Oxidation of Steroidal Ketones. V. Selenium Dioxide Catalyzed Hydrogen Peroxide Oxidation of Steroidal Conjugated Ketones[1]

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The previous investigations on the oxidation of 4-en-3-ones[3,4] were extended to other steroidal conjugated carbonyl systems. The various conjugated moieties did not react uniformly with this reagent.

The selenium dioxide catalyzed hydrogen peroxide oxidation of steroidal ketones was described in several communications from this laboratory.[3-5] When 4-en-3-ones were oxidized, the products formed were seco lactones XIV which rearranged with ease to the γ-lactones XV. We now wish to report the evaluation of the oxidation procedure for other steroidal conjugated ketones and for saturated 12-ketone.

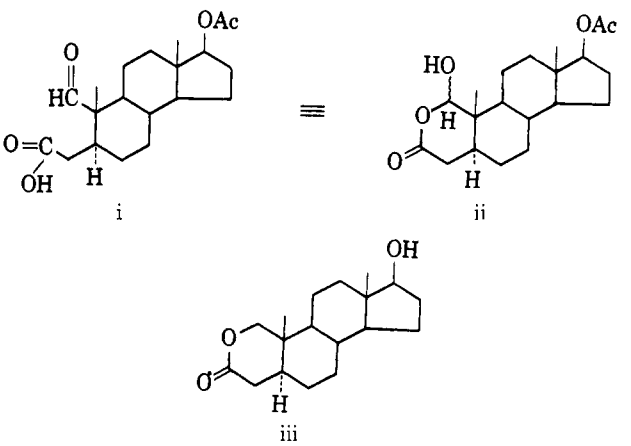
When 17β-acetoxy-5α-androst-1-en-3-one was oxidized for 6 hr., an acidic and a neutral fraction were obtained. The acid proved to be the 2,3-seco-2,3-dicarboxylic acid I and was identified by comparison with an authentic sample.[5a] The neutral product was assigned the 1α,2α-epoxy structure II on the basis of its identity to a sample prepared by the method of Hoehn.[6] When the oxidation was extended to 16 hr., the main component of the base-soluble fraction was again acid I. The base-insoluble residue was resolved by thin layer chromatography to yield a small amount of epoxide II and a larger amount of lactone III. The lactone III had a composition of $C_{19}H_{28}O_4$, did not absorb ultraviolet light, and had an infrared band at 1770 cm.$^{-1}$, characteristic of γ-lactones. Saponification provided the dihydroxy acid IVa, which could be reconverted to III by refluxing with acetic anhydride. When IVa was first treated with diazomethane, then oxidized with chromium trioxide in pyridine, the hydroxy ester IVb (3550, 1740, and 1720 cm.$^{-1}$) was obtained, demonstrating the presence of a tertiary hydroxyl. An n.m.r. spectrum of III had signals at τ 9.13 (18-methyl), 8.76 (19-methyl), 7.96 (acetate), and 5.36 (triplet 17α-H). The absence of other signals in the τ 5–6 region confirmed the tertiary nature of the lactonized hydroxyl. The observed deshielding of the 19-methyl with respect to the 19-methyl in 5α-androstane is 0.45 p.p.m. The deshielding of an 18-methyl in 17-oxa-16-oxo compounds (τ 8.81) relative to an 18-methyl in a D-homo-5α-androstane is 0.36 p.p.m. The deshielding of the 19-methyl and its magnitude provide additional support for structure III.

In an attempt to rationalize the results, we considered the possibility of epoxide II as the initial reaction product. To test the hypothesis, epoxide II was oxidized for 24 hr. under the same conditions. The acidic fraction was a complex mixture, and attempts to detect the 2,3-dicarboxylic acid I failed. Consequently, we are inclined to infer that the epoxide is apparently not a precursor of the diacid. From the neutral fraction, which proved also to be a complex mixture, the lactone III was obtained.[7]

It appears that the epoxide II might be the intermediate *en route* to γ-lactone III. The accumulation of II, when the reaction is carried out for a shorter time (6 hr.), provides some support for this hypothesis. However, other pathways (*e.g.*, *via* enol lactone V) cannot be excluded on the basis of the present evidence, especially in view of the ease with which conjugated ketones can be oxidized to enol lactones.[8]

The 16α,17α-epoxide[9] VIa was the only transformation product detected in the neutral fraction from oxidation of 3β-acetoxy-5β-pregn-16-en-20-one. Though an acidic residue was also obtained, no identifiable product could be isolated.

We then turned our attention to the oxidation of a ring C conjugated ketone, namely 9(11)-dehydrohecogenin acetate. The isolated acidic fraction consisted mainly, if not exclusively, of the 9,12-seco-11-norketo acid[10] VII. Confirmation of the structure was obtained



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(2) (a) Recipient of a Public Health Research Career Program Award CA-K3-16614 from the National Cancer Institute; (b) Postdoctoral Fellow on leave of absence from Hokkaido University, Sapporo, Japan.

(3) E. Caspi and S. N. Balasubrahmanyam, *Experientia*, **19**, 396 (1963).

(4) E. Caspi and S. N. Balasubrahmanyam, *J. Org. Chem.*, **28**, 3383 (1963).

(5) (a) E. Caspi, Y. Shimizu, and S. N. Balasubrahmanyam, *Tetrahedron*, **20**, 1271 (1964); (b) E. Caspi, and S. N. Balasubrahmanyam, *Tetrahedron Letters*, 745 (1963). An apparent directional influence of ring A/B junction on the course of oxidation indicated in this reference was reinvestigated and proved to be incorrect.[5a]

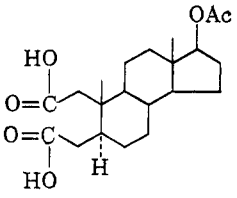
(6) W. M. Hoehn, *J. Org. Chem.*, **23**, 929 (1958).

(7) In addition to lactone III, a small amount of another product, insufficient for its characterization, was isolated. The unknown had infrared bands at 3200 (hydroxyl, rather sharp), 1730, and 1705 cm.$^{-1}$. It was considered possible that it might be the lactol ii; however, this possibility was disproved by the following experiments. Treatment of the unknown with diazomethane gave a sirup whose infrared spectrum was devoid of hydroxyl absorption and had a band at 1730 cm.$^{-1}$. Reduction of the sirup with sodium borohydride in the presence of sodium hydroxide and subsequent treatment with acid gave a solid which was distinctly different from the lactone iii described by R. Pappo and C. J. Jung, *Tetrahedron Letters*, 365 (1962). We are indebted to Dr. R. Pappo for the authentic sample of lactone iii.

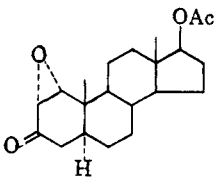
(8) (a) L. Velluz, G. Amiard, J. Martel, and J. Warnant, *Bull. soc. chim. France*, 879, 1485 (1957); (b) E. Caspi, Y. W. Chang, and R. I. Dorfman, *J. Med. Pharm. Chem.*, **5**, 714 (1962).

(9) R. E. Marker, E. M. Jones, and E. L. Wittbecker, *J. Am. Chem. Soc.*, **64**, 468 (1942).

(10) T. P. Kutney, I. V. Lattas, and G. W. Rao, *Can. J. Chem.*, **41**, 958 (1963).



I



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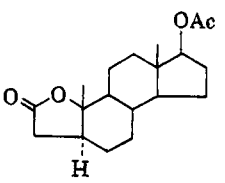

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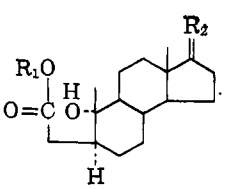
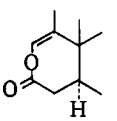
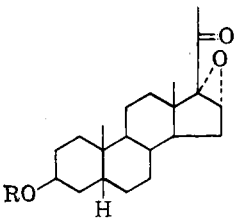


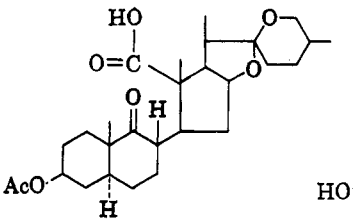
IVa, $R_1 = H$; $R_2 = OH(\beta)$, H(α)
b, $R_1 = CH_3$: $R_2 = O$



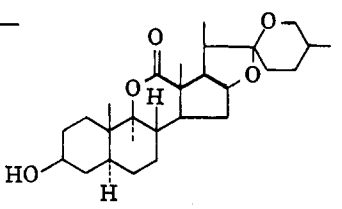
V



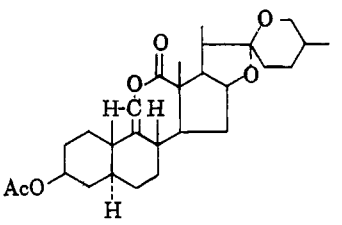
VIa, R = Ac
b, R = H



VII



VIII



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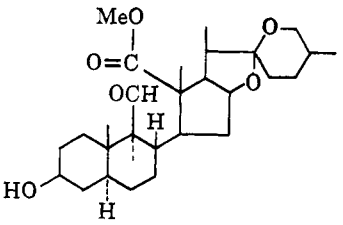
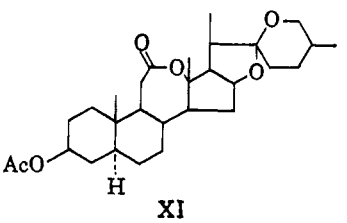
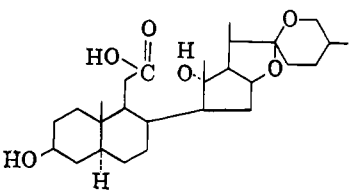


X



XI



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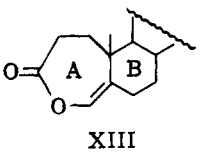
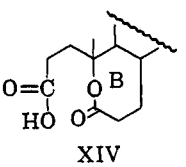
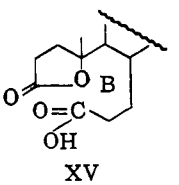


XIII



XIV



XV

by its conversion to lactone VIII by sodium borohydride and subsequent dehydration.[10] In considering the stereochemistry of VIII, it might be assumed that the reduction proceeded to give the more stable equatorial hydroxyl, hence the 9α-H assignment. The neutral residue of the oxidation contained mainly enol lactone IX. The product IX had the composition $C_{29}H_{42}O_6$, and its infrared spectrum had bands at 1738, 1730, and 1670 cm.$^{-1}$. The two bands at 1738 and 1670 cm.$^{-1}$ are characteristic of enol lactones and enol esters. Confirmation of the structure was provided by an n.m.r. spectrum which had, among others, a signal for a single proton at τ 3.89 (singlet). The fact that the proton gave rise to a singlet excluded the presence of hydrogens on neighboring carbons, and its chemical shift is consistent for a vinylic proton on a carbon bearing an oxygen function. Saponification of IX followed by esterification with diazomethane gave an amorphous aldehydo ester X. The product X showed a band at 2720 cm.$^{-1}$ in the infrared and a doublet at τ 0.45 (J = 5.0 c.p.s.) in the n.m.r. spectrum for the aldehyde proton.

The known hecolo lactone acetate XI was formed on oxidation of hecogenin acetate.[11] The lactone provided the dihydroxy acid XII on saponification. No efforts were made to isolate the alternative 11,12-iso lactone, if present.

(11) (a) E. S. Rothman, M. E. Wall, and C. R. Eddy, *J. Am. Chem. Soc.*, **76**, 527 (1954); (b) P. Bladon and W. M. McMeekin, *J. Chem. Soc.*, 3504 (1961).

Attempted oxidation of 7-ketocholesteryl acetate and 3β-acetoxy-12-keto-5β-chol-9(11)-enic acid led to the recovery of all of the starting material.

In considering a possible mechanism of oxidation for Δ^4-3-ketones, we have suggested[3,4] an initial attack of the reagent on the carbonyl and formation of peroxides or hydroperoxides. The peroxy intermediates could then collapse to enol lactones XIII which on further oxidation would yield XIV. The isolation of enol lactone IX and secoketo acid VII provides some support for the proposed mechanism and points to a possible similarity between oxidation of Δ^4-3-ones and the 5α-$\Delta^{9(11)}$-12-ketones. However, it may be observed that the oxidation of the Δ^1-3-ketone in the 5α-series and of the Δ^{16}-20-ketone in the 5β-series does not necessarily proceed in this manner. The resistance of a Δ^5-7-ketone and of a $\Delta^{9(11)}$-12-ketone of the 5β-series indicates that no general rule on the course of oxidation can be made at the moment.

Experimental[12]

Oxidation of 17β-Acetoxy-5α-androst-1-en-3-one. A.—A mixture of the 1-en-3-one (2.0 g.), *t*-butyl alcohol (90 ml.), hydrogen peroxide (50%, 4.5 ml.), and selenium dioxide (150 mg.) was re-

(12) Melting points were determined on a micro hot stage and are corrected. Infrared spectra were taken on solids incorporated in potassium bromide blotters. N.m.r. spectra were determined in $CDCl_3$. Thin layer chromatographies were performed with silica gel HF_{254} purchased from E. Merck, A. G., Darmstadt, Germany.

fluxed for 6 hr. After dilution with ethyl acetate, the solution was partitioned with aqueous sodium hydrogen carbonate into base-soluble and base-insoluble fractions. Following the conventional work-up,[4,5] a neutral (1.1 g.) and an acidic (0.59 g.) residue were obtained.

B.—A mixture of the 1-en-3-one (1.0 g.), *t*-butyl alcohol (45 ml.), hydrogen peroxide (50%, 2.5 ml.), and selenium dioxide (70 mg.) was refluxed for 16 hr. The mixture was processed as above to yield neutral (410 mg.) and acidic (580 mg.) fractions.

17β-Acetoxy-2,3-seco-5α-androstane-2,3-dioic Acid (I).—The acidic fractions from experiments A and B were crystallized from ethyl acetate to yield I: m.p. 223–225°; ν_{max} 3100, 2600, 1720, 1690, 1240 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{32}O_6$: C, 66.30; H, 8.48. Found: C, 66.09; H, 8.87.

The infrared spectrum of I was indistinguishable from that of an authentic sample.[5a]

17β-Acetoxy-1α,2α-epoxy-5α-androstan-3-one (II). A.—The neutral crystalline fraction from the 6-hr. oxidation (A) was recrystallized from methanol to yield II. The mother liquor consisted mainly of II as evidenced by thin layer chromatography (t.l.c.).

B.—A portion of neutral fraction from the 16-hr. oxidation (B, 300 mg.) was chromatographed on three 20 × 20 cm. t.l.c. plates prepared with silica gel HF_{254}. After development with chloroform–ethyl acetate (4:1), two zones were detected. Elution of the more mobile zone gave II (33 mg.).

C.—To a mixture of 17β-acetoxy-5α-androst-1-en-3-one (500 mg.), methanol (10 ml.), and hydrogen peroxide (30%, 0.5 ml.) at 15°, a 2 *N* methanolic solution of sodium hydroxide was added.[6] Within several minutes a crystalline solid separated and was collected by filtration after 10 min. Dilution of the mother liquor with water provided an additional amount of II. The epoxide was recrystallized from methanol (240 mg.).

All samples were recrystallized from methanol to m.p. 156–158° and did not depress the melting points mutually: ν_{max} 1725, 1710, 1240 cm.$^{-1}$. The infrared spectra of all samples were indistinguishable.

17β-Acetoxy-A-nor-1-oxa-5α-androstan-2-one (III). A.—The less mobile fraction recovered from the above-described t.l.c. was III (60 mg.).

B.—A mixture of the hydroxy acid IV (10 mg.) and acetic anhydride (1 ml.) was refluxed for 2 hr. The excess acetic anhydride was removed in a stream of nitrogen, and the residue was purified by t.l.c. (chloroform–ethyl acetate, 4:1). The recovered product was crystallized from aqueous methanol to yield III (4 mg.).

C.—The lactone was also isolated from the oxidation of the epoxide II (see below). All samples gave the same infrared spectra and did not depress their melting points mutually.

Recrystallization from aqueous methanol gave a sample: m.p. 110°; ν_{max} 1770, 1725, 1240 cm.$^{-1}$; n.m.r. τ 5.36 (triplet 17α-H), 7.63, 7.96 (acetate), 8.76 (19-Me), 9.13 (18-Me).

Anal. Calcd. for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.24; H, 8.94.

10α,17β-Dihydroxy-1,2-bisnor-3,10-seco-5α-androstan-3-oic Acid (IVa).—A solution of lactone III (10 mg.) in methanol (2.5 ml.) and 1 *N* sodium hydroxide (2.5 ml.) was refluxed under nitrogen for 2 hr. Ice was added and the mixture was carefully acidified with dilute hydrochloric acid. The acid was recovered with ethyl acetate in the conventional manner. Crystallization from ethyl acetate provided IVa: m.p. 217–220°; ν_{max} 3450, 2600 (broad), 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.54; H, 9.52.

Methyl 10α-Hydroxy-1,2-bisnor-3,10-seco-5α-androstan-17-on-3-oate (IVb).—The hydroxy acid IVa (20 mg.) was esterified with ethereal diazomethane, and the ether removed in a stream of nitrogen. To the residue a suspension of chromium trioxide (25 mg.) in pyridine (2 ml.) was added, and the mixture was stored for 6 hr. at ambient temperature. Ethyl acetate was added, and the precipitated solid was removed by filtration through Celite. The filtrate was washed with dilute hydrochloric acid and water, then dried and concentrated to a residue (17 mg.). Purification by t.l.c. (chloroform–ethyl acetate, 3:1) gave 13 mg. of crystalline IVb. The solid was recrystallized from ether–*n*-hexane (prisms): m.p. 118–119°; ν_{max}^{KBr} 3550, 1740 (17-ketone), 1720 (ester) cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.47; H, 9.10.

Oxidation of Epoxide II.—A solution of epoxide II (250 mg.) and selenium dioxide (25 mg.) in *t*-butyl alcohol (15 ml.) and hydrogen peroxide (50%; 0.7 ml.) was refluxed for 24 hr. After dilution with water, the steroids were recovered with ethyl acetate. Partitioning with sodium hydrogen carbonate led to acidic (90 mg.) and neutral (141 mg.) fractions.

The neutral fraction was resolved by t.l.c. (chloroform–ethyl acetate, 4:1), into about seven zones which were numbered in order of increased mobility. Zones 6 and 5 gave starting material (12 mg.) and lactone III (21 mg.), respectively.

From zone 2 a small amount of an unknown solid was obtained: ν_{max} 3200 (sharp), 1730, 1705 cm.$^{-1}$. Treatment with diazomethane gave a sirup, ν_{max} 1730 cm.$^{-1}$. A mixture of the sirup, methanol (0.3 ml.), 2 *N* sodium hydroxide (0.2 ml.), and sodium borohydride (5 mg.) was kept at ambient temperature for 16 hr. Water was added and the solution was extracted with ether. The aqueous phase was acidified with 1 *N* hydrochloric acid and extracted with ethyl acetate. The ethyl acetate solution was washed with a sodium hydrogen carbonate solution and water, dried, and concentrated. The residue was crystallized from ether–ethyl acetate to m.p. 195–199°. The infrared spectrum had bands at ν_{max} 3400, 1700 cm.$^{-1}$ and was different[7] from that of the lactone iii.

3β-Acetoxy-16α,17α-epoxy-5β-pregnan-20-one (VIa).—A mixture of 3β-acetoxy-5β-pregn-16-en-20-one (500 mg.), *t*-butyl alcohol (25 ml.), selenium dioxide (40 mg.), and hydrogen peroxide (50%; 1.2 ml.) was refluxed for 7 hr. The conventional work-up provided neutral (350 mg.) and acidic (112 mg.) fractions. Crystallization of the neutral residue from isopropyl ether and methanol gave the epoxide (220 mg.): m.p. 172° (lit.[9] m.p. 179–180°); ν_{max} 1730, 1715, 1250, 870, 800 cm.$^{-1}$. Chromatography of the mother liquor yielded some starting material and an additional amount of the epoxide.

Saponification of VIa in aqueous methanolic sodium hydroxide gave 3β-hydroxy-16α,17α-epoxy-5β-pregnan-20-one (VIb), m.p. 223–225° (lit.[9] m.p. 223–225°). The acidic residue resisted crystallization even after t.l.c.

Enol Lactone IX.—A mixture of 9(11)-dehydrohecogenin acetate (650 mg.), *t*-butyl alcohol (30 ml.), hydrogen peroxide (50%, 1.5 ml.), and selenium dioxide (50 mg.) was refluxed for 10 hr. Processing of the reaction mixture and partitioning with sodium carbonate led to acidic (312 mg.) and neutral (250 mg.) residues.

The neutral residue was crystallized from methanol–ethyl acetate to yield the enol lactone IX: m.p. 275–285°; ν_{max} 1738 (lactone), 1730 (acetate), 1670 (—O—C(H)=C<) cm.$^{-1}$; n.m.r. τ 3.89 (>C=C(H)—O—).

Anal. Calcd. for $C_{29}H_{42}O_6$: C, 71.57; H, 8.70. Found: C, 71.80; H, 9.02.

A mixture of the enol lactone (30 mg.), methanol (5 ml.), and 2 *N* sodium hydroxide (2 ml.) was refluxed for 2 hr. in an atmosphere of nitrogen. Most of the methanol was removed in a stream of nitrogen, then the mixture was acidified and the steroid was recovered with ethyl acetate. The extract was washed with water, dried, and concentrated to a residue. The amorphous solid was then treated with ethereal diazomethane and the ester submitted to t.l.c. The product, an amorphous powder, resisted crystallization: ν_{max} (film) 3240 (—OH), 2720 (—CHO), 1710 cm.$^{-1}$; n.m.r. τ 0.45 (doublet) (J = 5.0 c.p.s.) (>CH—CHO), 6.29 (3H, CO—OCH_3).

11-Nor-9,12-seco-9-keto-12-carboxylic Acid (VII).—The acidic residue from the above experiment was crystallized from ethyl acetate to yield plates: m.p.[13] 244–249° (lit.[10] m.p. 262–264°); ν_{max} 3200, 2000 (broad), 1725, 1710, 1240, 1055, 1030, and 880 cm.$^{-1}$.

Anal. Calcd. for $C_{28}H_{24}O_7$: C, 68.54; H, 8.63. Found: C, 68.69; H, 8.48.

11-Oxahecogenin (VIII).—To a solution of acid VII (10 mg.) in 1 *N* sodium hydroxide (1 ml.), sodium borohydride (20 mg.) was added. The mixture was stored for 16 hr. at ambient temperature. The reaction was terminated with aqueous hydro-

(13) When the melting points were determined on a Fisher-Johns apparatus, VII showed m.p. 260–262° and VIII, m.p. 269–271° as reported in ref. 10.

chloric acid, and the steroids were recovered with ethyl acetate. The ethyl acetate solution was washed with sodium bicarbonate and water, dried, and concentrated *in vacuo*. The residue was crystallized from aqueous methanol to yield prisms: m.p.[13] 257–261° (loss of water at 110°) (lit.[10] m.p. 274–276°); ν_{max} 3550, 1727 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{40}O_5$: C, 72.19; H, 9.32. Found: C, 72.14: H, 9.14.

Hecolo Lactone Acetate XI.—A mixture of hecogenin acetate (650 mg.), *t*-butyl alcohol (30 ml.), selenium dioxide (50 mg.), and hydrogen peroxide (50%, 1.5 ml.) was refluxed for 10 hr. Processing of the reaction mixture gave acidic (312 mg.) and neutral (250 mg.) residues.

The neutral residue crystallized from methanol to yield the lactone XI (200 mg.): m.p. 290–292° (lit.[11b] m.p. 290–295°); ν_{max} 1728, 1243, 1158, 983, 922, 897 cm.$^{-1}$.

The acidic residue was dissolved in methanol (2.5 ml.) and 1 *N* sodium hydroxide (2.5 ml.), and the mixture was refluxed for 1 hr. in an atmosphere of nitrogen. After the usual work-up, the seco acid XII was obtained and showed a double m.p. 185–189° and 242–252° (lit.[11b] m.p. 187° and 253–258°); ν_{max} 3400, 2600 (broad), and 1700 cm.$^{-1}$.

Condensation of 2-Aryl-1,3-dioxolanes with Alkyllithium Reagents. A New Synthesis of Alkyl Aryl Ketones from Aromatic Aldehydes[1]

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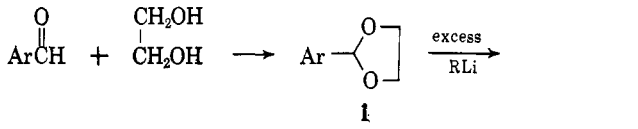
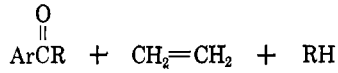
1,3-Dioxolanes of aromatic aldehydes have been found to react with alkyllithium reagents to give alkyl aryl ketones in good yield. The over-all process is thus replacement of hydrogen in the aromatic aldehyde by an alkyl substituent. An inverse addition of butyllithium to a dioxolane produced several compounds including butane which suggests initial hydrogen–metal exchange to yield an alicyclic carbanion. A mechanism is postulated in which the carbanion formed undergoes ring opening to give a β-arylcarboxyethyl anion. Decay of this anion is postulated to explain the products.

Facile conversion of one functional group to another is extremely valuable in synthetic problems. Results are now available which demonstrate that aromatic aldehydes can be smoothly transformed into alkyl aryl ketones through the following sequence.[4] Syntheses



1



2

1a, Ar = C_6H_5
b, Ar = *p*-$CH_3OC_6H_4$
c, Ar = *p*-$CH_3C_6H_4$

2a, Ar = C_6H_5, R = C_4H_9
b, Ar = C_6H_5, R = C_6H_{11}
c, Ar = *p*-$CH_3OC_6H_4$, R = C_4H_9
d, Ar = *p*-$CH_3C_6H_4$, R = C_4H_9

of 1,3-dioxolanes **1** are conventionally achieved by condensation of the appropriate aldehyde with a 1,2-diol in the presence of *p*-toluenesulfonic acid as a catalyst.[5] Although noted for marked stability to alkali bases,[6] 1,3-dioxolanes of aromatic aldehydes are conceivably vulnerable to attack by removal of a benzylic proton in analogy with the Wittig rearrangement involving the reaction of phenyllithium with benzyl ethers to give alcohols.[7,8]

In a typical experiment 2-phenyl-1,3-dioxolane (**1a**) in cyclohexane was slowly added to butyllithium in ether–cyclohexane under nitrogen. When the addition was complete (the temperature was maintained below 35°), the mixture was slowly heated to 60° (1 hr.). A large quantity of gelatinous precipitate was formed and gas was evolved. After an additional 1.5 hr. at 60°, the mixture was decomposed with water. Distillation of the organic layer gave *n*-valerophenone (**2a**) identified by infrared and n.m.r. spectroscopy. *n*-Hexyllithium and **1a** gave *n*-heptanophenone (**2b**), *n*-butyllithium and 2-*p*-methoxyphenyl-1,3-dioxolane (**1b**) gave *p*-methoxy-*n*-valerophenone (**2c**), and *n*-butyllithium and 2-*p*-tolyl-1,3-dioxolane (**1c**) gave *p*-methyl-*n*-valerophenone (**2d**) as shown in Table I. In all cases the ratio of lithium reagent to dioxolane was greater than 3. Butane and ethylene were produced in major quantity and were trapped over salt water and identified by infrared analysis. These observations imply that a nucleophilic attack by butyllithium on a carbon atom of the cyclic acetal is unlikely. In contrast the stability of benzylic anions is well known,[9] and loss of a benzylic proton from **1a** would produce such an anion.

TABLE I

ALKYL ARYL KETONES

Ketone	Yield, %	$\lambda_{max}^{C=O}$, μ
2a	87.5	5.95
2b	66.5	5.92
2c	78.0	5.98
2d	80.0	5.96

Fission of a carbon–oxygen bond in the carbanion **3** could occur to give **4** which may decompose to **5** and

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(2) Dow Chemical Co. Predoctoral Fellow, 1963–1964.

(3) College Teacher Research Participant supported by the National Science Foundation, summer 1964; National Science Foundation Faculty Fellow, 1964–1965.

(4) After this work was submitted, a paper appeared describing similar results from the reaction of 2-phenyl-1,3-dioxolane with phenyllithium: see P. S. Wharton, G. A. Hiegel, and S. Ramaswami, *J. Org. Chem.*, **29**, 2441 (1964). The one reaction studied did not provide a method of synthetic value nor was the postulated mechanism substantiated by the interception of benzoic acid. Neither was reference made to the earlier report of L. J. Nehmsman (ref. 8) who discovered the same reaction recently. In neither case was firm evidence provided for the existence of the anion **3**.

(5) M. Renoll and M. S. Newman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 502.

(6) R. C. Fuson, "Reactions of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 401.

(7) G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).

(8) Phenyllithium is reported to react with 2-phenyl-1,3-dioxolane to give benzophenone, tritanol, and ethylene as major products: see L. J. Nehmsmann, *Dissertation Abstr.*, **23**, 1929 (1962).

(9) G. A. Russell, *J. Am. Chem. Soc.*, **81**, 2017 (1959).