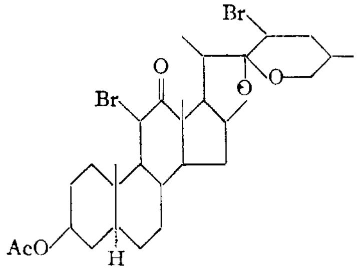

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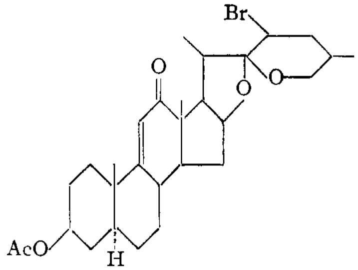

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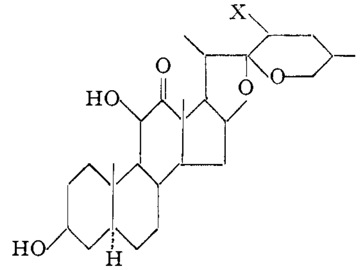

III (X = Br)
IV (X = H)

nin acetate (II), m.p. 228–230° (dec.),[3] $[\alpha]^{26}\text{D}$ −24.6° (chloroform), $\lambda^{95\%\ \text{alc.}}_{\text{max.}}$ 240 mμ (log ε 4.06), 311 mμ (log ε 2.08). Calcd. for $C_{29}H_{41}O_5Br$: C, 63.38; H, 7.52; Br, 14.54. Found: C, 63.79; H, 7.92; Br, 14.38. On cold, alkaline hydrolysis 11,23-dibromohecogenin acetate formed 11-hydroxy-23-bromohecogenin (III), m.p. 234.0–234.2° (dec.), $[\alpha]^{26}\text{D}$ −23.7° (dioxane). Calcd. for $C_{27}H_{41}O_5Br$: C, 61.70; H, 7.87; Br, 15.21. Found: C, 61.77; H, 7.65; Br, 14.83. Reduction of the latter with zinc in acetic acid yielded 11-hydroxyhecogenin (IV), m.p. 216–218.5°, $[\alpha]^{26}\text{D}$ −37.1° (dioxane). Calcd. for $C_{27}H_{42}O_5$: C, 72.61; H, 9.48. Found: C, 72.36; H, 9.68. Treatment with acetic anhydride in pyridine gave a diacetate, m.p. 230–231°, $[\alpha]^{26}\text{D}$ −70.7° (dioxane). Calcd. for $C_{31}H_{46}O_7$: C, 70.16; H, 8.74. Found: C, 69.95; H, 8.63.

The structures of III and IV follow tentatively from the identity of the hydrolysis conditions with those which yielded 11α- and 11β-hydroxy-12-ketocholanic acids from the corresponding 11β- and 11α-bromo derivatives.[2] Treatment of IV with hot alcoholic alkali, as with pyridine or chromatographic alumina, gave rise to a mixture of isomeric substances having the composition of hydroxyhecogenin and giving variously fractions melting in the range 210–220°, $[\alpha]\text{D}$ −27 to −37°. This indicates a rearrangement with the possible formation of some of the expected 11-keto-12-hydroxy isomer. In view of the pyridine–acetic anhydride conditions for formation of the diacetate as well as the failure of the latter to form an oxime, the structure of this compound is not assigned. Further investigation of the ketol rearrangement is in progress.

We wish to thank the Research Corporation for making this investigation possible.

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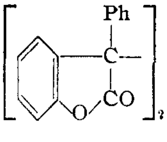
RECEIVED JANUARY 31, 1951

DEHYDROGENATION REACTIONS BY THE ACTION OF FREE RADICALS

Sir:

Very little seems to be known about the strong dehydrogenating power of long-lived free radicals. We have found that the compounds listed in Table I, which all dissociate into free radicals of long life, at least at high temperatures (see footnotes 1–5), dehydrogenate benzyl alcohol to benzaldehyde. Experimental details concerning temperature and duration of the experiment are shown below; no solvents were used. The dehydrogenation of the benzyl alcohol is accompanied by the reduction of the free radical corresponding to the substances mentioned in Table I. Thus, from (I) the lactone of *o*-hydroxydiphenylacetic acid (III) was obtained, tetraphenylhydrazine yielded diphenylamine and diphenyl disulfide yielded thiophenol.



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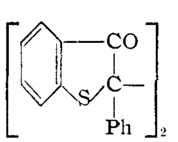

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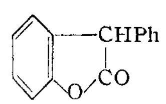

III

TABLE I

	Temp. °C.	Hours
2,2′-Diketo-3,3-diphenyl-3,3′-dicoumaranyl[1] (I)	110	2
2,2′-Diphenyl-thioindigo white[2] (II)	130	2
Tetraphenylsuccinodinitrile[3,6]	140	2
Tetraphenylhydrazine[4]	110	1
Diphenyl disulfide[5]	100	5

We found also that phenyliodo dichloride ($C_6H_5ICl_2$) converts benzyl alcohol into benzaldehyde when the two substances are heated at 110° for 20 minutes, whereas xanthhydrol was readily converted into xanthone. It is believed that these two reactions also proceed via a free radical mechanism, involving chlorine atoms. The yields of benzaldehyde (estimated through the 2,4-dinitrophenylhydrazone) were good, in some cases exceeding 70%.

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(1) Löwenbein and Simonis, *Ber.*, **57**, 2040 (1924).
(2) Kalb and Baeyer, *ibid.*, **46**, 3879 (1913).
(3) Löwenbein, *ibid.*, **58**, 606 (1925); Wittig, *ibid.*, **65**, 760 (1932).
(4) Wieland, *Annalen*, **381**, 200 (1911).
(5) Schönberg and Mustafa, *J. Chem. Soc.*, 889 (1949); Schönberg, Rupp and Gumlich, *Ber.*, **66**, 1932 (1933).
(6) This experiment was carried out with M. F. S. El-Hawary.

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RECEIVED DECEMBER 1, 1950

ABSOLUTE MOLAL ENTROPIES OF TRANSFER OF IONS

Sir:

In a recent paper[1] Goodrich, Goyan and others have calculated absolute molal entropies of trans-

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(1) J. L. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston and M. B. Young, THIS JOURNAL, **72**, 4411 (1950).