Ibanez [6], est moins favorable à la comparaison. Une interpolation à 20 °C des mesures données par [6] conduit à une contraction de 0,156 $cm^3 mole^{-1}$, de 12% inférieure à celle mesurée ici.

Le système cyclohexane + benzène est proposé par *Powell* pour servir [7] d'étalon aux déterminations de volumes d'excès. Ce choix est discutable car l'accord entre les nombreux expérimentateurs est loin d'être réalisé, comme le montre le tableau 10.

Tableau 10. *Système cyclohexane + benzène*, t = 25 °C; x = 0,5

– ce travail:	$V^E = 0{,}619\ cm^3\ mole^{-1}$
– *Powell* [7]:	$V^E = 0{,}639\ cm^3\ mole^{-1}$
– *Stockes* [8]:	$V^E = 0{,}650\ cm^3\ mole^{-1}$
– *Diaz-Peña* [9]:	$V^E = 0{,}635^e\ cm^3\ mole^{-1}$
– *Ridgway* [10]:	$V^E = 0{,}595\ cm^3\ mole^{-1}$

[e: extrapolé à partir de mesures à 20 °C]

Nous remercions le *Fonds National Suisse de la Recherche Scientifique* pour son soutien. Nos remerciements vont aussi à M. le Professeur *A. Jacot-Guillarmod* pour son appui, et à Mlle. *L. Rossetti* et M. *P. A. Berger* pour leur consciencieuse collaboration.

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134. Steroid Total Synthesis, Part VII[1]); (±)-Estr-4-ene-3, 17-dione and (±) 13β-Ethyl-gon-4-ene-3, 17-dione[2])

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(4. 4. 72)

Summary. An efficient and practical synthesis of the title compounds is described. The novel route is based on earlier results and uses (±)- 5-hydroxy-9,9-*o*-phenylenedioxy-decanoic acid lactone as the starting material. The results demonstrate the usefulness of pyrocatechol for the protection of an aliphatic ketone.

In two previous publications [1] [2] the use of the 3,5-dimethylisoxazole group [3] in the total synthesis of both racemic and optically active 19-nor-steroids

[1]) Part VI; see ref. [1].

[2]) Presented in part at the Third International Congress on Hormonal Steroids, Hamburg, Germany, 1970; Symposium Lectures, Abstr. 4.

has been reported. The synthetic scheme, which involves an interesting asymmetric induction, was based on earlier results [4] [5] [6] obtained with BCD-tricyclic intermediates. The present paper describes parallel syntheses of racemic estr-4-ene-3,17-dione and 13β-ethyl-gon-4-ene-3,17-dione, comprising the phenylenedioxy moiety (ketal derived from pyrocatechol) as the novel feature[3]).

Synthesis of (±)-Estr-4-ene-3, 17-dione (9a). – Based on the scheme and the reactions developed earlier [4]–[6] we first attempted the synthesis of the racemic 19-norsteroid **9a** utilizing the usual ethylene ketal moiety (see scheme, R = $-OCH_2CH_2O-$)[4]). However, it soon became obvious that this ketal group did not have the desired stability in the steps leading to the BCD-tricyclic intermediate **8**. Thus, difficulties arose in the formation of the diene **4a** and particularly in the oxidation step **6** → **7**, the ethylene ketal moiety suffering extensive hydrolysis[5]). Some improvement was gained by using *2,3*-butyleneglycol and *2,2*-dimethylpropane-1,3-diol for preparation of the necessary ketals[5]). A superior and nearly ideal ketal was the one derived from pyrocatechol[6]). The ketal formed readily[7]), proved stable under all the reaction conditions employed, and was easily removed in the last step (**8** → **9**) of the synthesis. Thus the steroid **9a** was conveniently prepared as described below.

First, the lactone **1** [10] was reacted with vinylmagnesium chloride in THF at –45° [5] to afford the vinyl ketone **2** (X = O). This was immediately converted to the more stable base **3** (addition of diethylamine) which was purified by acid extraction. This same base was also prepared by the condensation of the *Grignard* reagent from 2,2-phenylenedioxy-5-chloropentane with glutaraldehyde [10] followed by the addition of vinylmagnesium chloride and subsequent oxidation [5] of the alcohol **2** (X = H, OH) with manganese dioxide in the presence of diethylamine. In this manner the base **3** was obtained in an overall yield of 72%. Condensation [5] of the *Mannich* base **3** with 2-methylcyclopentane-1,3-dione in refluxing acetic acid/pyridine/toluene next gave an excellent yield of the diene **4a**. No attempt was made to separate the two diastereomers, since both lead to the same final product **9a**[8]). The crude 17-alcohol **5a** obtained from **4a** by reduction with lithium aluminium hydride was selectively hydrogenated in toluene over a palladium catalyst affording the C,D-*trans* fused compound **6a** as the major product. Treatment of crude **6a** with sulfuric acid in acetone followed by *Jones'* oxidation subsequently gave the triketone **7a**. The BCD tricyclic product **8a**, which was obtained from crude **7a** with potassium hydroxide in refluxing methanol, was purified by crystallization. The enone **8a** was finally hydrogenated over a palladium catalyst in tetrahydrofuran in the presence of a small amount of triethylamine and the crude hydrogenation product on treatment with hydrochlorid acid in refluxing aqueous methanol then gave (±)-estr-4-ene-3,17-dione

[3]) The synthesis of (+)estr-4-ene-3,17-dione by a similar route is presented in part VIII [7].

[4]) cf. [8] regarding the sequence **8a** → **9a** for R = $-OCH_2CH_2O-$.

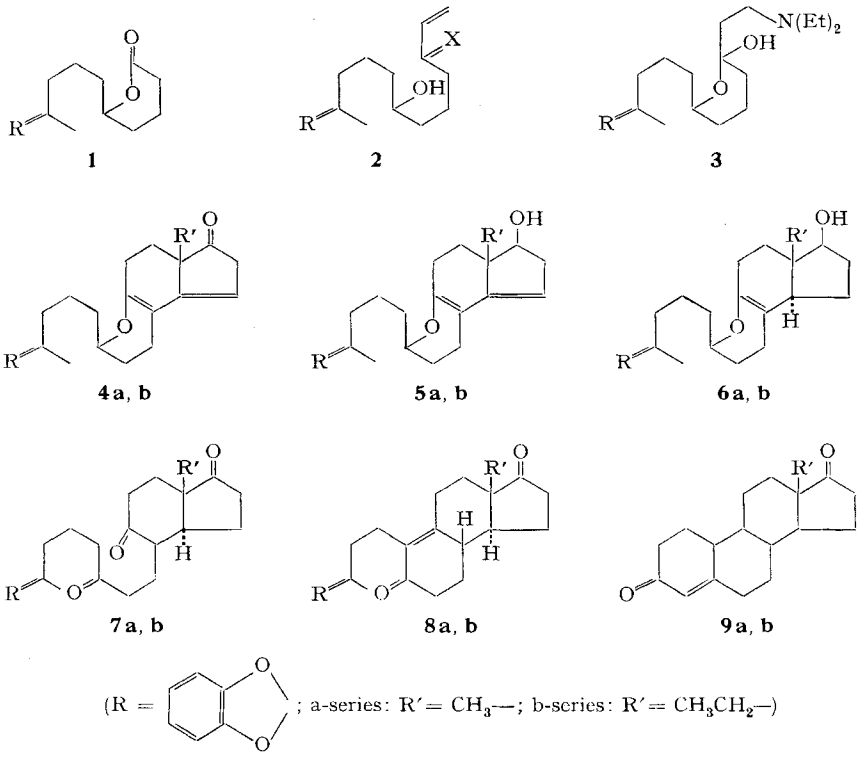
[5]) Experiments not described.

[6]) To our knowledge, pyrocatechol has only been used occasionally for protection of carbonyl groups; see e.g. [9].

[7]) The preparation of **1** from 5-chloro-2-pentanone has been described elsewhere [10].

[8]) It follows from earlier results [5] [6] and work with optically active **9a** [7] that the *trans*-enantiomer (13βmethyl, 5βH) predominates.

Synthesis of (±)-*Estr-4-ene-3,17-dione* (**9a**) *and* (±)*13β-Ethyl-gon-4-ene-3,17-dione* (**9b**)



(all compounds racemic)

9a [11]. This product was readily obtained in pure form by crystallization. Its correct stereochemistry follows from a comparison with authentic optically active material[9]). This preparation (**9a**) was found to be identical with the material prepared by us previously, using an alternate scheme [12]. The overall yield of pure **9a** from the base **3** was 27%.

The synthesis of the 13β-ethyl analog **9b** followed the same pattern and proved straightforward. Thus, condensation of the base **3** with 2-ethyl-cyclopentane-1,3-dione [13] first gave the diene **4b** (mixture of 2 racemates), which was transformed to (±)13β-ethyl-gon-4-en-3,17-dione (**9b**) using the procedures outlined above. None of the intermediates (**4b–8b**) of this synthesis were purified and the final product **9b** was readily obtained in pure form by crystallization. Its identity was established by comparison with an authentic sample [12]. The overall yield for the transformation **3** → **9b** was 19%. As described previously [12] the dione **9b** may serve as an intermediate for the preparation of *Norgestrel*. The results presented above demonstrate that the phenylenedioxy moiety is advantageous in terms of acid stability and because it imparts good crytsallinity to many intermediates. In order to expand these findings, we have also carried out the synthesis of (±)-estr-4-ene-3,17-dione (**9a**) using 4,5-

[9]) Prepared from 19-nortestosterone by oxidation.

dimethylcatechol and 2,3-naphthalenediol for protection of the initial keto group (**1** → **8a**, R = 4,5-dimethyl-1,2-phenylenedioxy- and 2,3-naphthalenedioxy-)[10]. The results obtained[5] (see ref. [10] for preparation of **1**) are very similar to those described above, both as regards acid stability and crystallinity of the intermediates.

Experimental Part

General. – Melting points (m.p.) are uncorrected. Thin layer chromatography (TLC.) was carried out on *Brinkman* F 254 silica gel plates using ethyl acetate/benzene 1:1. The spots were viewed under UV. light and developed by spraying with 50% aqueous *p*-toluenesulphonic acid and heating to 120° for 1–3 min followed by exposure to iodine vapour. Ultraviolet spectra (UV.) were measured in ethanol and were recorded with a *Carey* Model 14 spectrometer while infrared spectra (IR.) were determined with *Beckman* IR. 8 and IR. 9 spectrophotometers. NMR. spectra were recorded with *Varian* HA-60 and HA-100 spectrometers with tetramethylsilane as an internal standard.

Removal of solvents 'in vacuo' refers to removal at 20 mm at 45° on a *Büchi* rotavapor and finally at 0.5 mm.

(±)-*2-(2-Diethylaminoethyl)-6-(4,4-o-phenylenedioxypentyl)-tetrahydropyran-2-ol* (**3**). – A solution of 5-hydroxy-9,9-phenylenedioxy-decanoic acid lactone **1** (1.6 g) [10] in tetrahydrofuran (15 ml) was cooled to −45° and treated over a period of 2 min with a solution of vinylmagnesium chloride in tetrahydrofuran (3.4 ml, 2.7 molar). The mixture was stirred for a further 23 min under nitrogen at −45° and then quenched with methanol (5 ml) followed by an aqueous ammonium chloride solution (20 ml, 15%). The vinyl ketone **2** (X = O) was extracted into ether and the etherial solution was then exposed for $^1/_2$ h to diethylamine (5 ml) and dried over magnesium sulfate. After removal of the solids and the solvents the crude *Mannich* base **3** was redissolved in ether (75 ml) and extracted with aqueous sulfuric acid (1 N, 4 × 14 ml). Regeneration of the free base with potassium hydroxide solution (2 N, 35 ml) and isolation of the base with ether yielded the pure amine **3** (1.74 g) as a pale yellow colored mobile oil: IR. (film) 3150 (bonded-OH), 1480, 1240, and 730 cm^{-1} (pyrocatechol ketal). NMR. ($CDCl_3$): δ 6.75 (*s*, 4, phenyl protons); 1.6 (*s*, 3, side chain – CH_3) and 1.0 ppm (*t*, 6, $-N(CH_2-CH_3)_2$).

$C_{22}H_{35}NO_4$ Calc. C 69.99 H 9.35 N 3.71% Found C 70.21 H 9.64 N 3.99%

The same compound (**3**) was also prepared as follows: A solution of 4,4-*o*-phenylenedioxy-1-chloropentane (106.5 g) in tetrahydrofuran (750 ml) was converted to the *Grignard* reagent with magnesium powder (*Alpha Inorganics;* 18 g) at 35–37° under nitrogen [10]. This solution was then rapidly added (~15 min) at −45° to dry freshly distilled glutaraldehyde (48 g) dissolved in tetrahydrofuran (350 ml). After complete addition the mixture was warmed to room temperature (over 1 h) and stirred for a further 1 h. The resulting reaction mixture was then cooled to 0° treated with a solution of vinylmagnesium chloride in tetrahydrofuran (1.2 equiv., 2 M) and stirred at room temperature for 16 h. Aqueous ammonium chloride solution (200 ml, 15%) was then added at 5° and the solids formed were filtered off and washed with more tetrahydrofuran. The combined filtrates were dried over magnesium sulfate, filtered free of solids and taken to dryness 'in vacuo' to give the diol **2** (X = H, OH) as an oil (156 g). A portion of this material (5.5 g) yielded an analytically pure sample (4.4 g) after chromatography on silica gel: IR. ($CHCl_3$): 3600 and 3450 (hydroxyl), 1490 and 1240 (pyrocatechol ketal) and 930 cm^{-1} (mono-subst. olefin). NMR. ($CDCl_3$): δ 6.73 (*s*, 4, phenyl protons); δ 5.8 (*m*, 1, $-CH=CH_2$); δ 5.15 (*m*, 2, $-CH=CH_2$); 4.2 (*m*, 1, O—C*H*); 3.6 (*m*, 1, O—C*H*) and 1.6 ppm (*s*, 3, CH_3).

$C_{18}H_{26}O_4$ Calc. C 70.5 H 8.6% Found C 70.0 H 8.4%

The crude alcohol **2** (150 g) was dissolved in benzene (300 ml) and added to a slurry of manganese dioxide (1500 g; activated with nitric acid) [14] and benzene (4500 ml) containing diethylamine (450 ml) and stirred at room temperature under nitrogen for 23 h. The solids were filtered off, washed with benzene and the combined filtrate was taken to dryness 'in vacuo'. The crude amine was purified by acid extraction from ether as before to yield the *Mannich* base as a brown-colored oil (157 g). The material was then dissolved in hexane and filtered through a plug of alumina (300 g, grade III) to give a pale yellow colored oil (**3**) (134 g) identical in all respects with the material prepared above.

[10] Experimental work performed by *R. Müller*.

(±)-*3-(4,4-o-Phenylenedioxy-n-pentyl)-6a, β-methyl-1, 2, 3, 5, 6, 6a-hexahydrocyclopenta[f] chromen-7(8H)-one* (**4a**). – A solution of the *Mannich* base **3** (10.6 g) in toluene (80 ml) was added to a refluxing solution of 2-methylcyclopentane-1,3-dione (4.7 g) in toluene (50 ml), acetic acid (23 ml) and pyridine (7.2 ml) under nitrogen. After heating at reflux for 4 h the mixture was cooled to room temperature, treated with toluene (100 ml), washed with water, aqueous sodium bicarbonate solution and dried over magnesium sulfate. The solids were then filtered off and the solvents were removed 'in vacuo' giving the crude dienolether **4a** (10.8 g) as a pale orange colored crystalline solid: m.p. 115–120°. A sample recrystallized from benzene/hexane yielded the analytical sample: m.p. 126–129°. UV.-max. (C_2H_5OH): 254 nm (ε = 17,300). IR. ($CHCl_3$): 1745 (cyclopentanone), 1645 (dienol ether), 1490 and 1250 cm^{-1} (pyrocatechol ketal). NMR. ($CDCl_3$): δ 6.7 (*s*, 4, phenyl protons); 5.4 (*t*, 1, *J* = 3 Hz, vinyl proton); 1.63 (*s*, 3, side chain methyl) and 1.1 ppm (*s*, 3, 6a-CH_3).

$C_{24}H_{28}O_4$ Calc. C 75.76 H 7.47% Found C 75.80 H 7.50%

(±)-*trans-6-(3,3-o-Phenylenedioxybutyl)-3a, β-methyl-2, 3, 3a, 4, 5, 7, 8, 9, 9a, 9b-decahydro-1H-cyclopenta[a]-naphthalenc-3,7-dione* (**8a**). – A solution of the dienol ether (**4a**; 10.7 g; crude *cis/trans* mixture) in 100 ml tetrahydrofuran/ether 1:1 was added, under nitrogen, to a slurry of lithium aluminium hydride (4 g) in the same mixture of solvents (400 ml) and kept at 3° with cooling (salt-ice bath). After stirring a further 10 min at –5° and 2 h at room temperature, wet ether (100 ml) was added followed by a saturated aqueous solution of sodium sulfate (25 ml). The solids were filtered off, washed well with tetrahydrofuran and the combined filtrates were dried over magnesium sulfate and then taken to dryness 'in vacuo' yielding the alcohol **5a** (11.2 g) as an oil: IR. ($CHCl_3$): 3600 and 3450 (hydroxyl), 1640 (dienol ether) and 1480 cm^{-1} (pyrocatechol ketal).

This crude material **5a** (11.2 g) was dissolved in toluene (100 ml) and hydrogenated over a 5% palladium on carbon catalyst (2 g) until the hydrogen uptake stopped (700 ml consumed in $5^1/_2$ h at 23° and 755 mm). The solids were filtered off and removal of the solvents 'in vacuo' furnished the enol ether **6a** (10.4 g) as an oil: IR. (film): 3375 (hydroxyl), 1660 (enol ether), 1480, 1230 and 730 cm^{-1} (pyrocatechol ketal).

A solution of the crude enol ether (10.76 g) in acetone (210 ml) was treated with aqueous sulfuric acid (0.5 N, 50 ml) and left at room temperature for 2 h. Ether (500 ml) was added to the mixture and the solution was washed with saturated brine (5 × 100 ml), sodium bicarbonate solution (5%, 50 ml) and dried over magnesium sulfate. Removal of the solvents 'in vacuo' then yielded the hemiacetal (10.33 g) as a glass (the 1660 cm^{-1} band in the IR. was absent).

This material was dissolved in acetone (200 ml), cooled to ~0–5° in an ice bath and treated, over 10 min, with a fresh solution of *Jones'* chromic acid mixture (20 ml). The reaction mixture was then stirred for a further $1^1/_2$ h at room temperature and then quenched with an aqueous sodium bisulfite solution (10%; 100 ml) and saturated brine (100 ml). Extraction of the organic materials into benzene and washing the benzene extracts with sodium carbonate solution (10%) yielded the triketone **7a** (8.6 g) as a pale yellow colored oil on removal of the solvents: IR. (film): 1730 (cyclopentanone), 1705 (saturated carbonyl), 1480, 1240 and 730 cm^{-1} (pyrocatechol ketal).

The crude triketone **7a** (8.26 g) was dissolved in a solution of potassium hydroxide (1 g) in methanol (250 ml) and heated at reflux under nitrogen for 1 h. Benzene (500 ml) was added and the mixture was washed with aqueous sulfuric acid (0.5 N), sodium bicarbonate solution (5%) and dried over magnesium sulfate. Removal of the solvents 'in vacuo' yielded the crude tricyclic diketone **8a** (6.75 g) as an oily solid. Crystallization from ethanol yielded crystalline material (4.85 g): m.p. 166–170° (92% pure by UV.). The analytical sample (colorless crystals from ethanol) had m.p. 173–175°; UV.-max.: 238 nm (ε = 14,100); IR. ($CHCl_3$): 1740 (cyclopentanone), 1660 and 1605 (cyclohexenone), 1485 and 1240 cm^{-1} (pyrocatechol ketal). NMR. ($CDCl_3$): δ 6.75 (*s*, 4, aromatic protons), 1.62 (*s*, 3, side chain methyl) and 0.98 ppm (*s*, 3, 6aβ-CH_3).

$C_{24}H_{28}O_4$ Calc. C 75.76 H 7.42% Found C 75.79 H 7.27%

(±) *Estr-4-ene-3,17-dione* (**9a**). – The crystalline diketone **8a** (4.01 g; 92% purity) was dissolved in tetrahydrofuran (45 ml) containing triethylamine (0.8 ml) and hydrogenated at room temperature and pressure over a 5% palladium on carbon catalyst (400 mg). After the uptake of hydrogen ceased (280 ml at 23° and 765 mm) the solids were filtered off and the solvents were removed 'in vacuo' yielding the crude hydrogenation product as an oil (4.3 g). IR. (film): 1735 (cyclopentanone) 1705 (cyclohexanone), 1480, 1240 and 740 cm^{-1} (pyrocatechol ketal). This crude material was dissolved

in methanol (70 ml), treated with aqueous hydrochloric acid (4 N, 35 ml) and heated at reflux under nitrogen for 6 h. The mixture was then treated with benzene (200 ml) and washed with water, aqueous sodium hydroxide solution (1 N, 3 × 100 ml) and brine and then taken to dryness 'in vacuo'. Crystallization of the solid residue from dichloromethane/isopropyl ether yielded pure **9a** (2.01 g): m.p. 155–157°. This material was identical [IR. ($CHCl_3$); NMR., UV. and TLC.] with a sample prepared by an alternate route [12].

(±)-*13β-ethyl-gon-4-ene-3,17-dione* (**9b**). – A solution of 2-ethyl-cyclopentane-1,3-dione [13] (71 g) in toluene (670 ml) and acetic acid (335 ml) was heated to reflux under nitrogen. To this refluxing solution was added, in one portion, the *Mannich* base **3** (134 g) dissolved in toluene (340 ml). The resulting solution was then heated for a further 1 h at reflux and then for 1 h more in conjunction with a *Dean* and *Stark* water separator. The cold (it is important to cool these reaction mixtures before working up in order to minimize air oxidation) mixture was washed with brine, aqueous sodium carbonate solution (5%) and taken to dryness 'in vacuo' to yield the dienol ether **4b** (134.8 g) as an orange colored mobile liquid: IR. (film): 1740 (cyclopentanone) 1637 (dienol ether), 1480, 1230, 730 cm^{-1} (pyrocatechol ketal). The crude material (134.8 g) was dissolved in tetrahydrofuran (400 ml) and added to a slurry of lithium aluminium hydride (17.2 g) in tetrahydrofuran (600 ml) held at −10° (dry ice-acetone bath used). The mixture was then stirred a further 3 h at room temperature and then treated with a saturated aqueous solution of sodium sulfate (this was added until a fine white granular precipitate was formed). The solids were filtered off and washed with tetrahydrofuran and the combined filtrates were taken to dryness 'in vacuo'. The resulting crude alcohol (140 g, IR. showed no 1740 cm^{-1} band) was dissolved in toluene (800 ml) and hydrogenated at room temperature and pressure over a 5% palladium on carbon catalyst (15 g) until the hydrogen uptake stopped. The solids were filtered off, the solvents were removed 'in vacuo' and the residue (132 g, IR.: no band at 1637 cm^{-1}, new band at 1675 cm^{-1} (enol ether)) was dissolved in acetone (1,4 liters) and treated with aqueous sulfuric acid (140 ml, 0.5 N). After $2^1/_2$ h at room temperature (TLC. and IR. showed no enol ether present) the mixture was cooled to 5° and treated over 25 min with a fresh solution of *Jones'* chromic acid mixture (340 ml). After stirring a further $2^1/_2$ h at room temperature aqueous sodium bisulfite solution was added (130 ml; 20%) followed by brine (1.5 liters) and the products were extracted into benzene. The benzene extracts were washed well with aqueous sodium carbonate solution (20%) and taken to dryness 'in vacuo'. The resulting crude triketone **7b** (109 g; IR. (film): 1737 (cyclopentanone), 1705 (cyclohexanone and alkyl carbonyl), 1480, 1240 and 735 cm^{-1} (pyrocatechol ketal)) was dissolved in methanol (950 ml) containing potassium hydroxide (11.8 g) and heated at reflux for 1 h under nitrogen. Brine (1 liter) was added and the products were extracted into benzene; removal of the solvents 'in vacuo' gave the crude tricyclic material **8b** (88 g) as an oil: IR. ($CHCl_3$): 1735 (cyclopentanone), 1660 and 1600 (cyclohexanone) and a minor band at 1705 cm^{-1} (cyclohexanone). Chromatography failed to give crystalline material.

A solution of crude **8b** (88 g) in ethanol (1.1 liter) containing triethylamine (8.8 ml) was hydrogenated at room temperature and pressure over a 5% palladium on carbon catalyst (18 g) until the hydrogen uptake stopped. The solids were filtered off and the filtrate was exposed to aqueous hydrochloric acid (880 ml; 2 N) and heated at reflux for 4 h. Most of the ethanol was removed 'in vacuo', the products were isolated with benzene and the combined extracts were washed free of pyrocatechol with sodium hydroxide solution (2 N) and then treated with charcoal (5 g). The solids were filtered off and the solvents were removed 'in vacuo' to give a syrup (62.5 g) which was dissolved in isopropyl ether and left to crystallized. Recrystallization from dichloromethane/isopropyl ether gave pure **9b** (19.2 g): m.p. 159–161°. UV.-max.: 237 nm (ε = 17,600). IR. ($CHCl_3$): 1730 (cyclopentanone) 1665 and 1620 cm^{-1} (cyclohexenone).

$C_{19}H_{26}O_2$ Calc. C 79.68 H 9.15% Found C 79.57 H 9.36%

This preparation (**9b**) was found to be identical with authentic material [12].

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VI. Internationaler Kongress für grenzflächenaktive Stoffe

vom 11.–15. September 1972 in Zürich

Die Vorträge sind in drei Sektionen eingeteilt:

A. Chemie
B. Physikalische Chemie
C. Applikationen der grenzflächenaktiven Stoffe

Vortragsprogramm und Anmeldeformulare: Schweiz. Gesellschaft für Chemische Industrie, Nordstrasse 15, 8035 Zürich.

IUPAC Internationales Symposium on Photochemical Processes in Polymer Chemistry

12.–15. June 1972 in Leuven (Belgien)

Information: Prof. Dr. *F. C. De Schryver*, Secr. Microsymposium 1972, Dep. Scheikunde, Celestijnenlaan 200 F, 3030 Heverlee (Belgien).
