

ORGANIC SYNTHESIS BY ELECTROLYSIS III  
ANODIC ALLYLIC SUBSTITUTION

Tatsuya Shono and Tōru Kōsaka

Department of Synthetic Chemistry, Faculty of Engineering,  
Kyoto University, Kyoto, Japan

(Received in Japan 28 October 1968; received in UK for publication 7 November 1968)

Anodic acetoxylation, cyanidation, methoxylation and isocyanation of both nuclear and side chain of aromatic compounds have been studied by several workers<sup>1)</sup>.

In our continuing study on the electrolysis of aliphatic compounds, we have found a novel anodic allylic substitution reaction which may be an unique method to synthesize some allylic compounds from aliphatic olefins. The experimental results are shown in Table I. The electrolysis was carried out at room temperature with a carbon anode and cathode using a ceramic diaphragm until a roughly theoretical number of coulombs was passed (except 1-Octene). The yield may be improved with the increase in the number of coulombs passed. The reaction yielded some higher boiling by-products which were presumed to be disubstituted compounds whose structures were uncertain as yet. The allylic acetoxylation of some olefins has been observed in the reaction of t-butyl peracetate with olefins in the presence of copper salt catalysts<sup>2)</sup>. The present electrochemical method of allylic substitution is obviously more useful in view of the variety of the substituent. Although the establishment of the reaction mechanism is the subject of future investigation, the mechanism might be similar to that proposed for the perester reaction, in which the process of the oxidation of a radical to a carbonium ion is involved.

Table I. Reaction Condition and Yield

| Olefin<br>(mole)                  | Solvent<br>(mole)  | Electrolyte<br>(mole)                     | Current<br>(A)      | Terminal<br>Voltage(V) | Time<br>(hr) | Yield <sup>a</sup><br>(%) |
|-----------------------------------|--|---|---------------------|------------------------|--------------|---------------------------|
| Cyclohexene<br>(0.122)            | AcOH<br>(1.67)   | M.K. Salt <sup>h</sup><br>(0.03)          | 0.2                 | 28                     | 30           | 54.8 <sup>c</sup>         |
| Cyclohexene<br>(0.122)            | AcOH<br>(1.67)   | AcONa<br>(0.122)                          | 0.2                 | 44                     | 33           | 8.4 <sup>c</sup>          |
| Cyclohexene<br>(0.122)            | MeOH<br>(1.57)   | M.K. Salt<br>(0.03)                       | 0.3                 | 8                      | 22           | 21.0 <sup>d</sup>         |
| Cyclohexene<br>(0.122)            | MeOH<br>(1.57)   | NH <sub>4</sub> NO <sub>3</sub><br>(0.05) | 0.3                 | 6                      | 22           | 16.2 <sup>d</sup>         |
| Cyclohexene<br>(0.122)            | CH <sub>3</sub> CN<br>(2.44)<br>H <sub>2</sub> O<br>(0.03) | M.K. Salt<br>(0.03)                       | 0.5                 | 9                      | 13           | 17.0 <sup>b,e</sup>       |
| 1-Octene<br>(0.040)               |  | AcOH<br>(1.67)                            | M.K. Salt<br>(0.03) | 0.2                    | 34           | 125                       |
| 1,5-Cyclo<br>Octadiene<br>(0.100) | AcOH<br>(1.67)   | M.K. Salt<br>(0.03)                       | 0.2                 | 34                     | 34           | 13.6 <sup>g</sup>         |
| 1,5-Cyclo<br>Octadiene<br>(0.100) | AcOH<br>(1.67)   | AcONa<br>(0.122)                          | 0.2                 | 45                     | 34           | 4.8 <sup>g</sup>          |

<sup>a</sup> Measured by V.P.C.<sup>b</sup> Determined by isolation<sup>c</sup> Product is 3-acetoxycyclohexene-1<sup>d</sup> Product is 3-methoxycyclohexene-1<sup>e</sup> Product is 3-acetoaminocyclohexene-1<sup>f</sup> Product is 3-acetoxyoctene-1<sup>g</sup> Product is 3-acetoxycyclooctadiene-1,5<sup>h</sup> Tetraethylammonium p-toluenesulfonate

We are extremely grateful to Professor R.Oda of Kyoto University for his kind encouragement.

## References

- 1) V.D.Parker and B.E.Burgert Tetrahedron Letters, No 29 3341 (1968), and references cited therein
- 2) C.Walling and A.A.Zavitsas, J. Am. Chem. Soc., 85, 2084 (1963)