CHEMISTRY LETTERS, pp. 5-6, 1982.

A VERY SIMPLE SYNTHESIS OF NATURAL SATURATED δ-SUBSTITUTED δ-LACTONES. THE PHEROMONE OF *Vespa orientalis*

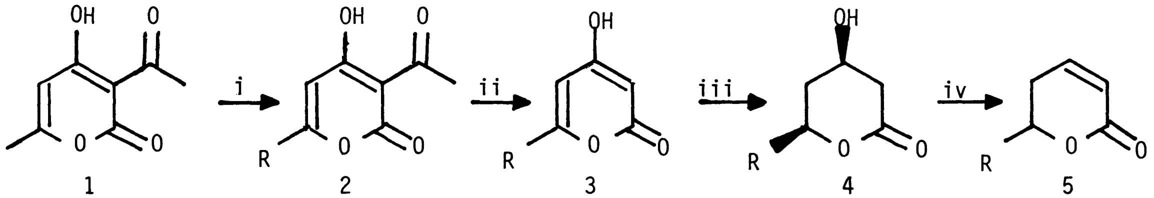
Ramón BACARDIT and Marcial MORENO-MAÑAS*
Departamento de Química Orgánica. Universidad Autónoma de
Barcelona. Cerdanyola. Barcelona. Catalunya. Spain

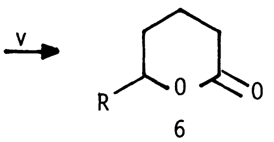
Very facile syntheses of racemic massoia lactone and the pheromone of *Vespa orientalis* have been achieved starting from dehydroacetic acid.

δ-Lactones are widely spread in nature; some of them are flavouring substances in plants and others are significant in insect behaviour[1].

The availability of simple syntheses for important products, requiring the use of cheap and easily available reagents and starting materials is a matter of the uppermost interest. With this idea in mind we reasoned that the industrially available dehydroacetic acid, 1, could be an appropriate starting material for the preparation of the mentioned lactones. We describe now original and very efficient synthesis of 6-*n*-undecyltetrahydro-2-pyrone, 6b, pheromone of the oriental hornet (*Vespa orientalis*)[2] and of 6-*n*-pentyl-5,6-dihydro-2-pyrone, 5a, called massoia lactone, present in *Cryptocaria massoia*[3,4,5], in *Polianthes tuberosa L*[6], and in two species of formicine ants of the genus *Camponotus*[7].

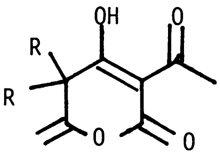
Sequential alkylation[8], deacetylation[9], and hydrogenation[10,11] afford the hydroxylactones 4[12], easily transformed into 5 and 6[13] (see scheme). The overall yields for 5a and 6b were 47 and 42%. By-products in the alkylation steps were isolated and characterized as 7-10 (a, R = = *n*-C_4H_9; b, R = *n*-$C_{10}H_{21}$)[14] by spectroscopic methods. They were derived from the trianion of 1.



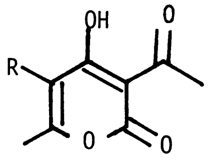


a.- R= *n*-C_5H_{11}
b.- R= *n*-$C_{11}H_{23}$

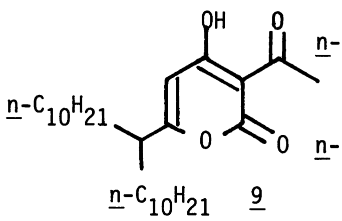
i.- 1) 3 $NaNH_2$/liq. NH_3; 2) *n*-C_4H_9Br or *n*-$C_{10}H_{21}Br$.
ii.- 90% H_2SO_4/130°/ 18 minutes.
iii.- H_2/1 atm./r.t./Ra-Ni/EtOH.
iv.- TsOH/Benzene/reflux.
v.- H_2/1 atm./r.t./10% Pd-C/AcOEt.



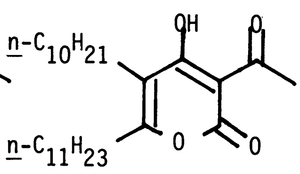
7



8



9



10

Acknowledgements.- We acknowledge financial support from the "Comisión Asesora de Investigación" and a grant (to R.B.) from INAPE (Ministerio de Educación y Ciencia). We are very much indebted to Prof. Pirkle (Univ. of Illinois) for spectroscopic data of 6b.

References

1) a) G. Ohloff; Fortschr. Chem. Org. Naturstoffe, 35, 431, (1978); b) J.M. Brand, J.C. Young, R.M. Silverstein; ibid., 37, 1, (1979).
2) W.H. Pirkle, P.E. Adams; J. Org. Chem., 44, 2169, (1979) and references cited therein.
3) H. Benoni, K. Hardebeck; Arzneim. Forsch., 14, 40, (1964) and references cited therein.
4) W.H. Pirkle, P.E. Adams; J. Org. Chem., 45, 4117, (1980).
5) K. Mori; Agric. Biol. Chem., 40, 1617, (1976).
6) R. Kaiser, D. Lamparsky; Tetrahedron Letters, 1976, 1659.
7) G.W.K. Cavill, D.V. Clark, F.B. Whitfield; Aust. J. Chem., 21, 2819, (1968).
8) T.M. Harris, C.M. Harris, M.P. Wachter; Tetrahedron, 24, 6897, (1968).
9) J.N. Collie; J. Chem. Soc., 59, 607, (1891).
10) R. Bacardit, M. Moreno-Mañas; Tetrahedron Letters, 21, 551, (1980).
11) B. Nedjar, M. Hamdi, J. Périé, V. Hérault; J. Heterocyclic Chem., 15, 1153, (1978).
12) The cis configuration is assigned by comparison of the pmr spectrum of 4a and 4b with that of 4 (R = CH_3)[10].
13) Compounds 2-6 were fully characterized by comparison with reported data and/or authentic samples. Correct elemental analysis were secured for all new compounds. Induction of enantioselectivity at the hydrogenation step is under consideration.
14) M.p. or b.p. (oven temp./mm Hg): 2a: 42-3°; 2b: 70-1°; 3a: 53-4°(Lit.[15], 46-7°); 3b: 87-8° (Lit.[15], 80°); 4a: liquid partially converted into 5a upon vacuum distillation; 4b: 53-6°; 5a: 100-5°/0.2; 5b: 32-4°(Lit.[16], 27-9°); 6a: 100-5°/0.2; 6b: 29-30°(Lit.[17], 29.5-30°); 7a: 105°/0.15; 7b: 73-7°; 8a: 90-3°/0.25; 8b: 140-5°/0.2; 9: 198-201°/0.2; 10: 200-3°/0.1.
15) F. Kögl, C.A. Salemink; Rec. Trav. Chim., 71, 779, (1952).
16) P.C. Wailes; Aust. J. Chem., 12, 173, (1959).
17) G.M. Robinson; J. Chem. Soc., 1930, 745.

(Received September 7, 1981)