Tetrahedron Vol. 43, No. 15, pp. 3505 to 3508, 1987
Printed in Great Britain.

0040–4020/87 \$3.00+.00
Pergamon Journals Ltd.

A NEW METHOD FOR PREPARATION OF DIHYDRODINAPHTHOPYRANOPYRANS

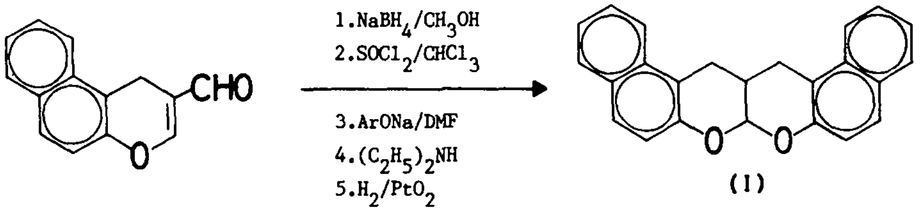
NACIYE TALINLI, AHMET AKAR* and A.CEVDET AYDOGAN

Department of Chemistry, Faculty of Science,
Technical University of Istanbul, Turkey

(*Received in UK* 11 *June* 1987)

Abstract: The syntheses of 7a,15a-dihydro-15a-methylnaphtho[2,1-b] naphtho [1',2': 5,6] pyrano[3,2-e] pyran (II) and 7a,15a-dihydro-7a-methyl-15a-isopropyl naphtho[2,1-b] naphtho [1',2':5,6] pyrano[3,2-e] pyran (III) from 2-naphthol and corresponding dimethylol ketones in one step were described. Amberlyst-15® was used as catalyst.

7a,15a-dihydro-naphtho[2,1-b] naphtho[1',2': 5,6] pyrano[3,2-e] pyran(I) has been produced in several steps starting from naphtho[2,1-b] pyran carboxaldehyde[1].

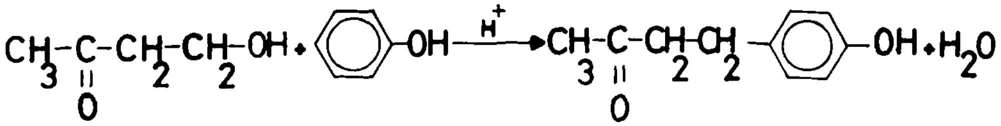


(I)

This method was only used for compound(I). However, no method for the preparation of angular alkyl derivatives of (I) has been described so far. The present paper gives a new and simple method having only one step, for the preparation of pyranopyran compounds containing angular alkyl groups, using simple organic compounds, i.e., 2-naphthol and dimethylol ketones.

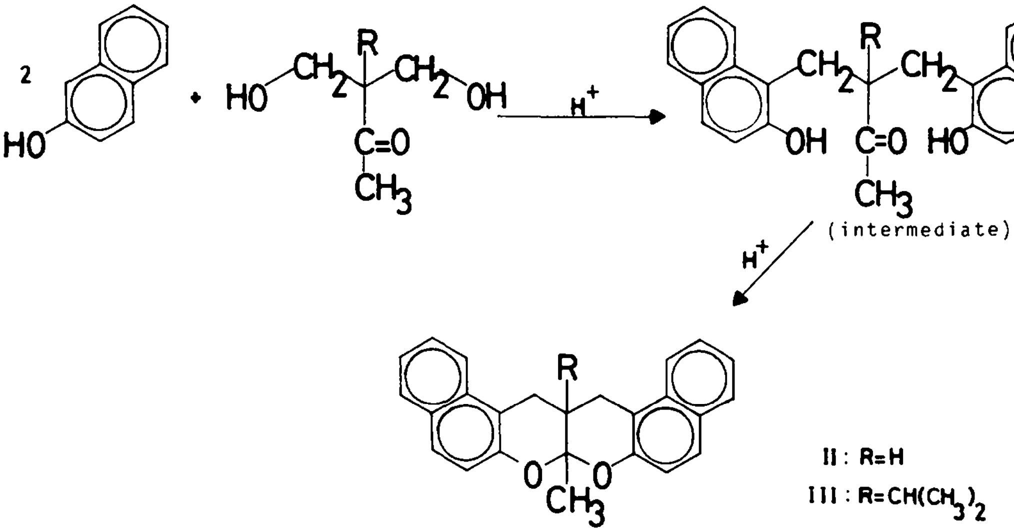
RESULTS AND DISCUSSION

Condensation of 4-hydroxy-2-butanone (monomethylol acetone) with phenol in the presence of mineral acids and strong acid ion exchange resin was studied and found that the yield was higher if ion exchange resin was used as acid catalyst[2,3].



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-OH + C_6H_5OH \xrightarrow{H^+} CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_2-C_6H_4-OH + H_2O$$

In order to extend this work, condensation of dimethylol ketones with 2-naphthol was studied. Dimethylol ketones were prepared by the modified methods reported before and then reacted with 2-naphthol using Amberlyst-15® as catalyst. Unexpectedly, pyranopyran type compounds were obtained instead ketodinaphthol. Pyranopyran could only occur if ketodinaphthol, which was the expected condensation product of one mole of dimethylol ketone and two moles of 2-naphthol, undergoes intramolecular acetalization reaction by the effect of strong acid catalyst, Amberlyst-15®, present in the reaction media. Similar intramolecular acetalization reactions in strong acid medium have been reported earlier[4,5]. Here, Amberlyst-15® should be acting as catalyst for both condensation and acetalization. Amberlyst-15® is a macroporous dry resin and preffered as catalyst if any water should be removed during a reaction[6].



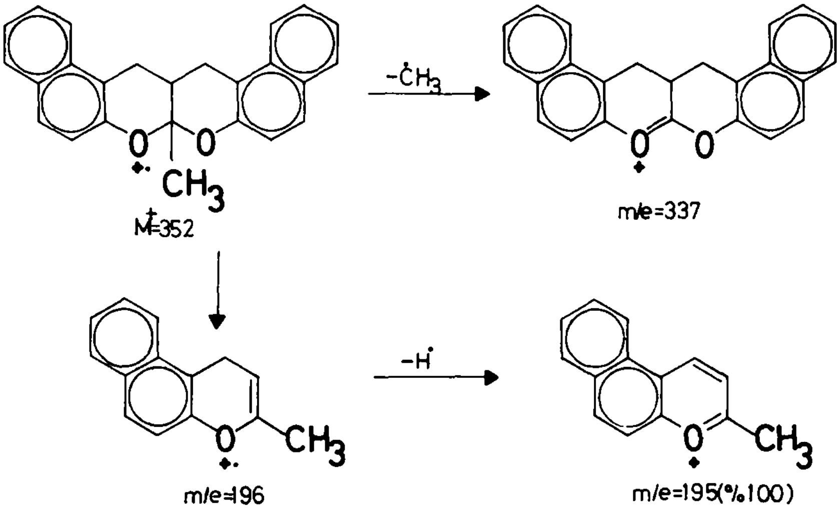
The structure of (II) and (III) was proved by their IR, PMR and MASS spectra and compared with spectral data of similar compounds[1,7,8,9]. The spectral data was collected in table 1. The PMR spectrum of the compound(II) suggests that only one stereoisomer is present, i.e. cis- structure of (II). Trans stereoisomer of this type of compound was reported to be highly strained[8]. The signal at 1.74 ppm is about angular methyl group and multiplet at 2.6-3.5 is about five protons of pyranopyran ring. The compound(III) is a mixture of cis and trans stereoisomers.

Table 1: Spectral Data of the compounds (II) and (III)

	Compound (II)	Compound (III)
IR(cm^{-1})	3050, 2950, 2850, 1620, 1600, 1223, 1100, 820, 750	3050, 2950, 2850, 1600, 1340, 1225, 1100, 810, 750
PMR (δ) ($CDCl_3$)	1.74(s-3H), 2.6-3.5(m-5H) 7.05-7.85(m-12H)	1.02(d-6H,j=6), 1.88 and 1.95(s-cis and s-trans,3H) 2.05-2.4(septet-1H), 2.6-3.5(m-4H), 7.0-7.8(m-12H)
MASS m/e(%)	352(48.4), 337(11.5), 195(100.0), 181(34.5), 152(10.3), 128(8.6), 44(7.9)	394(48.2), 337(63.1), 250(27.8), 181(76.5), 157(26.1), 128(15.7), 44(10.0)

The two singlets at 1.88 and 1.95 ppm are about the angular methyl group of cis and trans isomers respectively. Methyl group of trans isomer is affected by two naphthol rings, thus its singlet appears at lower region than that of cis isomer. The compound (III) showed two spots on TLC. This also supports above suggestion.

MASS spectrometry provided further evidence for the proposed structure of (II) and (III) and major peaks could be explained in terms of the fragmentation. The fragmentation pattern of the compound (II) is as follows:



EXPERIMENTAL

Materials

Amberlyst-15® is a macroporous styrene/divinylbenzene resin containing sulphonic acid groups and a commercial product of Rohm-Haas, USA.

4-hydroxy-3-hydroxymethyl-2-butanone(1,1-dimethylol acetone) was prepared as follows[9,10]:

Two moles of acetone and one mole of formaldehyde(as formalin) was mixed and pH was brought to 10 with 10% NaOH at room temperature. After about 30 min., the mixture was neutralized with dilute sulphuric acid. Dimethylol acetone was isolated from the mixture by fractional distillation at reduced pressure. Boiling range: 120-125°C/10 mmHg. Yield: 10g.

Preparation of 3,3-Bishydroxymethyl-4-methyl-2-pentanone (methyl isobutyl ketone dimethylol)

1 mole 2-pentanone and 2 moles formaldehyde were mixed and about 25 ml ethanol was added in order to achieve homogeneous mixture. Then, 0.8 g calcium oxide was added and stirred at room temperature.After about 18 hours, the mixture was neutralized with dry-ice and calcium carbonate was filtered off. After distillation of ethanol, the upper organic layer was separated, dried over sodium sulphate and distilled under reduced pressure. Boiling range: 140-150°C/18 mmHg.

Preparation of the compound (II)

10 g of Amberlyst-15®, 28 g of 2-naphthol and 50 ml of ethanol were placed in a three-necked round bottomed flask equipped with a mechanical stirrer, condenser and a dropping funnel.The mixture was heated to 70°C with stirring. 9.7 g acetone dimethylol was added dropwise from the funnel to the reaction mixture in 3 hours. At the end of this period, Amberlyst-15® was filtered and the solution was allowed to stand overnight. The precipitated white crystals were filtered and recrystallised from the mixture of acetone/water (6/1), m.p. 223°C, the yield: 2.2 g.(Found: C, 84.5; H, 5.4; $C_{25}H_{20}O_2$; requires: C, 84.7; H, 5.7 %).

Preparation of the compound (III)

The procedure was essentially the same as for the compound(II) afforded 1.8 g of the compound (III) from 25 g 2-naphthol and 10 g methyl isobutyl ketone dimethylol. The material was recrystallised from ethanol/carbon tetrachloride(1/1), m.p.153-155° C. (Found:C, 84.8; H, 7.08; $C_{28}H_{26}O_2$ requires: C, 85.1; H, 7.05%).

Acknowledgement: The authors are grateful to Dr.B.M.Watson and Dr.P.Brook,Department of Organic Chemistry, University of Leeds for PMR and MASS spectra and H.Ersen for Amberlyst-15® which was kindly supplied.

REFERENCES

1. Selvaraj, S., Sanjevi Babu, K.G. and Balasubramanian, K.K., Tetrahedron Letters, 24, 2509(1983)
2. Fisher, R., Körnic, W., German Patent, 2,145,308 (1971)
3. Yoshio, Y., Masahiko, N. and Yukiyasa, T., German Patent, 3,028,917 (1980)
4. Ellis, G.P., Ed., "Chromanones and Chromones", The Chemistry of Hetereocyclic Compounds;31 Jhon-Wiley and Sons (1977)
5. Baker, W. and Walker, J., J. Chem.Soc., Part 1, 646 (1935)
6. Pitochelli, F., Ion Exchance Catalysis and Matrix effect, Rohm-Haas Technical Bulletin (1980)
7. Bates, D.K. and Jones, M.C., J. Org. Chem., 43, 3856 (1978)
8. Cotteril, D.W., Iqbal,M., Livingstone, R. and Walshaw, M.V., J.Hetereocyclic Chem.,11, 283(1974)
9. Cagniant, D., Charaux, C. and Cagniant, P., Bull. Soc. Chim. France, 11, 3644 (1966)
10. Ellis, C., "The Chemistry of Synthetic Resins", vol.1.,p.543, Reinhold Publ. Corp. (1935)
11. Flemming, W. and Horst, H.D., German Patent, 544,887 (1932)