Tetrahedron Letters No.17, pp. 9-11, 1960. Pergamon Press Ltd. Printed in Great Britain

A NOVEL PREVOST REACTION

L. H. Briggs, B. F. Cain and B. R. Davis

Department of Chemistry, University of Auckland, New Zealand

(Received 29 June 1960)

ISOPHYLLOCLADENE, whose formulation as Ia is now secure,[1] undergoes a novel reaction with silver iodobenzoate (Prévost's reagent[2]). This complex normally reacts with olefins to produce the corresponding glycol dibenzoate[3] but when isophyllocladene in dry, refluxing benzene was treated with iodine and silver benzoate it gave, in high yield, an unsaturated monobenzoate, m.p. 161-163° (Found: C, 82.3, 82.3; H, 9.4, 9.0. $C_{27}H_{36}O_2$ requires C, 82.6; H, 9.2. Infra-red bands at 1709 and 853 cm^{-1}) which we now show to possess structure Ib. On hydrolysis Ib afforded the alcohol (Ic), m.p. 126-127° (Found: C, 83.2; H, 11.0. $C_{20}H_{32}O$ requires: C, 83.3; H, 11.2. Infra-red bands at 3279, 1015 and 837 cm^{-1}) which in refluxing acetic anhydride gave the acetate (Id), m.p. 37-38° (Found: C, 79.9; H, 10.4. . $C_{22}H_{34}O_2$ requires: C, 79.9; H, 10.4. Infra-red bands at 1745 and 841 cm^{-1}) and with benzoyl chloride in refluxing pyridine reformed Ib.

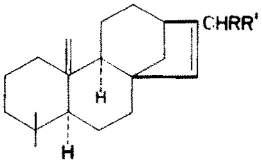
On oxidation with chromium trioxide-pyridine Ic affords the α β-unsaturated aldehyde (Ie), m.p. 125-127°, in almost quantitative yield [Found: C, 84.2;

---

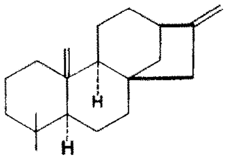
[1] L. H. Briggs, B. F. Cain and R. C. Cambie, Tetrahedron Letters No. 8, 17 (1959) and references there cited; P. K. Grant and R. Hodges, Tetrahedron 8, 261 (1960).

[2] C. V. Wilson in Adams' Org. Reactions IX, 350 (1957).

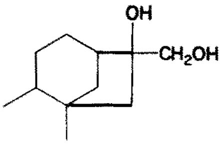
[3] K. B. Wiberg and K. A. Saegebarth, J. Amer. Chem. Soc. 79, 6256 (1957).



I a R=R'=H
b R=H, R'=OBz
c R=H, R'=OH
d R=H, R'=OAc
e RR'=O
f RR'=N.NH.CO.NH$_2$



II



III

H, 10.2. $C_{20}H_{30}O$ requires: C, 83.9; H, 10.6. Infra-red bands at 2817, 2717, 1681, 1597 and 856 cm^{-1} λ_{max}^{EtOH} 253 and 258 mμ (log ε 3.87 and 3.88)]. The long wavelength of these bands [cf. cyclopent-1-enealdehyde λ_{max}^{EtOH} 237-238 mμ (log ε 4.13)][4] is probably an indication of strain in the bicylo [3:2:1] octane system.[5,6] The aldehyde yielded a semicarbazone (If), m.p. 262-264° [Found: C, 73.6; H, 9.6. $C_{21}H_{33}ON_3$ requires: C, 73.4; H, 9.7. λ_{max}^{EtOH} 275.5 mμ (log ε 4.54) and a 2,4-dinitrophenylhydrazone, m.p. 234° [Found: C, 67.5; H, 7.2; N. 12.0. $C_{26}H_{34}O_4N_4$ requires C, 66.9; H, 7.4; N, 12.0. λ_{max}^{EtOH} 234, 255, 291 and 384 mμ (log ε 4.32, 4.32, 4.18 and 4.51)].

That these structural assignments are correct was shown in three ways. On oxidation with selenium dioxide phyllocladene (II) or isophyllocladene gave the aldehyde (Ie) (identified by m.p. and mixed m.p.; semicarbazone identified by m.p. and mixed m.p.) while the semicarbazone (If), on Wolff-Kishner reduction, gave phyllocladene (identified by m.p., mixed m.p., infra-red spectrum). These reactions constitute the first conversion of isophyllo-

---

[4] J. B. Brown, H. B. Henbest and E. R. H. Jones, J. Chem. Soc. 3634 (1950).

[5] R. N. Moore and G. S. Fisher, J. Amer. Chem. Soc. 78, 4362 (1956).

[6] W.Bottomley, A.R.H. Cole and D.E. White, J. Chem. Soc. 2624 (1955).

cladene to phyllocladene. Finally, the diol (III),[7] obtained by oxidation of phyllocladene, on treatment with benzoyl chloride in refluxing pyridine underwent simultaneous dehydration and benzoylation to yield the benzoate (Ib) (identified by m.p. and mixed m.p.).

When the variant of the Prévost reaction developed by Woodward and Brutcher[8] was employed, the same allylic oxidation occurred. Isophyllocladene in moist acetic acid was treated with iodine and silver acetate. The reaction product, on hydrolysis, then yielded the alcohol (Ic) (identified by m.p. and mixed m.p.).

Finally, phyllocladene, in dry benzene, when treated with silver benzoate and iodine also gave the benzoate (Ib). This unexpected result was explained by subsequently finding that phyllocladene is isomerized to isophyllocladene by a trace of iodine in benzene.

Acknowledgements - We gratefully acknowledge assistance from the Chemical Society, the Rockefeller Foundation of New York, the Australian and New Zealand Association for the Advancement of Science and the Research Grants Committee of the University of New Zealand and two of us (B.F.C. and B.R.D.) the award of Research Fund Fellowships.

---

[7] C. W. Brandt, New Zealand J. Sci. Tech. **34** B, 46 (1952).

[8] R. B. Woodward and F. V. Brutcher, Jr., J. Amer. Chem. Soc. **80**, 209 (1958).