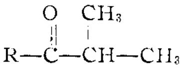
TABLE II

KETONES FROM DECARBOXYLATION OF $\alpha$-ALKYL-$\beta$,$\beta$-DIMETHYLGLYCIDIC ACIDS,



$R-C(=O)-CH(CH_3)-CH_3$

| R | Yield, % | B.p. °C. | B.p. Mm. | $n^{20}D$ | $d^t_4$ | $t$, °C. | Carbon, % Found | Carbon, % Calcd. | Hydrogen, % Found | Hydrogen, % Calcd. |
|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$[7] [a] | .. | 96 | Atm. | .... | .... | .. | ... | ... | ... | ... |
| $C_2H_5$[8] | 51 | 113 | Atm. | 1.3971 | 0.8105<br>.8349 | 20<br>0 | ... | ... | ... | ... |
| $C_3H_7$[8] | 57.5 | 133 | Atm. | 1.4042 | .8091<br>.8340 | 20<br>0 | ... | ... | ... | .. |
| $C_4H_9$[9] | 40 | 158 | Atm. | 1.4115 | .8163<br>.8333 | 20<br>0 | ... | ... | ... | ... |
| $C_5H_{11}$[10] | 69.5 | 72 | 20 | 1.4172 | .8176<br>.8340 | 20<br>0 | ... | ... | ... | .. |
| $C_6H_{13}$ | 51.5 | 77 | 4 | 1.4226 | .8215<br>.8369 | 20<br>0 | 76.80 | 76.86 | 12.64 | 12.90 |
| $C_7H_{15}$ | 61 | 79 | 3 | 1.4261 | .8243<br>.8387 | 20<br>0 | 77.11 | 77.48 | 12.55 | 13.02 |
| $C_8H_{17}$ | 75.5 | 94 | 4 | 1.4300 | .8268<br>.8419 | 20<br>0 | 78.19 | 78.19 | 12.82 | 13.12 |
| $C_9H_{19}$[11] | 73.5 | 111 | 4 | 1.4340 | .8293<br>.8441 | 20<br>0 | 78.55 | 78.72 | 13.19 | 13.21 |

[a] Isolated as the 2,4-dinitrophenylhydrazone.

TABLE III

DERIVATIVES OF THE 2-METHYL-3-ALKANONES

| R | 2,4-Dinitrophenylhydrazone M.p., °C. | Nitrogen, % Found | Nitrogen, % Calcd. | Lit. m.p. °C. | Semicarbazone M.p., °C. | Lit. m.p. °C. |
|---|---|---|---|---|---|---|
| $CH_3$ | 122 | ... | ... | 122[7] | 113 | 113[7] |
| $C_2H_5$ | 110 | ... | ... | 109[8] | 81 | 80[8] |
| $C_3H_7$ | 97.5 | 19.17 | 19.04 | ... | 119 | 119[8] |
| $C_4H_9$ | 73 | 18.14 | 18.17 | ... | 110 | 110[9] |
| $C_5H_{11}$ | 92.5 | 16.86 | 17.19 | ... | 77 | 75[10] |
| $C_6H_{13}$ | 82 | 16.66 | 16.66 | 83[a] | Oil | Oil[a] |
| $C_7H_{15}$ | 103 | 15.70 | 15.96 | Oil?[a] | Oil | Oil[a] |
| $C_8H_{17}$ | 125 | 15.77 | 15.38 | 125.5[a] | 57[c] | .. |
| $C_9H_{19}$ | 28 | 14.45 | 14.77 | 36,[11,b]<br>27[a] | Oil | Oil[a] |

[a] Alternate synthesis product. Mixed melting point determinations showed no depression. [b] Apparently this value is incorrect. [c] Calcd.: N, 16.72. Found: N, 16.73.

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# Triphenylethylene Derivatives. II

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Although triphenylhaloethylenes with estrogenic properties and triphenylethanes with low estrogenic activity are well known,[1] the estrogenic properties of triphenylhaloethanes have not been reported. The author has prepared some examples of the latter type in order to study their biological behavior.

1,2,2-Triphenylethanone, obtained by the Friedel–Crafts condensation of desyl bromide with benzene, was converted to the corresponding ethanol by reduction with sodium borohydride. The ethanol, on treatment with thionyl chloride, gave the desired 1,2,2-triphenyl-1-chloroethane.

Although diphenylacetic acid is converted to the crystalline acid chloride by treatment with phosphorus trichloride, only the acid anhydride was obtained in crystalline form from *p*-anisylphenylacetic acid by this treatment. The slow crystallization of the acid anhydride from a benzene–petroleum ether solution of the reaction product was accompanied by the faint, but continuous, evolution of hydrogen chloride. Presumably, the intermediate ketene was formed spontaneously and reacted with the trace of moisture present to give the acid anhydride.

## Experimental

**1,2,2-Triphenylethanone**[2] (I).—Compound I was obtained by the condensation of desyl bromide with benzene in the presence of aluminum chloride in 85% yield, m.p. 136–138°.

**1,2,2-Triphenylethanol** (II).—Compound I (0.27 g., 0.001 mole) was dissolved in hot methanol (30 ml.). When the solution was cooled to 30°, sodium borohydride (0.05 g., 0.0013 mole in 1 ml. of water) was added dropwise with stirring. After standing for 30 minutes at room temperature, the reaction mixture was concentrated to 15 ml. on a water-bath and water (50 ml.) added. The precipitate which was collected after a few hours (0.27 g. of the crude product) was recrystallized from hot 60% acetic acid as colorless needles, m.p. 88–89°, reported m.p. 87°,[3] m.p. 87.5–88.5°.[4]

**1,2,2-Triphenyl-1-chloroethane** (III).—To a cold solution of II (0.27 g., 0.001 mole) in pyridine (0.15 ml., 0.0019 mole) was added thionyl chloride (0.1 ml., 0.0013 mole) with stirring. After the slurry had stood overnight at room temperature, water (10 ml.) was added and the solid material collected. The crude product (0.28 g.), on crystallization

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from ethanol yielded colorless prisms (0.21 g., 72.4%) which after several recrystallizations, melted at 99–100°, reported m.p. 84°.[5]

*Anal.* Calcd. for $C_{20}H_{17}Cl$: C, 82.04; H, 5.85; Cl, 12.11. Found: C, 81.79; H, 5.95; Cl, 12.17.

A mixture of III (0.1 g.) and 10% ethanolic potassium hydroxide (2 ml.) was refluxed on a water-bath for 2 hours. Then the reaction mixture was poured into water (20 ml.) and kept overnight in a refrigerator. The precipitate recrystallized from methanol as colorless prisms which were identified as triphenylethylene, m.p. 69–71°, reported m.p. 69–70°.[6]

Although 1,1,2-triphenyl-1-chloroethane is converted to triphenylethylene by heating for 5 hours with pyridine,[7] III was recovered unchanged after this treatment.

A mixture of II (0.27 g.), phosphorus trichloride (0.1 g.) and benzene (1 ml.) was heated under reflux for 3 hours. After cooling, the benzene layer was washed with water, dried over calcium chloride and evaporated to dryness. The resinous residue was treated with methanol to give a halogen-free, crystalline product (m.p. 65–66.5°) which showed no depression of the melting point on admixture with authentic triphenylethylene

**1-*p*-Anisyl-2,2-diphenylethanol (IV).**—IV was prepared from the corresponding *p*-methoxy ketone[8] as described for II; a satisfactory yield (83.3%) was obtained when twice the amount of sodium borohydride was used. The crude product was recrystallized from hot benzene to give colorless prisms (m.p. 160–161°) which were sparingly soluble in benzene, alcohol and glacial acetic acid.

*Anal.* Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62; mol. wt., 304.4. Found: C, 83.06; H, 6.48; mol. wt. (Rast), 308.6.

The acetate of IV separated as colorless platelets from glacial acetic acid; m.p. 121–123°.

*Anal.* Calcd. for $C_{23}H_{22}O_3$: C, 79.75; H, 6.36. Found: C, 80.03; H, 6.32.

The treatment of IV in glacial acetic acid with bromine (1 molar equivalent) yielded a bromine-containing compound which crystallized from methanol as almost colorless prisms, m.p. 128–129°; Carter, *et al.*,[9] reported that 1-*p*-anisyl-2,2-diphenylbromoethylene melted at 130°.

**4-Methoxybenzil.**—4-Methoxydesoxybenzoin (11.3 g., 0.05 mole) and selenium dioxide (7.5 g., 0.067 mole) in pyridine (15 ml.) were heated at 100° for 1 hour, and at 120° for another 2 hours with occasional stirring. After cooling, the selenium (4 g.) was filtered and washed with ethanol (10 ml.). The filtrate and washings were poured into water (300 ml.), and the yellowish precipitate collected and washed with water; yield 11.6 g. (96.7%). After crystallization from benzene–petroleum ether, it melted at 64–65°, reported m.p. 62–63°.[10,11]

*p*-Methoxybenzilic acid[12] was obtained by the benzilic acid rearrangement of 4-methoxybenzil; yield 90%.

***p*-Anisylphenylacetic Acid (V).**—A mixture of *p*-methoxybenzilic acid (5.2 g., 0.02 mole), stannous chloride hydrate (15 g., 0.066 mole), concentrated hydrochloric acid (30 ml.) and glacial acetic acid (40 ml.) was stirred for 2 hours at 30°, and then for 10 minutes at 70°. The mixture, when cool, was poured into water (400 ml.) and kept overnight in a refrigerator. The resulting crystals, yield 4.6 g. (94.7%), were recrystallized from benzene–petroleum ether; m.p. 104–105°, reported m.p. 100°.[13] V is very soluble in glacial acetic acid, benzene and ethanol, sparingly in hot water and insoluble in ligroin.

*Anal.* Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.16; H, 5.42.

**Diphenylacetic acid** was prepared from benzilic acid as described above; yield 90%.

**Action of Phosphorus Trichloride on *p*-Anisylphenylacetic Acid (V).**—A mixture of V (1.45 g., 0.0060 mole), phosphorus trichloride (0.5 g., 0.0036 mole) and benzene (3 ml.) was refluxed over a water-bath for 3 hours and then cooled. The benzene solution was decanted and the benzene and excess phosphorus chloride distilled, leaving a brown oily residue which was thought to be the acid chloride. A solution of this residue in benzene-petroleum ether, on standing in a refrigerator for 2 months, gradually deposited crystals (0.5 g.); this was accompanied by the faint evolution of hydrogen chloride. The colorless platelets (m.p. 120–121°) obtained by several recrystallizations from benzene–petroleum ether gave a negative Beilstein test for chlorine and analytical data corresponding to those of the acid anhydride. Upon hydrolysis with ethanolic potassium hydroxide, the starting acid was recovered quantitatively.

*Anal.* Calcd. for $C_{30}H_{26}O_5$: C, 75.10; H, 5.58; mol. wt., 466.5. Found: C, 75.18; H, 5.18; mol. wt. (Rast), 477.5.

After standing for a few days at room temperature, a mixture of the oily acid chloride and concentrated aqueous ammonia solidified. Crystallization from hot benzene gave the colorless amide as prisms, m.p. 136–137°.

*Anal.* Calcd. for $C_{15}H_{15}O_2N$: N, 5.81. Found: N, 5.86.

Our attempts to prepare $\alpha$-phenyldesoxyanisoin by the condensation of the oily acid chloride with anisole in the presence of aluminum chloride or stannic chloride yielded a glassy resin from which no compound could be isolated chromatographically.

The author wishes to thank Mr. K. Matsumura for advice and encouragement.

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## Synthesis of 2,3-Bis-($\beta$-Hydroxyethoxyethoxy)-dioxane

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The synthesis and physical properties of a series of chlorophenoxyethoxyethanols from polychlorobenzenes has been reported recently from this Laboratory.[1] An analogous reaction has been applied now to the preparation of $\beta$-hydroxyethoxy derivatives of dioxane by the reaction of 2,3-dichlorodioxane with the sodium salts of glycols.

The reaction of 2,3-dichlorodioxane and ethylene glycol in equimolar quantities has been reported by Boeseken.[2,3] Hexahydro-*p*-dioxino[b]-*p*-dioxin was the main product.

In the present study using an excess of diethylene glycol at 60°, 2,3-bis-($\beta$-hydroxyethoxyethoxy)-dioxane was obtained in 39% yield. This was confirmed in a second experiment at 70° from which a 35% yield of this compound was obtained. Although ethylene, triethylene and thiodiethylene glycols reacted with 2,3-dichlorodioxane under similar conditions, products of definite composition were not isolated from these respective reaction mixtures by distillation.

### Experimental

**2,3-Bis-($\beta$-hydroxyethoxyethoxy)-dioxane.**—Ten moles (1061 g.) of diethylene glycol was placed in a three-liter 3-necked flask and heated to 80° and 46 g. of sodium metal

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