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Communications

Alkylation of Orcinol with Nerol in Modified Lewis Acid

Chan-Nam Yook, Seung-Hwa Baek*, Sung-Dong Cho†,
and No-Yeun Park‡

Department of Health Hygienic, Wonkwang Public Health Junior College, Iri 570-750
**Department of Chemistry, Wonkwang University, Iri 570-749*
† Department of Chemistry, Chosun University, Kang Ju 501-759
‡ Department of Research and Development, Kayang Co., Pyongtaik 451-860

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The alkylation of orcinols with cyclic allyic alcohols using modified Lewis acid reagent has received some attention in the recent years[1]. These investigations have been promoted by proposals of mechanism for the syntheitc cannabinoids, and they have been aimed to perform the alkylation in mild media[2].

We wish to report here another development of this method, *viz.* the alkylation of orcinol with nerol using Lewis acid in nonagueous medium, to isomerize new derivatives of orcinol[3].

The alkylation of orcinol (**2**) was performed with BF_3-etherate in the presence or in the absence of alumina. The products were separated by Flash Chromatography on silica gel and when necessary, by Thin Layer Chromatography.

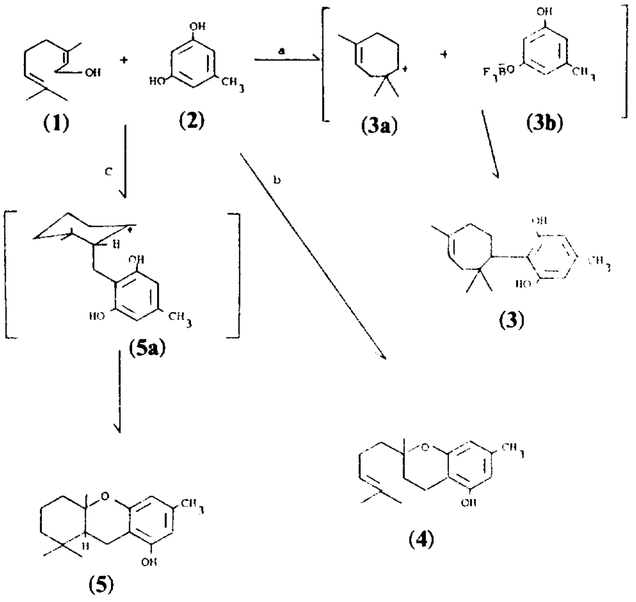
The alkylation of (**2**) with nerol (**1**) using BF_3-etherate in the presence of alumina gave a bicyclic compound (**3**)[4] in 33% yield.

We think that the postulated carbocation (**3a**) can be produced by treatment of nerol with Lewis acid[2]. The structure of this product was established on the basis of its molecular weight (mass spectrum) and NMR spectrum. In the above reaction intramolecular cyclization was not observed resulting from the addition of one of the hydroxyl groups to a double bond. This is undoubtedly due to the "mildness" of BF_3-etherate with alumina reagent which catalyses a Friedel-Crafts type reaction but apparently does not attack olefins (or attacks them at a low rate) to form a cationic center.

When the above described reaction is undertaken with BF_3-etherate, the condensation reaction was followed by cyclization (**4**)[5].

The condensation of nerol with orcinol gave the *cis* tricyclic ompound (**5**)[6] in 40% yield under the condition of general procedure[7]. This result is in sharp contrast to intermolecular alkylation (**3**) obtained (under somewhat different experimental conditions) by catalysis with BF_3-etherate on alumina.

We suppose that the observed stereochemical variation are due not to any basic mechanistic difference but to the rate of ring closure of the hypothetical intermediate (**5a**) at the monocyclic state. The nucleophilic phenolic group apparently reacts with the monocyclic carbocation before the achievement of conformational equilibration or the elimination of a proton[3].



a) BF_3-etherate, alumina, CH_2Cl_2, Imin, reflux.
b) BF_3-etherate, CH_2Cl_2, Imin, reflux.
c) BF_3-etherate, alumina, CH_2Cl_2, 3 hr, RT.

Scheme 1.

All reaction products described in the notes were identified by comparison of their physical data (m.s., n.m.r. and i.r.).

References

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2. R. K. Razdan, H. C. Dalzell, and G. R. Handrick, *J. Am. Chem. Soc.*, **96**, 5860 (1974).
3. (a) B. Cardillo, L. Merlini, and S. Servi, *Tetrahedron Lett.*, 945 (1972); (b) R. Mechoulam and B. Yagen, *Tetrahedron Lett.*, 5349 (1969).
4. Physical data of compound (3); an oil (172 mg, 33%), NMR ($CDCl_3$), δ 1.76 (6H, S, CH_3), 2.18 (3H, S, arom. CH_3), 3.85 (1H, brd, $J=7.9$ Hz, Benzylic H), 5.50 (1H, brs, olefinic H), 6.20 (2H, brs, arom. H); MS (107°) m/e, 260 (M^+, 23), 190 (19), 175(100); IR (film), 3300, 1620, 1585, 1450 cm^{-1}.
5. Physical data of compound (4); an oil (213 mg, 42%); NMR ($CDCl_3$), δ 1.26 (3H, s, CH_3), 1.76 (6H, brs, CH_3), 2.18 (3H, S, arom. CH_3), 3.46 (2H, brd, $J=7.7$ Hz, benzylic H), 5.48 (1H, brs, olefinic H), 6.09 (1H, s, arom. H), 6.23 (1H, d, $J=2.3$ Hz, arom. H); MS (102°), m/e 260 (M^+, 32), 175 (100); IR (film), 3425, 1628, 1585, 1450 cm^{-1}.
6. Physical data of compound (5); an oil (208 mg, 40%); NMR ($CDCl_3$), δ 0.94 (3H, d, $J=7.1$ Hz, CH_3), 1.08 (3H, d, $J=7.9$ Hz, CH_3), 1.33 (3H, s, CH_3), 2.20 (3H, S, arom. CH_3), 3.33 (2H, d, $J=2.3$ Hz, benzylic H), 6.11 (1H, s, arom. H), 6.26 (1H, S, arom. H); MS (59°), m/e 260 (M^+, 15), 175 (100); IR (film), 3350, 1623, 1580, 1440 cm^{-1}.
7. The general procedure is as follows; BF_3-etherate (0.4 m*l*) was added under nitrogen to a stirred suspension of basic aluminum oxide (woelm, grade I) (4 g) in dry dichloromethane (40 m*l*). The mixture was stirred for 5 min, at room temperature. Nerol (1) (308 mg, 2.0 mmol) and orcinol (2) (284 mg, 2.0 mmol) in dichloromethane 6 m*l*) were added to the suspension by syring and the reaction was quenched after 5 min with 10% aqueous solution of sodium bicarbonate (20 m*l*). Ether (100 m*l*) and an additional proportion of the above sodium bicarbonate solution (100 m*l*) were added. The organic layer was washed with brine, dried and evaporated to dryness. The oil obtained was separated by Flash Chromatography (240-400 mesh ASTM, silica gel 60, for column chromatography; elution with ethyl ether to *n*-Hexane 5 : 95).

Epoxidation of Styrene Catalyzed by Ni(II)- and Cu(II)-Macrocyclic Complexes

Yu Chul Park* and Seong Su Kim

Department of Chemistry, Kyungpook National University,
Taegu 702-701

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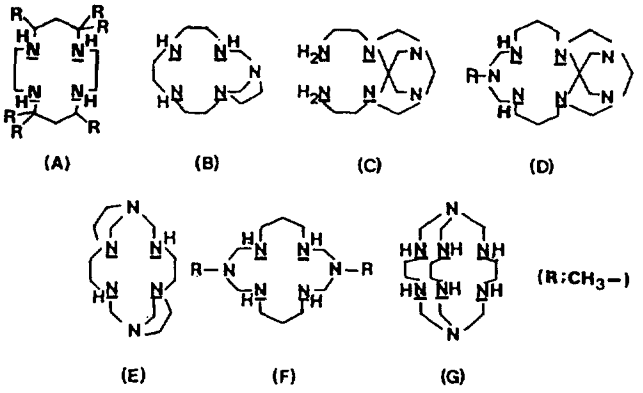


N= coordinated nitrogen on complex

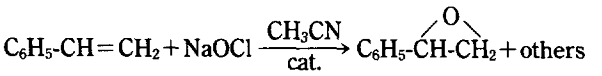
Figure 1.

The direct oxidation of olefins is a field of both academic and industrial importance and challenge. Catalysis by metal complexes plays a central role in partial selective oxidation of olefins to useful products. The use of transition metal complexes as catalysts for epoxidation reaction has received an increased attention during the past two decades. There are many reasons for this increased interest; *e.g.*, the requirement for functionalization of lower alkenes formed as byproducts in the manufacture of gasoline by gas oil cracking, the interest in understanding reactions of biological importance, the need for partial selective oxidation, and the preparation of compounds with a specific spatial structure[1]. Recently epoxidation reaction by macrocyclic complexes has been studied in conjunction with mimicking the enzymatic reaction[2-5].

We now report that nickel(II) and copper(II) complexes of macrocyclic ligand ranging from tetraazamacrocycle to octaazamacrocycle are highly effective catalysts for styrene epoxidation by sodium hypochlorite in acetonitrile and that unlike previously reported systems, we observed various selectivity for styrene oxide depending on the types of polyazamacrocyclic ligand coordinated to nickel(II) and copper(II).

The macrocyclic complexes used as catalysts were prepared by the literatures methods[6-10] and the ligands were shown in Figure 1.

The catalytic epoxidation of styrene by macrocyclic complexes could be described as Eq. (1).



$$C_6H_5\text{-}CH{=}CH_2+NaOCl \xrightarrow[cat.]{CH_3CN} C_6H_5\text{-}\overset{\;\;O}{CH\text{-}CH_2}+\text{others} \qquad (1)$$

In a typical experiment, sodium hypochlorite (4 mmol) was slowly added in the air over a period of 30 minutes to a solution of the complex (0.05 mmol) and styrene (1 mmol) in 5 m*l* of acetonitrile. The reaction was monitored by a Hwelett-Packard 5890 gas chromatography (GC) equipped with a 50 m FFAP capillary column and FID detector (oven temperature = 150℃ ; carrier gas pressure = 30 psi; split ratio = 30 : 1).

In the absence of the metal complexes, conversions of styrene were about 5-6% and formation of styrene oxide was only trace. All the nickel(II) complexes were active catalysts for the styrene oxidation. $Ni(A)^{2+}$ (tetraazamacrocyclic complex) gave 94% of styrene oxide and 1% of phenylacetalde-