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Spectroscopic Methods for Distinguishing Primary and Secondary Alkylation Products

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Due to the great biological interest of resorcinols, a number of syntheses of the primary alkylation products and of the secondary products obtained by acid-induced cyclization have been reported.[1]

The key step of many of these syntheses, including the most used and efficient ones, is the alkylation of 5-alkylresorcinol with a cyclic allylic alcohol. In principle, this reaction can give two cyclic compounds, the so-called "bicyclic" ones, and the "tricylic" ones.

The alkylation of resorcinol was performed with BF_3-etherate in the presence or in the absence of alumina. The products were separated by medium pressure liquid chromatography on silica gel and when necessary, by thin layer chromatograpy.

Mechoulam[2,3] has observed that the most reactive alkylation site of olivetol and 5-(1,1-dimethylhepthyl) resorcinol[4] is between the two hydroxyls, whereas the same does not hold for orcinol.

In this paper we report a convenient single step synthesis of inter and intramoleuclar Friedel-Crafts alkylation products.

In typical reactions the general procedure (A) is as follows: BF_3 etherate (0.2-0.4 ml) was added under nitrogen to a stirred suspension of basic aluminum oxide (Woelm, grade I) (2.0-4.0 g) in dry dichloromethane (10 ml). Cyclic allylic alcohols (1.0-2.0 mmol) and resorcinols (1.0-2.0 mmol) in dichloromethane (3 ml) were added to the solution *via* syringe and the mixture was stirred for 5 min at room temperature. The reaction was quenched with 10% aqueous solution of sodium bicarbonate (10 ml). Ether (50 ml) and an additional portion of sodium bicarbonate solution (50 ml) were added. The organic layer was washed with brine, dried and evaporated to dryness. The oil obtained was separated by medium pressure liquid chromatography (230-400 mesh ASTM, silica gel 60 for column chromatography, elution with ethylacetate to petroleum ether 2.5 : 97.5).

The general procedure (B) is as follows: The experimental method is the same reaction condition of procedure A in the absence of alumina.

In the above reaction (Scheme 1) a benzoxocin ring is formed. BF_3 etherate in methylene chloride initiates the ring closure which probably proceeds by the mechanism indicated through the hypothetical intermediate cation (4). The cyclohexene ring is expected to exist predominantly in a chair conformation.[3,5,6]

When the bicyclic compounds (3) were reacted with BF_3-etherate, intramolecular cyclisation took place by the addition
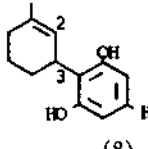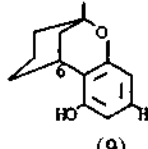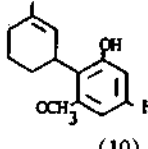

a) BF_3 etherate

Scheme 1.

a) BF_3 etherate
b) BF_3 etherate, Alumina
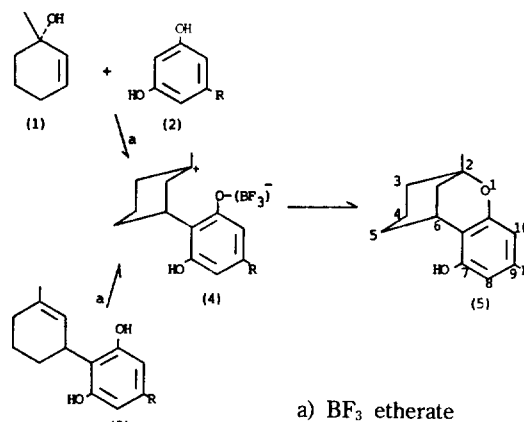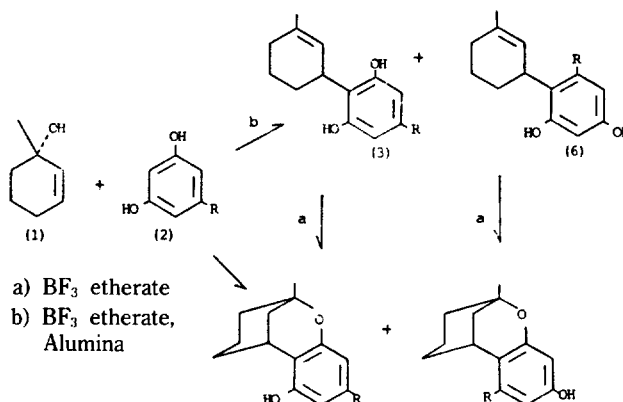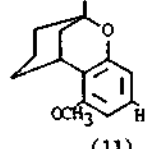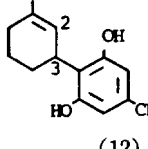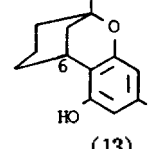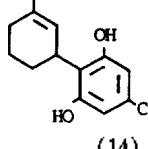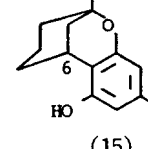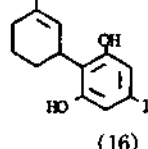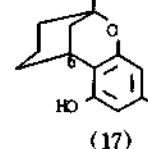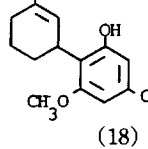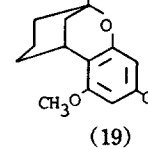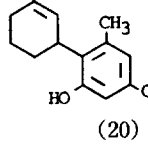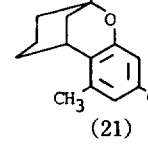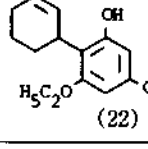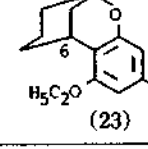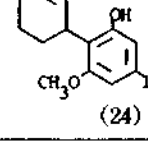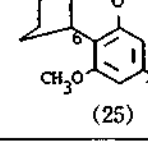
Scheme 2.

of one of the phenolic group to a suitably placed double bond (Scheme 2).[7-9]

The bicyclic compounds (3) contain double bonds which are on the cyclohexene ring. As the ultraviolet spectra eliminate the possibility of conjugation with either the double bond or the aromatic ring, the cyclohexene double bond has to occupy position C-1. This position is supported additional indicated that it is deshielded by both the double bond and the aromatic ring. Such an effect is possible only if the double bond occupies the C-1 position (Table 1).[10]

In the tricyclic compounds (5) the corresponding benzylic C-6 proton is shielded. Molecular models show that this proton is out of the plane of the aromatic ring. It is of interest to compare the chemical shifts of the C-3 and C-6 protons in the bicyclic and tricyclic compounds. The C-3 proton in the bicyclic compounds is deshielded as compared to the corresponding C-6 proton in the tricylic compounds. In the bicyclic compounds, the aromatic ring, which can rotate freely, is most probably in the same plane as the C-3 hydrogen, which is therefore deshielded (Table 1).[10,11]

We hope that these simple empirical rules, together with the difference in TLC behaviour (bicyclic compounds are usually less polar than tricyclic ones) prove useful in rapid

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Table 1. NMR Sepctra of Alkylation Products Formed Cyclic Allylic Alcohols and Resorcinols[a]

Compound	C-2H C-3H arom-H	Yield (%)	Compound	C-6H (or C-5H as indicated) arom-H	Yield (%)
(8)	3.44 (1H, m) 5.52 (1H, brs) 6.27 (1H, d, $J=2$ Hz) 6.38 (1H, d, $J=2$ Hz) 7.08 (1H, d, $J=8$ Hz)	40	(9)	3.01 (1H, br) 6.30 (2H, m) 6.76, 6.93 (1H, s, d, $J=2$ Hz)	32
(10)	3.93 (1H, br) 5.60 (1H, brs) 6.38 (1H, brs) 6.51 (1H, d, $J=2$ Hz) 7.06 (1H, t, $J=8$ Hz)	7	(11)	3.00 (1H, br) 6.40 (2H, t, $J=2$ Hz) 6.88 (1H, d, $J=8$ Hz)	65
(12)	5.59 (1H, brs) 3.77 (1H, br) 6.17 (2H, brs)	21	(13)	3.31 (1H, brs) 6.12 (1H, brs) 6.25 (1H, brs)	37
(14)	5.65 (1H, brs) 3.89 (1H, br) 6.22 (2H, S)	34	(15)	3.31 (1H, br) 6.12 (1H, d, $J=2$ Hz) 6.27 (1H, brs)	60
(16)	5.64 (1H, brs) 3.76 (1H, br) 6.34 (2H, S)	21	(17)	3.28 (1H, br) 6.25 (1H, d, $J=2$ Hz) 6.38 (1H, brs)	80
(18)	5.61 (1H, brs) 3.48 (1H, br) 6.23 (1H, s) 6.29 (1H, brs)	69	(19)	3.35 (1H, br) 6.21 (1H, brs) 6.29 (1H, brs)	60
(20)	5.61 (1H, brs) 3.48 (1H, br) 6.18 (1H, brs) 6.27 (1H, brs)	46	(21)	3.18 (1H, br) 6.24 (1H, brs)	34
(22)	5.54 (1H, brs) 3.50 (1H, m) 6.06 (1H, s) 6.25 (1H, brs)	18	(23)	3.37 (1H, br) 6.18 (1H, brs) 6.26 (1H, brs)	58
(24)	5.63 (1H, brs) 3.95 (1H, br) 6.40 (1H, s) 6.44 (1H, d, $J=1$ Hz)	80	(25)	3.31 (1H, br) 6.36 (1H, d, $J=2$ Hz) 6.43 (1H, d, $J=2$ Hz)	84
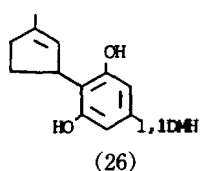
5.57 (1H, brs)
4.49 (1H, br)
6.33 (2H, s)   73

(26)
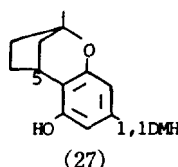
3.32 (1H, br)
6.84 (1H, brs)
6.99 (1H, d, $J=6$ Hz)   91

(27)

ᵃSpectra were determined on a Bruker WH-60 spectrometer in deuteriochloroform. Values given in ppm relative to tetramethylsilane as internal standard. Numbers in parentheses determined by integration of areas. Letters in parentheses donate singlet (s); doublet (d); broad (br); and multiplet (m).

structural elucidation of new alkylation products.

The preparation and structural proof for the new compounds 8, 9, 10, 11, 14, 15, 17, 22, 23, 25, 26, 27 will be reported in a forthcoming paper.[12] The other substance 12, 13, 16, 18, 19, 20, 21, 24 were reported.[13]

Acknowledgement. The author would like to thank Professor R. Mechoulam, and the Department of Natural Products, the Hebrew University of Jerusalem for financial support of this project.

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Spectroelectrochemical Behavior of Polypyrrole Coated on SnO₂ in Aqueous Solutions

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Polypyrrole (PPy) has received a great deal of attention because of its good electrical conductivity, ability to enhance the stability of photoelectrodes, and interesting redox properties[1-3]. Modified electrodes with PPy have been applied as potentiometric sensors[4]. The response behavior of those sensors would be closely related to the chemical status of the pyrrolylium nitrogens, the nature of doping anions as well as the interaction between pyrrolylium nitrogen and doping anions[5].

Accordingly, it is important to obtain a better understanding of the electrochemical nature of the PPy and its interaction with anions. In this connection, it is appropriate to compare the chemical structures corresponding to various oxidation states of PPy. In this paper we report the spectroelectrochemical studies on the formation of radical cations (or polarons) and dications (or bipolarons) in PPy for the first time as a function of potential cycling and the reaction of the cations with OH⁻.

Figure 1a and 1b show a series of absorption spectrum changes of the PPy film at various stage of oxidation on a working electrode immersed in a 1.0 cm×1.0 cm absorption cell at pH 2 and pH 12, respectively. The PPy coated working electrode was prepared on SnO₂ from an aqueous solution containing 50 mM pyrrole and 1.0 M HNO₃ using cyclic voltammetry as described previously[3]. During the absorbance measurements the potential was applied continuously in the range from −0.4 V to 0.4 V at 5 mV/sec with a Princeton Applied Research Model 273 potentiostat/galvanostat. All the potentials given here are referred to a Ag /AgCl electrode. The transparent SnO₂ on glass coated with PPy film was placed in a sepctrochemical cell fixed in a rapid scan Hewlett Packard 8542A diode array spectrophotometer. The absorptrum of the PPy film was recorded instantaneously in the wavelength range from 300 nm to 800 nm at a certain applied potential.

Similar spectral changes of PPy film as shown in Figure