benzoic acid, m.p. 63.5–64°. A trace of a neutral oil was isolated from this reaction but it failed to give a test with 2,4-dinitrophenylhydrazine reagent.

In connection with the preparation of isobutylbenzoic acid it may be noted that an attempt to reduce 7.06 g. of 3-hydroxy-3-isopropylphthalide with hydrazine hydrate (5 ml.) and sodium hydroxide (5 g.) in diethylene glycol (80 ml.) by the Huang-Minlon procedure[20] yielded, instead of a reduction product, 6 g. (87%) of a crystalline solid, m.p. 154–156°; melting point after recrystallization from benzene-hexane, 158–159°; infrared absorption, 3.14, 3.28, 3.34, 6.04 (very strong), 12.68, 13.28 μ. The analysis, mode of formation, and spectrum indicate that this product is 4-isopropylphthalazone.

Anal. Calcd. for $C_{11}H_{12}ON_2$: C, 70.19; H, 6.43; N, 14.89. Found: C, 69.57; H, 6.36; N, 14.93.

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[20] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

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

Experiments in the 4-Arylcycloalk-2-en-1-one Series. V[1]

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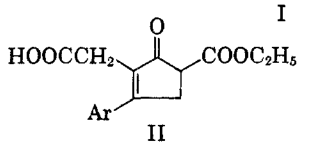
Some new cases are reported, in which the Stobbe reaction of γ-keto esters leads to cyclopent-2-enone derivatives.

Recently, it has been reported[2] that the Stobbe condensation of ethyl 3-benzoylpropionate (Ia) with diethyl succinate leads unexpectedly to 4-carbethoxy-5-oxo-2-phenylcyclopent-1-enylacetic acid (IIa). Elimination of the 4-carbethoxy group gave 5-oxo-2-phenylcyclopent-1-enylacetic acid (IIIa), characterized by its conversion into 4-hydroxy-3′-oxo-1,2-cyclopentenonaphthalene (IV), which had been prepared before by a different route.

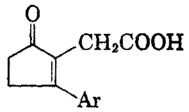
It had escaped our attention that Turner[3] had observed the analogous reaction with methyl β-(5,6,7,8-tetrahydro-2-naphthoyl)propionate (Ib), yielding 5-oxo-2-(5,6,7,8-tetrahydro-2-naphthyl)cyclopent-1-enylacetic acid (IIIb).[4,5] In fact, the reaction seems to be general for esters of 3-aroylpropionic acids. Thus, ethyl 3-(2-naphthoyl)propionate (Ic) gave with diethyl succinate in the presence of sodium hydride an oily acidic product, to which according to the spectrum formula (IIc) was assigned. It could not be isolated in pure form, but was converted, by treatment with boiling alcoholic sulfuric acid, into ethyl 2-(2-naphthyl)-5-oxocyclopent-1-enylacetate and, by subsequent hydrolysis, to the corresponding acid (IIIc) which had the same melting point as a product which Robinson[6] had obtained by a different route and to which he assigned formula (IIIc). This was confirmed by conversion of the compound into 4-acetoxy-3′-oxo-1,2-cyclopentenophenanthrene (V), a compound possessing the steroid skeleton. The oily product obtained from ethyl 3-(*p*-anisoyl)propionate (Id) and diethyl succinate was obviously 4-carbethoxy-2-(*p*-methoxyphenyl)-5-oxocyclopent-1-enylacetic acid (IId), as it could be converted into ethyl 2-(*p*-methoxyphenyl)-5-oxocyclopent-1-enylacetate and the corresponding acid (IIId) which had been prepared before by Turner by a different route.[7] It was cyclized by boiling acetic anhydride to 4-acetoxy-6-methoxy-3′-oxo-1,2-cyclopentenonaphthalene (VI).

$ArCOCH_2CH_2COOC_2H_5$

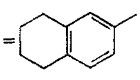
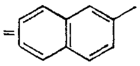
I



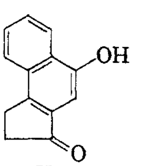
II



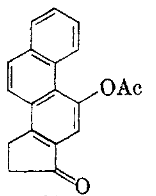
III

a, Ar = C_6H_5 b, Ar =  c, Ar = 

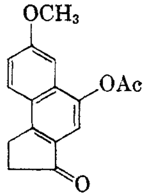
d, Ar = $p\text{-}CH_3O\cdot C_6H_4$



IV



V



VI

In Table I, the ultraviolet spectra of compounds IIIa, c, and d, of their 2,4-dinitrophenylhydrazones, and of IV, V, and VI are compared. In III, the naphthyl and even more the *p*-methoxyphenyl

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[1] Part IV. E. D. Bergmann and S. Yaroslavsky, *Tetrahedron*, **82**, in press.

[2] E. D. Bergmann, S. Yaroslavsky, and H. Weiler-Feilchenfeld, *J. Am. Chem. Soc.*, **81**, 2775 (1959).

[3] D. L. Turner, *J. Am. Chem. Soc.*, **75**, 1257 (1953).

[4] We are indebted to Dr. D. L. Turner, Jefferson Medical College, Philadelphia, for drawing our attention to his paper.

[5] Another example which—at least formally—belongs to this group is the Stobbe reaction of 2-carbethoxymethyl-1-hydrindone. B. P. Sen, A. Chatterjee, S. K. Gupta, and B. K. Bhattacharyya, *J. Indian Chem. Soc.*, **35**, 751 (1958) [*Chem. Abstr.*, **53**, 16086 (1959)].

[6] R. Robinson, *J. Chem. Soc.*, 1390 (1938).

[7] D. L. Turner, *J. Am. Chem. Soc.*, **71**, 612 (1949). The same acid has recently been described by G. S. Grinenko and V. I. Maksimov [*Zhur. Obshcheĭ Khim.*, **28**, 528 (1958); *Chem. Abstr.*, **52**, 14544 (1958)], m.p. 146°. Turner and we both observed a melting point of 132°.

groups cause a bathochromic effect, corresponding to the extension of the absorbing conjugated system. On the other hand, V absorbs at longer wave lengths than IV and VI; this effect could also be expected.

TABLE I

Compound	Ultraviolet Spectra,[a] mμ (log ε)
IIIa[b]	278 (4.26)
IIIc	215 (4.65); 267 (4.57); 295 (4.28)
IIId	225 (4.43); 301 (4.43)
DPN of IIIa ethyl ester	268 (4.36); 300 (4.08); 393 (4.53)
DNP of IIIc ethyl ester	262 (4.40); 315 (4.10); 400 (4.56)
V	263 (4.89); 288 (4.51); 302 (4.29); 339 (3.28); 356 (3.46); 375 (3.51)
VI	215 (4.39); 232 (4.30); 250 (4.62); 260 (4.71); 297 (4.05); 305 (4.15); 311 (4.13); 330 (3.87); 345 (3.75)
IV	222 (4.45); 262 (4.54); 290 (3.65); 366 (3.76)

[a] In ethanol. [b] See ref. 2.

EXPERIMENTAL

3-(2-Naphthoyl)propionic acid,[8] m.p. 171°, was converted into its *ethyl ester* (Ic) with ethanol and sulfuric acid in a yield of 80%. The ester boiled at 178° (0.5 mm.) and solidified slowly on standing.

Ethyl 2-(2-naphthyl)-5-oxocyclopent-1-enylacetate (as IIIc). When a mixture of 64 g. of ethyl 3-(2-naphthoyl)propionate (Ic), 11 g. of sodium hydride, 130 g. of diethyl succinate, 250 ml. of benzene, and 2.5 ml. of ethanol was stirred at room temperature, a slow reaction took place which quickened gradually and reached after 30 min. its maximum rate, indicated by a temperature rise to 40–50°. When the temperature of the reaction had returned to normal, the stirring was continued for 2 hr. and the product treated with 50 ml. of glacial acetic acid. Addition of water and ether, separation of the organic layer, extraction with sodium carbonate solution, and acidification of the alkaline extract gave an oil (58 g., 69%) which did not crystallize. It had the spectrum expected for 4-carbethoxy-2-(2-naphthyl)-5-oxocyclopent-1-enylacetic acid (IIc). [$\lambda_{\max}^{C_2H_5OH}$ 220 (4.66); 268 (4.30); 304 mμ (4.00)] and was directly treated as follows:

The product (54 g.) was refluxed for 8 hr. with 200 ml. of anhydrous alcohol, containing 1 g. of concd. sulfuric acid. The solution was concentrated, diluted with water, and extracted with ether. The extract was washed with sodium carbonate solution and water, dried, and distilled; b.p. 220° (1 mm.); yield, 18 g. (38%). In spite of the sharp boiling point, the 4-carbethoxy group had not been completely eliminated, as the analysis indicated. However, the spectrum showed the expected bands and an analytically pure 2,4-dinitrophenylhydrazone could easily be prepared. $\lambda_{\max}^{C_2H_5OH}$ 215 (4.72); 268 (4.58); 302 mμ (4.74).

The *2,4-dinitrophenylhydrazone* formed, after recrystallization from nitromethane, red crystals, m.p. 235–236°; $\lambda_{\max}^{CHCl_3}$ 262 (4.40); 315 (4.10); 400 mμ (4.56).

Anal. Calcd. for $C_{25}H_{22}N_4O_6$: C, 63.3; H, 4.6. Found: C, 62.9; H, 4.6.

2-(2-Naphthyl)-5-oxocyclopent-1-enylacetic acid (IIIc). A mixture of 10 g. of the foregoing ester, 10 g. of sodium hydroxide, and 100 ml. of water was refluxed for 5 hr. Acidification of the filtered solution with hydrochloric acid at ice temperature gave 8 g. (90%) of the acid which was recrystallized from dilute acetic acid and benzene and formed yellowish crystals, m.p. 169–170° (lit.,[6] m.p. 170°). $\lambda_{\max}^{C_2H_5OH}$ 215 (4.65); 267 (4.57); 295 mμ (4.28); $\bar{\nu}_{\max}^{KBr}$ 1725 cm^{-1}.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.9; H, 5.5.[9] The *2,4-dinitrophenylhydrazone* formed red crystals, m.p. 320° (after recrystallization from nitrobenzene).

Anal. Calcd. for $C_{23}H_{18}N_4O_6$: C, 61.9; H, 4.0. Found: C, 62.0; H, 4.1.

4-Acetoxy-3′-oxo-1,2-cyclopentenophenanthrene (V). When 1 g. of the foregoing acid had been refluxed for 30 min. with 10 ml. of acetic anhydride, a solid substance began to separate upon cooling. The solid was filtered after addition of much water and recrystallized from butanol. It formed slightly brownish leaflets, m.p. 207° (lit.,[6] m.p. 207°), Yield, 1 g. (90%).

$\lambda_{\max}^{C_2H_5OH}$ 263 (4.89); 288 (4.51); 302 (4.29); 339 (3.28); 356 (3.46); 375 mμ (3.51). $\bar{\nu}_{\max}^{KBr}$ 1700, 1757 cm^{-1}.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.6; H, 4.8. Found: C, 78.4; H, 5.0.

Ethyl 3-(p-anisoyl)propionate (Id). 3-(*p*-Anisoyl)propionic acid was prepared from anisol and succinic anhydride[10] and recrystallized from ethanol, m.p. 147° (lit.,[10] m.p. 147°); yield, 50%. The *ethyl ester*, obtained in 80% yield, boiled at 160° (0.04 mm.).

Ethyl 2-(p-methoxyphenyl)-5-oxocyclopent-1-enylacetate (as IIId). The reaction between 85 g. of the foregoing ester, 187 g. of diethyl succinate, 26 g. of sodium hydride in 360 ml. of benzene, and 3 ml. of anhydrous ethanol was carried out as described for the analogous 2-naphthyl compound. The acidic product (67 g.; 60%) obtained was an oil which absorbed at 223 (4.30) and 301 mμ (4.14) and was directly heated for 8 hr. with 300 ml. of anhydrous ethanol, containing 1 g. of concd. sulfuric acid. The neutral product (34 g., 58%) boiled at 200° (1 mm.), but was not analytically pure, a small part of the carbethoxy group not having been eliminated. However, the *2,4-dinitrophenylhydrazone* could be obtained in pure form, as red crystals, m.p. 210° (from butanol).

Anal. Calcd. for $C_{22}H_{22}N_4O_7$: C, 58.2; H, 4.8. Found: C, 58.4; H, 4.7.

2-(p-Methoxyphenyl)-5-oxocyclopent-1-enylacetic acid (IIId). A mixture of 20 g. of the ester, 20 g. of sodium hydroxide, and 400 ml. of water was refluxed for 5 hr. and the filtered solution acidified with cold dilute hydrochloric acid. The product (16 g.; 90%) was recrystallized from water and benzene and formed slightly yellowish crystals, m.p. 132° (lit.[7] m.p. 132°). $\lambda_{\max}^{C_2H_5OH}$ 225 (4.43); 301 mμ (4.43). $\bar{\nu}_{\max}^{KBr}$ 1700 cm^{-1}.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.8; H, 5.2. The *2,4-dinitrophenylhydrazone* of IIId was recrystallized from a mixture (1:1) of glacial acetic acid and ethyl acetate and formed red crystals, m.p. 252–253°.

Anal. Calcd. for $C_{20}H_{18}N_4O_7$: C, 56.4; H, 4.2. Found: C, 56.0; H, 4.5. The *semicarbazone of* (IIId) was recrystallized from aqueous alcohol and formed yellowish crystals, m.p. 225°.

Anal. Calcd. for $C_{15}H_{17}N_3O_4$: C, 59.4; H, 5.6. Found: C, 59.3; H, 5.6.

4-Acetoxy-6-methoxy-3′-oxo-1,2-cyclopentenonaphthalene (VI). A solution of 1 g. of the foregoing acid in 7 ml. of acetic anhydride was refluxed for 30 min., cooled, and treated with an excess of water. The precipitate was filtered and recrystallized from butanol; it formed leaflets, m.p. 193°; yield, 0.9 g. (82%). $\lambda_{\max}^{C_2H_5OH}$ 215 (4.39); 232 (4.30); 250 (4.62); 260 (4.71); 297 (4.05); 305 (4.15); 311 (4.13); 330 (3.87); 345 mμ (3.75). $\bar{\nu}_{\max}^{KBr}$ 1700, 1757 cm^{-1}.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.2; H, 5.2. Found: C, 71.3; H, 5.4.

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(8) W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 472 (1939). *Cf.* M. S. Newman, R. B. Taylor, T. Hodgson, and A. B. Garrett, *J. Am. Chem. Soc.*, **69**, 1784 (1947).

(9) Good analytical figures were only obtained when the acid was dried at 100° in a vacuum of 1 mm. for 48 hr.

(10) O. Poppenberg, *Ber.*, **34**, 3257 (1901).