STUDIES IN THE CYCLIZATION OF THE PRODUCTS OF STOBBE CONDENSATION WITH PROPIOPHENONE

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Received August 7, 1964

ABSTRACT

The isomeric mixture of the half-esters resulting from the Stobbe condensation of propiophenone with diethyl succinate is cyclized with stannic chloride as well as with sodium acetate in acetic anhydride. Cyclization of the ethyl half-ester chlorides with stannic chloride gives the keto-ester "4-carbethoxy-2-methyl-3-phenylcyclopent-2-enone." This on acid hydrolysis and decarboxylation yields 2-methyl-3-phenylcyclopent-2-enone, from which 2-methyl-3-phenylcyclopentanone is prepared by catalytic reduction. The keto-ester on Clemmensen reduction gives the corresponding unsaturated ester from which 3-methyl-2-phenylcyclopentane-1-carboxylic acid is obtained by catalytic hydrogenation and hydrolysis. 2-Methyl-3-phenylcyclopentanone and 3-methyl-2-phenylcyclopentane-1-carboxylic acid are of interest as intermediates for analogues of steroid hormones. From the latter 3-methyl-2-phenylcyclopentyl hydroxymethyl ketone and its acetate are prepared.

Cyclization of the isomeric mixture of the ethyl half-esters with sodium acetate in acetic anhydride gives methyl 4-acetoxy-1-ethyl-2-naphthoate which is converted into 1-ethyl-4-methoxy-2-naphthoic acid.

In previous studies propiophenone was shown to condense with diethyl succinate in the presence of sodium ethoxide (1) or potassium *tert*-butoxide (2) giving a quantitative yield of an oily isomeric mixture of the half-esters (I*a*, main product, and I*b* *cis* and *trans*; R = C_2H_5). Stobbe (1) was able to separate and identify the three isomeric dibasic acids (I*a*, 80% and I*b* *cis* and *trans*, 9%; R = H). In the present investigation the cyclization of this isomeric mixture of half-esters was carried out aiming to synthesise a cyclopentenone by the use of anhydrous stannic chloride as well as a mixture of fused sodium acetate in acetic anhydride as cyclizing agents. The Stobbe condensation products from alicyclic (3) and aliphatic ketones (4) give normally cyclopentenones on cyclization, but as far as we are aware, no alkyl aryl ketone products have been cyclized in this way.

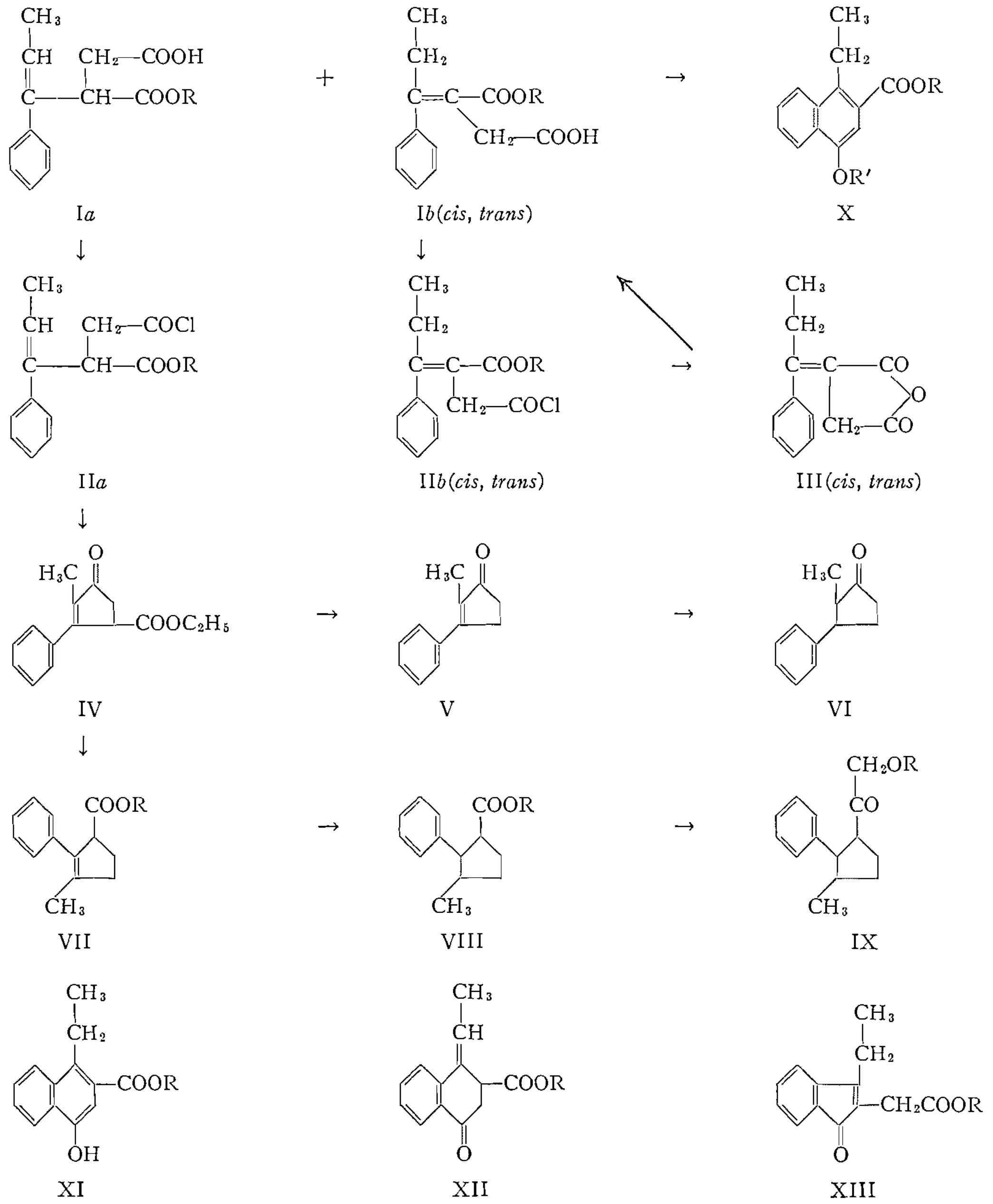
Stannic Chloride Method

The mixture of the ethyl half-esters was converted into its acid chlorides (II*a* and *b*) by the action of thionyl chloride in the presence of one molecular proportion of pyridine (5). Cyclization of the crude half-ester chlorides was achieved with anhydrous stannic chloride (4). The mixture of products thus obtained was completely neutral to carbonate but partially soluble in cold dilute sodium hydroxide solution. The alkaline solution was acidified and the solid product obtained was acidic to carbonate and melted over a wide range. This mixture when boiled with aqueous caustic soda gave a single substance which was identified as γ-ethyl-γ-phenylisoitaconic acid (I*b* *trans* Ph—CH_2COOH, R = H) (1). This result showed that the alkali-soluble fraction was exclusively the anhydride mixture (III) which was hydrolyzed by the cold alkali to the corresponding known dibasic acid mixture (I*b* *cis* and *trans*, R = H) and then converted by the boiling alkali to I*b* *trans* Ph—CH_2COOH, (R = H). This same isomerization and a similar one were previously reported (1, 6). Now the possibility of the formation of the phenolic ester (XI) can be excluded. The neutral fraction was an oil, which showed bands in the infrared region at 1 750 (m), 1 720 (s), 1 690 (s); 1 610 (m); 765 (s), and 700 (s) cm^{-1}, characteristic of the stretching frequencies of the carbonyl groups of esters, ketones, and conjugated esters and ketones; the stretching frequencies of olefinic linkages; and the bending frequencies (out of plane) of aromatic 5H atoms adjacent respectively (7, 12). It gave a single semicarbazone and one 2,4-dinitrophenylhydrazone. Theoretically, such a product may be an unsaturated γ-keto-ester which can have any one of the structures IV, XII, or XIII. Acid hydrolysis and decarboxylation of the product was effected by refluxing with a mixture of glacial acetic acid, constant-boiling hydrobromic acid, and water (8) to yield the previously reported unsaturated ketone (V), as a crystalline solid, m.p. 53–55° (cf. ref. 9*a*, *b*, *c*, *d*, m.p. 50–51°, 47–48°, 49–50°, 51–52° respectively). This ketone gave a semicarbazone, m.p. 251–253° (cf. ref. 9*b*, m.p. 238°), and a 2,4-dinitrophenylhydrazone, m.p. 232–233° (cf. refs. 9*a*, *c*, *d*, m.p. 232–233°, 232–232.5°, 218–220° respectively). Since there are some variations in the published melting points of this ketone and its derivatives, it was thought necessary to confirm its structure through oxidation with concentrated sulfuric acid and mercuric sulfate (10). Benzoic acid was found to be the only insoluble product from this experiment. This indicated that the cyclization took place on the olefinic linkage and not on the aromatic ring, giving 4-carbethoxy-2-methyl-3-phenylcyclopent-2-enone (IV) from the half-ester chloride (II*a*, R = C_2H_5). This agrees with the findings of Dahn (11) in a similar cyclization. The infrared spectrum of the unsaturated ketone showed the expected stretching frequencies at 1 700 and 1 620 cm^{-1} (cf. ref. 9*c*, *e*) and aromatic γ-CH at 765 and 700 cm^{-1}, characteristic of 5H adjacent (12) which further confirmed structure V. Both the unsaturated keto-ester and ketone showed absorption maxima in the ultraviolet spectra at 270, 243, 236 mμ (log ϵ 4.06, 4.02, 4.00), and 275 mμ (log ϵ 4.23) respectively (for the unsaturated ketone, cf. ref. 9*c* and *d*, λ_{max} 279.5, 242 mμ (log ϵ 4.013, 3.18) and 278 mμ (log ϵ 4.28) respectively; for similar compounds, cf. ref. 13, λ_{max} 276 mμ (log ϵ 4.20)).

The unsaturated ketone (V) was then hydrogenated at a platinum oxide catalyst, absorbing 1 mole of hydrogen and giving the known 2-methyl-3-phenylcyclopentanone VI (9*a*, *b*), as a colorless oil. Its infrared spectrum showed the expected stretching frequencies at 1 745 cm^{-1} and bending frequencies (out of plane) at 765 and 700 cm^{-1} (7, 12). It gave a semicarbazone, m.p. 220–221° (cf. ref. 9*b*, m.p. 209–210°) and a 2,4-dinitrophenylhydrazone, m.p. 199–200° (cf. ref. 9*a*, m.p. 203–204°).

Clemmensen reduction of the keto-ester (IV) yielded a mixture of neutral (main product) and acid fractions. The neutral fraction consisted mainly of the unsaturated ester (VII; R = C_2H_5), which on alkaline hydrolysis gave the corresponding acid (VII; R = H). This was characterized as *p*-toluidide. The acid fraction was found to be the unsaturated acid (VII; R = H), as it gave the same *p*-toluidide derivative. The structure of the unsaturated ester and its acid was inferred from their ultraviolet spectra ($\lambda_{max}^{ethanol}$ 248.5 mμ; log ϵ 3.57 and 243 mμ; log ϵ 3.58, respectively) which showed a styryl structure (14).

The unsaturated ester (VII; R = C_2H_5) was then hydrogenated with Adam's catalyst. It absorbed 1 mole of hydrogen to yield the ester (VIII; R = C_2H_5), whence alkaline hydrolysis gave the corresponding acid (VIII; R = H). 2-Methyl-3-phenylcyclopentanone (VI) and 3-methyl-2-phenylcyclopentane-1-carboxylic acid (VIII; R = H) are of interest, as they could serve as intermediates in the preparation of analogues of steroid hormones. 3-Methyl-2-phenyl-cyclopentane-1-carboxylic acid on treatment with thionyl cloride (15) yielded the corresponding acid chloride, which with diazomethane (16) gave the corresponding diazomethyl ketone. This when treated with glacial acetic acid or with 2 *N* sulfuric acid gave 3-methyl-2-phenylcyclopentyl acetoxymethyl ketone (IX, R = $COCH_3$) or 3-methyl-2-phenylcyclopentyl hydroxymethyl ketone (IX, R = H) respectively. Both compounds (IX, R = H and R = $COCH_3$) reduced ammoniacal silver

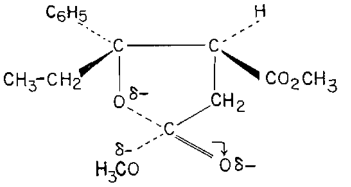


Ia, Ib(*cis*, *trans*), X, IIa, IIb(*cis*, *trans*), III(*cis*, *trans*), IV, V, VI, VII, VIII, IX, XI, XII, XIII

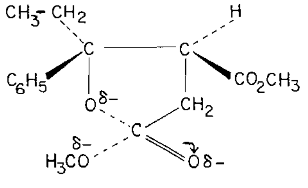
nitrate solution, and their infrared spectra showed the expected stretching frequencies at 3 600 (—OH), 1 720 ($\rangle$C=O) and 1 730 (—$COCH_2OCO$—) cm^{-1} respectively. They also showed the aromatic γ-CH at 765 and 700 cm^{-1}.

Sodium Acetate Acetic Anhydride Method

Cyclization of the crude mixture of the half-esters using fused sodium acetate in acetic anhydride (17) gave a mixture of acid and neutral fractions. The acid fraction, probably unreacted half-ester, was a viscous brownish oil, which on hydrolysis with baryta solution gave the known dibasic acid (I*a*, R = H) (1). The neutral fraction was a viscous oil and found to be ethyl 4-acetoxy-1-ethyl-2-naphthoate (X, R = C_2H_5, R′ = CH_3CO) formed from the half-ester I*b* *cis* (Ph—CH_2COOH). Trials to isolate any trace of the half-ester I*b* *trans* (Ph—CH_2COOH) were unsuccessful, indicating that it is present in a very small amount. The fact that the *cis* isomer in the *cis–trans* mixture of the alkylidene succinic half-ester (I*b*) is predominant can be explained by consideration of the two conformations which are favorable for the formation of the two intermediate paraconic esters. These two conformers are represented by XIV and XV. It is clear that the conformer XIV, which leads to the *cis* isomer, is more stable because of the eclipse of the bulky phenyl group with the small hydrogen atom (18).



XIV



XV

The crude acetoxy ester (X, R = C_2H_5, R′ = CH_3CO) on alkaline hydrolysis afforded 1-ethyl-4-hydroxy-2-naphthoic acid (X, R = R′ = H) in a higher yield than expected. Although Stobbe (1) stated that the ratio of I*a* to I*b* is 9:1, yet the above cyclization yield evokes the possibility of partial conversion of I*a* to I*b* under the conditions of the experiment. The hydroxynaphthoic acid was then treated with dimethyl sulfate and potassium carbonate in acetone to give the methoxy methyl ester (X, R = R′ = CH_3), which on alkaline hydrolysis yielded the methoxynaphthoic acid (X, R = H, R′ = CH_3) as a colorless crystalline solid.

EXPERIMENTAL*

4-Carbethoxy-2-methyl-3-phenylcyclopent-2-enone (IV)

The crude ethyl half-ester (14 g) obtained from the Stobbe condensation of propiophenone with diethyl succinate (2), in dry benzene (140 ml) was treated with pyridine (7 ml) and then redistilled thionyl chloride (6 ml) at 0° for half an hour. The benzene solution of the acid chlorides (II*a* and II*b*) was decanted from the solid cake, which was then pulverized and washed by decantation with benzene. The acid chlorides solution and washings were treated with stannic chloride (10 ml) for 15 h at 0°; the benzene solution was then poured on ice and concentrated hydrochloric acid (40 ml) and shaken. The benzene layer was separated and the aqueous layer washed with ether. The combined ether–benzene extract was washed with saturated sodium bicarbonate solution. Acidification of the bicarbonate washings gave no products. The organic layer was then extracted with cold 10% sodium hydroxide solution. Acidification of the sodium hydroxide washings with cold dilute hydrochloric acid gave a colorless solid, m.p. 158–175° (2.2 g). This mixture was completely soluble in $NaHCO_3$ solution and when refluxed in 10% sodium hydroxide solution (30 ml) for 1.5 h it gave after acidification γ-ethyl-γ-phenylisoitaconic acid (I*b* *trans* Ph—CH_2COOH, R = H), m.p. 184–185° (from water) (cf. ref. 1).

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.36; H, 5.85.

The organic layer after drying (Na_2SO_4), evaporation of the solvents, and distillation gave 4-carbethoxy-2-methyl-3-phenyl-cyclopent-2-enone, IV, (6.8 g, 52% crude yield), b.p. 120–122° at 0.3 mm. Infrared spectrum (liquid): 1 700, 1 690, 1 610, 765, 700 cm^{-1}. Ultraviolet spectrum: $\lambda_{max}^{ethanol}$ 270, 243, 236 $m\mu$ (log ϵ, 4.06, 4.02, 4.00).

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.23; H, 6.69.

It gave a semicarbazone, m.p. 195–196° (from benzene). Ultraviolet spectrum $\lambda_{max}^{ethanol}$ 290 $m\mu$ (log ϵ 4.39).

Anal. Calcd. for $C_{16}H_{19}O_3N_3$: C, 63.77; H, 6.36; N, 13.95. Found: C, 63.56; H, 6.58; N, 13.83.

**All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord 137B spectrophotometer. The ultraviolet absorption spectra were determined with a Perkin-Elmer Spectracord 4000A.*

Its 2,4-dinitrophenylhydrazone melted at 192–193° (from ethanol). Ultraviolet spectrum: $\lambda_{max}^{CHCl_3}$ 389 mμ (log ϵ 4.46).

Anal. Calcd. for $C_{21}H_{20}O_6N_4$: C, 59.43; H, 4.75; N, 13.20. Found: C, 59.30; H, 4.87; N, 13.24.

2-Methyl-3-phenylcyclopent-2-enone (V) (9)

The keto-ester IV (12 g distilled) was refluxed with glacial acetic acid (120 ml), constant-boiling hydrobromic acid (80 ml) and water (40 ml) for 1 h, during which carbon dioxide was evolved. The acidic mixture was cooled and poured carefully on crystalline sodium carbonate (320 g) in sufficient water to form a slurry. The ketone was extracted with ether and dried over Na_2SO_4, and the solvent was evaporated to give a brown oily residue (8.4 g). This after distillation, b.p. 101–103° at 0.35 mm, solidified on standing giving 2-methyl-3-phenylcyclopent-2-enone (V) as colorless needles, m.p. 53–55° (from petroleum ether, b.p. 40–60°). Infrared spectrum (Nujol mull): 1 700, 1 620, 765, 700 cm^{-1}. Ultraviolet spectrum: $\lambda_{max}^{ethanol}$ 275 mμ (log ϵ 4.23).

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.86; H, 7.04.

It gave a semicarbazone, m.p. 251–253° (from ethanol).

Anal. Calcd. for $C_{13}H_{15}ON_3$: N, 18.33. Found: N, 17.74.

Its 2,4-dinitrophenylhydrazone melted at 232–233° (from acetic acid).

Anal. Calcd. for $C_{18}H_{16}O_4N_4$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.11; H, 4.81; N, 15.51.

The unsaturated ketone (1 g) was treated with mercuric sulfate (0.6 g) and concentrated sulfuric acid (8 ml) at 250° for 10 min, then at 300–310° for 50 min using a metal bath and an air condenser. A colorless solid sublimed and was collected from the air condenser, m.p. 119–121°. This on admixing with an authentic specimen of benzoic acid, m.p. 122° (B.D.H.), gave no depression.

2-Methyl-3-phenylcyclopentanone (VI) (9a, b)

A solution of 2-methyl-3-phenylcyclopent-2-enone (2.5 g) in glacial acetic acid (30 ml) was shaken with hydrogen in presence of Adams platinum oxide (0.2 g) until the absorption of hydrogen was ceased. After filtration, the acetic acid was neutralized with sodium carbonate solution. The product was extracted with ether and dried over Na_2SO_4, and the solvent was evaporated to give an oily residue. This on distillation yielded 2-methyl-3-phenyl-cyclopentanone as a colorless liquid (2.3 g), b.p. 81–82° at 0.25 mm. Infrared spectrum (liquid): 1 745, 765, 700 cm^{-1}.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.24; H, 8.54.

It gave a semicarbazone, m.p. 220–221° (from methanol).

Anal. Calcd. for $C_{13}H_{17}ON_3$: C, 67.50; H; 7.41; N, 18.17. Found: C, 67.56; H, 7.37; N, 18.15.

Its 2,4-dinitrophenylhydrazone melted at 199–200° (from acetic acid).

Anal. Calcd. for $C_{18}H_{18}O_4N_4$: C, 61.01; H, 5.12; N, 15.81. Found: C, 60.93; H, 5.38; N, 15.92.

Clemmensen Reduction of the Keto-ester (IV)

To amalgamated zinc wool (80 g) in water (70 ml) and concentrated hydrochloric acid (160 ml) was added the ethyl keto-ester (IV) (20 g) in toluene (150 ml). The whole was refluxed for 30 h; every 6 h, 30 ml of hydrochloric acid was added. After cooling, the toluene layer was separated from the aqueous layer, the latter was extracted with ether, and then the ether–toluene mixture was extracted with sodium bicarbonate solution. The organic layer, after washing with water and drying (Na_2SO_4), afforded a pale-yellow oil (13.4 g), which on distillation gave ethyl 3-methyl-2-phenylcyclopent-2-ene-1-carboxylate (VII; R = C_2H_5), b.p. 97–101° at 0.2 mm. Ultraviolet spectrum: $\lambda_{max}^{ethanol}$ 248.5 mμ (log ϵ 3.57).

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.44; H, 7.84.

The bicarbonate solution after washing with ether and acidification afforded a viscous oil (6.2 g) which on distillation yielded 3-methyl-2-phenylcyclopent-2-ene-1-carboxylic acid (VII; R = H), b.p. 130–135° at 0.45 mm. Ultraviolet spectrum: $\lambda_{max}^{ethanol}$ 243 mμ (log ϵ 3.58).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.67; H, 6.48.

It gave a *p*-toluidide, m.p. 131–133° (from methanol).

Anal. Calcd. for $C_{20}H_{21}ON$: C, 82.41; H, 7.26; N, 4.81. Found: C, 82.70; H, 7.25; N, 4.47.

Alkaline hydrolysis of the unsaturated ester (VII; R = C_2H_5) (1.2 g) for 2 h yielded an unsaturated acid (1 g), which gave the same *p*-toluidide as that obtained directly from the Clemmensen reduction, m.p. and mixed m.p. 130–133°.

Ethyl 3-Methyl-2-phenylcyclopentane-1-carboxylate (VIII; R = C_2H_5)

A solution of the unsaturated ethyl ester (VII; R = C_2H_5) (3.6 g) in glacial acetic acid (40 ml) was shaken with hydrogen in presence of Adams platinum oxide (0.3 g). The hydrogenation was ceased when 1 mole of hydrogen absorbed. After filtration and removal of acetic acid under reduced pressure, the residual oil was distilled at 92–96° at 0.2 mm, to give ethyl 3-methyl-2-phenylcyclopentane-1-carboxylate (VIII; R = C_2H_5) as colorless liquid (3.3 g);

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.76; H, 8.38.

The ester failed to decolorize bromine in carbon tetrachloride.

3-Methyl-2-phenylcyclopentane-1-carboxylic acid (VIII, R = H)

A mixture of the ester (VIII; R = C_2H_5; 5.3 g) and 10% sodium hydroxide solution (70 ml) was refluxed for 3 h; after cooling it was ether-extracted. The ice-cold alkaline solution was acidified with hydrochloric acid and was then ether-extracted. The ethereal solution was dried over sodium sulfate and the solvent was removed. The residue (4 g) gave the acid (VIII; R = H) as a colorless viscous oil, b.p. 132–135° at 0.7 mm.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.13; H, 7.63.

3-Methyl-2-phenylcyclopentyl Acetoxymethyl Ketone (IX, R = CH_3CO)

3-Methyl-2-phenylcyclopentane-1-carboxylic acid (VIII; R = H; 2.2 g) in dry benzene (20 ml) was allowed to stand 3 d at room temperature with redistilled thionyl chloride (20 ml). Excess thionyl chloride and benzene were removed *in vacuo*, and the final traces of thionyl chloride were removed by addition and subsequent removal of two 10 ml portions of dry benzene. The dry residue was then dissolved in dry ether (30 ml) and added to an ethereal solution of diazomethane (350 ml) (from 20 g of *N*-nitrosomethyl urea) at 0°; after standing for 30 min at 0° and then overnight at room temperature, removal of ether and excess diazomethane *in vacuo* left the corresponding diazoketone as a residual oil (3.5 g). This was dissolved in glacial acetic acid (50 ml); and gradually heated on a water bath. After 45 min (nitrogen evolution complete), the contents of the flask were diluted with water and ether-extracted. After the ether solution was washed with 5% sodium carbonate and then water, it was dried (Na_2SO_4) and evaporated to give a pale-yellow oil (2.5 g). This on distillation gave 3-methyl-2-phenylcyclopentyl acetoxymethyl ketone, b.p. 130–135° at 0.4 mm, which darkens on keeping. This oil reduced ammoniacal silver nitrate. Infrared spectrum (liquid): 1 730, 765, 700 cm^{-1}.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.35; H, 7.42.

3-Methyl-2-phenylcyclopentyl Hydroxymethyl Ketone (IX, R = H)

The diazoketone from 1.7 g 3-methyl-2-phenylcyclopentane-1-carboxylic acid, as in the previous experiment, was dissolved in 40 ml pure dioxane, and 20 ml 2 *N* sulfuric acid was added. The evolution of nitrogen started when the mixture was warmed on a water bath and ceased after 45 min. The mixture was then diluted with water and thoroughly extracted with ether. The ethereal solution was washed with small amounts of 5% sodium bicarbonate solution, then with sodium chloride solution. After drying, the ether was removed *in vacuo* and the residual oil (1.8 g) distilled at 112–115° at 0.2 mm. This oil reduced ammoniacal silver nitrate solution.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.21; H, 8.42.

1-Ethyl-4-hydroxy-2-naphthoic Acid (X, R = R′ = H)

The crude ethyl half-ester (10 g) and anhydrous sodium acetate (5 g) in acetic anhydride (80 ml) were refluxed for 5 h and then worked up by removing the acetic anyhdride under reduced pressure, adding water, and extracting the precipitate with ether. The ethereal solution was washed with sodium bicarbonate solution, washed with water, and dried (Na_2SO_4). Evaporation left crude methyl 4-acetoxy-1-ethyl-2-naphthoate (X; R = CH_3, R′ = CH_3CO) as a brown viscous oil (5 g), which on hydrolysis with 10% sodium hydroxide solution (100 ml; 2 h refluxing), gave after acidification pale brownish needles (2.5 g). This on crystallization from aqueous ethanol yielded 1-ethyl-4-hydroxy-2-naphthoic acid (X; R = R′ = H), m.p. 189–191°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.34; H, 5.83.

This phenolic acid gave a violet color with alcoholic ferric chloride solution. Acidification of the carbonate washing gave a viscous brown oil (3.6 g), which on treatment with hot saturated barium hydroxide solution (100 ml; 2 h refluxing), gave after acidification γ-ethylidene-γ-phenyl methylsuccinic acid (I*a*; R = H) (1) as colorless crystals (2.4 g), m.p. 136–138° (from water). Its mixed melting point with an authentic specimen, m.p. 137–138°, which had been prepared by alkaline hydrolysis ($Ba(OH)_2$) of the crude half-ester followed by fractional crystallization, gave no depression.

Methyl 1-Ethyl-4-methoxy-2-naphthoate (X; R = R′ = CH_3)

The phenolic acid (X, R = R′ = H; 6 g), dimethyl sulfate (18 g), and anhydrous potassium carbonate (24 g) in acetone (180 ml) were refluxed for 12 h, affording a solid (5.8 g). This after crystallization from methanol gave methyl 1-ethyl-4-methoxy-2-naphthoate (X; R = R′ = CH_3) as colorless plates, m.p. 92–93°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.79; H, 6.57.

1-Ethyl-4-methoxy-2-naphthoic Acid (X; R = H, R′ = CH_3)

Hydrolysis of the ester (X; R = R′ = CH_3; 0.9 g) using 10% sodium hydroxide solution (20 ml) for 1.5 h refluxing, gave a solid (0.7 g). This on crystallization from methanol afforded 1-ethyl-4-methoxy-2-naphthoic acid as colorless crystals, m.p. 199–200°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.15; H, 6.26.

ACKNOWLEDGMENT

The authors thank Dr. F. G. Baddar, Professor of Organic Chemistry, Faculty of Science, Ain Shams University, for spectral determinations.

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