. of methyl iodide. The mixture was refluxed for 45 minutes and the ether evaporated and replaced by 60 ml. of dry benzene. At the temperature of 25° a solution of 3.3 g. of fluorene-1-carboxylic acid chloride[1] in 20 ml. of benzene was added during 15 minutes and the product again refluxed for 1 hour. Decomposition with ice and dilute sulfuric acid, extraction with ether and distillation yielded an oil (b.p. 165° (0.8 mm.)) which crystallized spontaneously. From isopropyl alcohol colorless rods, m.p. 88–89°, yield 2.2 g. (73%), were obtained; $\lambda_{\max}^{\mathrm{EtOH}}$ 253 mμ (log ε 4.47), 321 mμ (3.71).

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.4; H, 5.8. Found: C, 86.2; H, 5.6.

Ethyl α-Cyano-β-(1-fluorenyl)-crotonate.—A mixture of 3 g. of ethyl cyanoacetate, 4 g. of 1-acetylfluorene, 1 ml. of glacial acetic acid, 1 ml. of piperidine and 20 ml. of benzene was subjected to azeotropic distillation. The mixture was diluted with 100 ml. of ether, washed with sodium bicarbonate solution and water and distilled; b.p. 175° (0.02 mm.), yield 4.7 g. (80%).

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(5) L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **129**, 79 (1939); **139**, 263 (1941).

(6) G. R. Clemo and D. G. I. Felton, *J. Chem. Soc.*, 1660 (1952); M. Orchin and R. A. Friedel, THIS JOURNAL, **71**, 3002 (1949); see also F. Bandow, *Z. physik. Chem.*, **196**, 329 (1951); A. B. Klevens, *J. Chem. Phys.*, **18**, 1063 (1950).

Anal. Calcd. for $C_{20}H_{17}NO_2$: N, 4.6. Found: N, 4.6.

β-(1-Fluorenyl)-crotonic Acid.—(a) A mixture of 4 g. of the foregoing ester with 20 ml. of concentrated hydrochloric acid was refluxed for 25 hours and evaporated *in vacuo* to dryness. The residue was recrystallized from nitromethane and gave needles of m.p. 152°, yield 1.5 g. (45%).

(b) A mixture of 9.3 g. of 1-acetylfluorene, 14.9 g. of ethyl bromoacetate, 5.9 g. of mossy zinc (activated with a trace of iodine) and 50 ml. of benzene was heated gently until the reaction set in. When it had subsided (30 minutes), the mixture was refluxed for 30 minutes and decomposed with ice and dilute sulfuric acid. Ether was added and the organic layer washed with 5% sodium hydroxide solution, water, 10% sulfuric acid and again with water and dried over sodium sulfate. The solvents were evaporated and the residue heated *in vacuo* at 120° for a few minutes. The remaining reddish oil (9.8 g.) was then heated with 10 g. of powdered potassium hydrogen sulfate at 200° for 2 hours. Extraction with ether, treatment of the ethereal solution with 10% sodium hydroxide solution and water, drying and distillation gave 9 g. (97%) of *ethyl β-(1-fluorenyl)-crotonate* b.p. 162–163° (0.02 mm.), $n^{13}{}_D$ 1.6150, $d^{13}{}_4$ 1.330; λ_{max}^{EtOH} 265 mμ (4.58), 300 mμ (3.84).

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5; *MR*, 72.88. Found: C, 81.5; H, 6.6; *MR*, 72.94.

The ester (9 g.) in methanol (30 ml.) was refluxed for 3 hours with a solution of 3.6 g. of potassium hydroxide in 10 ml. of water. The methanol was driven off *in vacuo* and the acid, liberated by acidification, extracted with ether. The ether residue crystallized and was purified by recrystallization from nitromethane; m.p. 152°, yield 8.2 g. (98%); λ_{max}^{EtOH} 257 mμ (4.52), 300 mμ (3.72); ν_{max}^{KBr} 1680, 1625 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.3; H, 5.7.

β-(1-Fluorenyl)-butyric Acid (II).—A solution of 8 g. of the foregoing acid in 100 ml. of anhydrous dioxane was hydrogenated in the presence of 200 mg. of platinum oxide at 3 atmospheres pressure and elevated temperature. The reaction was complete within 45 minutes. The filtered solution was concentrated *in vacuo* and the residue recrystallized from nitromethane. Needles of m.p. 127°, yield 8 g. (quantitative), ν_{max}^{KBr} 1700 cm.$^{-1}$, were obtained.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.9; H, 6.8.

3′-Keto-1′-methyl-1,2-cyclopentenofluorene (III).—A mixture of 2 g. of II and 60 g. of polyphosphoric acid was heated at 100° for 2 hours and the red mass poured onto 100 g. of ice. Extraction with ether and evaporation of the solvent gave a solid product which was recrystallized from isopropyl alcohol and formed needles of m.p. 132°, yield 1.6 g. (86%), λ_{max}^{EtOH} 309 mμ (4.47).

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.1; H, 6.0. Found: C, 87.3; H, 6.0.

1′-Methyl-1,2-cyclopentenofluorene (I, $R_1 = CH_3$, $R_2 = H$).—A mixture of 600 mg. of III, 0.7 g. of powdered potassium hydroxide, 2 ml. of hydrazine hydrate (85%) and 10 ml. of diethylene glycol was subjected to the Huang-Minlon reduction. The product was diluted with 50 ml. of water, acidified with hydrochloric acid and extracted with chloroform. The hydrocarbon was purified by distillation *in vacuo* (b.p. 145–150° (0.2 mm.)) and recrystallization from methanol; needles of m.p. 71°, yield 0.5 g. (88%).

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.3.

1′,3′-Dimethyl-1,2-cyclopentadienofluorene.—A solution of 500 mg. of III in benzene was added slowly to the Grignard solution, prepared from 0.7 g. of magnesium and 4.2 g. of methyl iodide. The mixture was refluxed for 3 hours and worked up as usual. The crude product was dissolved in toluene and subjected to azeotropic distillation in the presence of 1 g. of anhydrous oxalic acid. Then the solution was washed with alkali and water, dried and evaporated, and the residue recrystallized from 80% acetic acid to give needles of m.p. 125–126°, yield 470 mg. (95%); λ_{max}^{EtOH} 297 mμ (4.46), 322 mμ (4.30).

Anal. Calcd. for $C_{18}H_{16}$: C, 93.0; H, 7.0. Found: C, 93.2; H, 6.8.

1′,3′-Dimethyl-1,2-cyclopentenofluorene (I, $R_1 = R_2 = CH_3$).—A solution of 450 mg. of the preceding hydrocarbon in 50 ml. of anhydrous ethanol was hydrogenated in the presence of 150 mg. of platinum oxide. The residue of the filtered solution solidified spontaneously and was recrystallized from methanol; needles of m.p. 82°, yield quantitative.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 92.2; H, 7.8.

Chloride of β-(1-Fluorenyl)-propionic Acid.—From 2 g. of the acid[1] and 5 ml. of freshly distilled thionyl chloride, the acid chloride was prepared at reflux temperature (3 hours); it was purified by distillation *in vacuo* (b.p. 210° (1 mm.)) and crystallized from benzene in prisms of m.p. 73°, yield 1.7 g. (79%).

Anal. Calcd. for $C_{16}H_{13}ClO$: C, 74.8; H, 5.1. Found: C, 74.6; H, 5.6.

γ-(1-Fluorenyl)-butyric Acid (VI).—A solution of 1.5 g. of the acid chloride in 50 ml. of ether was added at −10° to an ethereal solution of 5 g. of diazomethane. After 12 hours at room temperature, the ether was removed *in vacuo*; the diazoketone (1.5 g.) melted at 79–80°. It was dissolved in 5 ml. of dry benzyl alcohol and 5 ml. of γ-collidine and the solution brought into an oil-bath, which had been heated at 180°. Within 10 minutes, the liberation of nitrogen ceased. The product was cooled, dissolved in 50 ml. of ether and washed with hydrochloric acid (5%) and water. After evaporation of the ether, the reaction product was dissolved in 20 ml. of methanol and hydrolyzed with 1 g. of potassium hydroxide in 5 ml. of water for 5 hours at boiling temperature. The solvents were evaporated *in vacuo*, and the residue was diluted with 20 ml. of water and extracted with ether. Acidification gave the desired acid VI, which was recrystallized from glacial acetic acid and formed leaflets of m.p. 154°, yield 1.2 g. (80%), ν_{max}^{KBr} 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.7; H, 6.5.

4′-Keto-1,2-cyclohexenofluorene (VII).—A mixture of 1 g. of VI and 30 g. of polyphosphoric acid was heated for 2 hours at 100° and worked up as usual. From isopropyl alcohol, needles of m.p. 195°, yield 0.65 g. (72%), λ_{max}^{EtOH} 309 mμ (4.44), were obtained.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.1; H, 6.0. Found: C, 87.2; H, 6.2.

1,2-Cyclohexenofluorene (IV).—The method of Huang-Minlon was applied to a mixture of 500 mg. of VII, 5 ml. of diethylene glycol, 0.7 g. of powdered potassium hydroxide and 1.5 ml. of hydrazine hydrate (85%). The product was recrystallized from methanol and formed needles of m.p. 130–131°, yield 0.4 g. (85%).

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.7; H, 7.2.

2,3-Dimethylnitrobenzene.[7]—At 25°, a mixture of 120 g. of sulfuric acid (80%) and 117 g. of nitric acid (d. 1.42) was added to 170 g. of *o*-xylene and 180 g. of 80% sulfuric acid during 60 minutes; the stirring was continued for 30 more minutes and the mixture poured onto ice and extracted with ether. The extract was washed with 10% sodium hydroxide solution, dried and distilled; b.p. 131° (20 mm.), yield 200 g. (82%).

2,3-Dimethylaniline.—A solution of 80 g. of 2,3-dimethylnitrobenzene in 150 ml. of anhydrous ethanol was hydrogenated in the presence of 2 g. of 10% palladium–charcoal, at ordinary temperature and under a pressure of 3 atmospheres; b.p. 114° (20 mm.), yield 60 g. (94%).[8]

2,3-Dimethylcyanobenzene.—A solution of 60 g. of the amine in 127 ml. of concentrated hydrochloric acid and 127 ml. of water was diazotized at 0° with 36 g. of sodium nitrite in 75 ml. of water, and the resulting solution added during 30 minutes to a 85° hot solution of cuprous cyanide, prepared from 98 g. of copper sulfate, 78 g. of potassium cyanide and 185 ml. of water. The mixture was heated on the steam-bath for one hour and the nitrile isolated by steam distillation and extraction with ether; b.p. 80° (3 mm.), $n^{23}{}_D$ 1.5366, yield 88 g. (58%).[9]

2,3-Dimethylbenzoic Acid.[9]—The hydrolysis of 32 g. of the nitrile was accomplished by refluxing it for 8 hours with 80 g. of sodium hydroxide in 300 ml. of water and 50 ml. of methanol. The methanol was removed *in vacuo* and the

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[7] K. A. Kobe and P. W. Pritchett, *Ind. Eng. Chem.*, **44**, 1398 (1952).

[8] L. I. Smith and J. W. Opie, *J. Org. Chem.*, **6**, 427 (1941).

[9] O. Brunner, H. Hofer and R. Stein, *Monatsh.*, **63**, 79 (1933).

alkaline solution acidified, then crystallized from nitromethane, m.p. 145°, yield 17 g. (47%).

2,3-Dimethylbenzoyl chloride[9] was prepared from 16 g. of the acid, which was refluxed for 4 hours with 15 g. of thionyl chloride; b.p. 98–100° (3 mm.), yield 13 g. (68%).

(2,3-Dimethylbenzoyl)-cyclohexene (VIII).—Following the method of Christ and Fuson,[10] 10.5 g. of aluminum chloride was added (in 5 portions), at 0° and during 1 hour, to a well-agitated mixture of 13 g. of 2,3-dimethylbenzoyl chloride, 6.5 g. of cyclohexene and 50 ml. of carbon disulfide. The reaction mixture was stirred at 0° for another 6 hours, decomposed with ice and hydrochloric acid and concentrated *in vacuo*. The residue was refluxed for 3 hours with a solution of 4.4 g. of potassium hydroxide in 20 ml. of ethanol and the alcohol removed *in vacuo*. The residue was then diluted with water, extracted with ether and distilled; b.p. 133–135° (0.4 mm.), n^{26}D 1.5598, yield 9 g. (55%), ν^{liq}_{max} 1631 cm.$^{-1}$; λ^{EtOH}_{max} 255 mμ (4.20), inflection at 327 mμ (2.42).

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.6. Found: C, 83.2; H, 8.6.

The **2,4-dinitrophenylhydrazone** crystallized from isopropyl alcohol as orange needles, m.p. 155°; $\lambda^{CHCl_3}_{max}$ 258 mμ (4.45), 295 mμ (4.26), 394 mμ (4.48).

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 63.9; H, 5.6. Found: C, 63.6; H, 5.5.

1,2-Dimethyl-5,5a,6,7,8,8a-hexahydrofluorenone (IX).—A mixture of 7 g. of VIII, 17 g. of phosphoric acid (90%) and 55 g. of formic acid (98%) was kept at room temperature for 12 hours and at 85–90° for 6 hours, diluted with water and extracted with ether. The product IX was isolated by distillation *in vacuo*; b.p. 122–123° (0.15 mm.), n^{26}D 1.5633, yield 4.2 g. (60%); λ^{EtOH}_{max} 256 mμ (4.11), 291 mμ (3.40); ν^{KBr}_{max} 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.4. Found: C, 83.6; H, 8.0.

The **2,4-dinitrophenylhydrazone** crystallized from butanol as red needles, m.p. 213°, $\lambda^{CHCl_3}_{max}$ 398 mμ (4.52).

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 63.9; H, 5.6. Found: C, 64.4; H, 6.3.

1,2-Dimethylfluorenone.—A mixture of 4 g. of IX and 2 g. of sulfur was heated at 250° for 5 hours and the product extracted with benzene. It was purified by chromatography on alumina, but proved to be an oil; b.p. 127–130° (0.7 mm.), yield 3 g. (79%); λ^{EtOH}_{max} 264 mμ (4.62), 397 mμ (4.50); ν^{liq}_{max} 1715 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.7; H, 5.9.

The **2,4-dinitrophenylhydrazone** was obtained from nitromethane as orange-red crystals, m.p. 257°.

Anal. Calcd. for $C_{21}H_{16}N_4O_4$: C, 64.9; H, 4.1. Found: C, 64.3; H, 4.2.

1,2-Dimethylfluorene (V).—The hydrocarbon, obtained from 2.5 g. of 1,2-dimethylfluorenone, 1.5 g. of powdered potassium hydroxide, 1.5 ml. of hydrazine hydrate (100%) and 12 ml. of diethylene glycol, was an oil, b.p. 125–128° (2 mm.), yield 2 g. (87%).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.8; H, 7.2. Found: C, 93.1; H, 7.3.

JERUSALEM, ISRAEL

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(10) R. E. Christ and R. C. Fuson, THIS JOURNAL, **75**, 3306 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AIN SHAMS UNIVERSITY]

The Stobbe Condensation of Diethyl Phenylsuccinate with Cycloheptanone

BY A. M. ISLAM AND M. T. ZEMAITY

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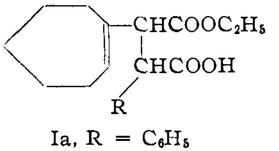
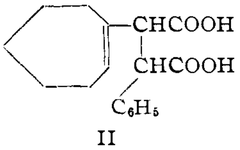
Condensation of diethyl phenylsuccinate and cycloheptanone in the presence of potassium *t*-butoxide gives β-carbethoxy-β-(cyclohepten-1-yl)-α-phenylpropionic acid (Ia). This is cyclized to 9-phenylbicyclo[5:3:0]dec-1(7)-en-8-one (IV), together with α-cycloheptenyl-β-phenylsuccinic acid (II). Saponification of Ia with alkali gives cycloheptylidenephenylsuccinic acid (IIIa).

The aim of the present investigation was to study the Stobbe condensation of diethyl phenylsuccinate with cycloheptanone in the hope of obtaining the bicyclic ketone IV.

Condensation of diethyl phenylsuccinate with cycloheptanone in the presence of sodium ethoxide gives only ethyl α-phenylhydrogensuccinate. In the presence of potassium *t*-butoxide, however, the product is almost entirely the cycloheptenyl half-ester Ia.

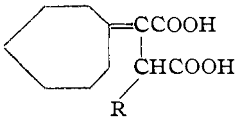


Ia, R = C_6H_5
Ib, R = H

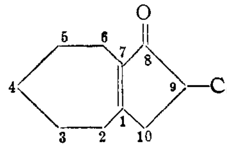


II

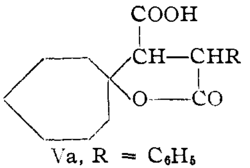
The ultraviolet absorption spectrum of Ia is very similar to that of phenylsuccinic acid and thus the double bond is pictured in the endocyclic position. This is in agreement with Stobbe's generalization[1] that compounds with methylene groups flanking the carbonyl group usually assume the pyrotartaric acid structure.



IIIa, R = C_6H_5
IIIb, R = H



IV



Va, R = C_6H_5
Vb, R = H

Treatment of this half-ester Ia with a hot mixture of acetic acid and hydrochloric acid furnishes a product which gives carbon and hydrogen figures corresponding to the three isomeric compounds II, IIIa and Va.

In contrast to Cook, *et al.*,[2] who isolated the cycloheptylidene compound IIIb together with the paraconic acid Vb on treating the half-ester Ib with acetic acid–hydrochloric acid mixture, our product is almost entirely the cycloheptenyl acid II. Its

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(1) H. Stobbe, *Ann.*, **321**, 83 (1902).

(2) J. W. Cook, R. Philip and A. R. Somerville, *J. Chem. Soc.*, 164 (1948).