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REGIOSELECTIVITY IN ELECTROCHEMICAL ADDITIONS OF THE ALLYL GROUPS IN SUBSTITUTED ALLYL HALIDES TO α,β-UNSATURATED ESTERS OR ACETONE

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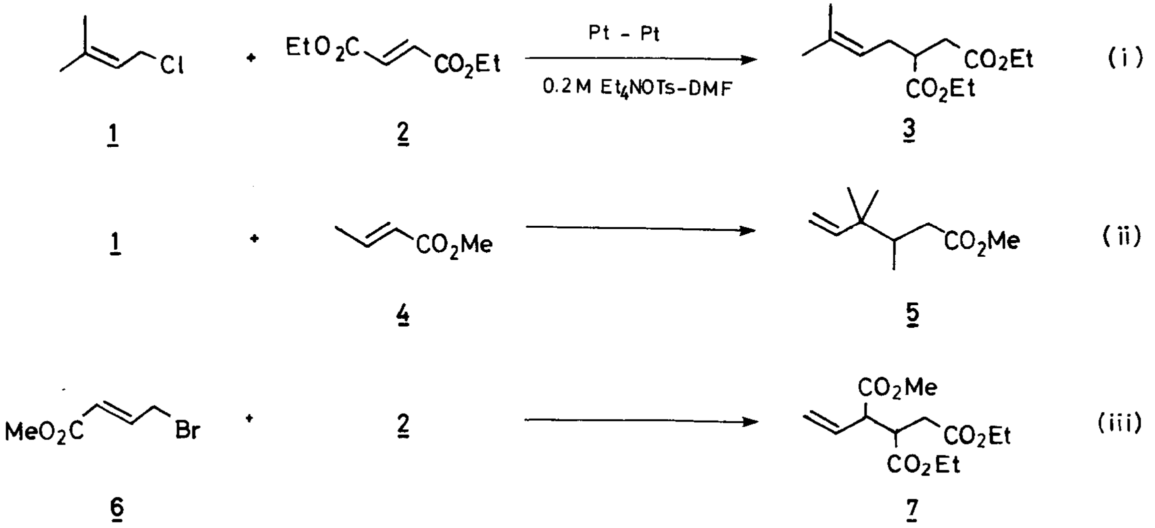
Summary: Electrochemical additions of the allyl groups in substituted allyl halides to some α,β-unsaturated esters took place in a regioselective manner at either of their α- or γ-carbon terminus, whereas regioselectivity in the addition to acetone was found to be controlled by changing a cathode material or an electrolytic potential.

The introduction of the allylic units to organic substrates is of importance in organic synthesis. A number of methods which use allyl halides as electrophiles[1] or allylic organometallic compounds as nucleophiles[2] are available. Substituted allylic organometallics undergo a nucleophilic addition to ketone,[2] aldehydes,[2] or α,β-unsaturated ketones[3] at their more highly substituted carbon termini almost exclusively. It has recently been found that allyl groups of allyl halides can be introduced to α,β-unsaturated esters by electrochemical reduction.[4,5]

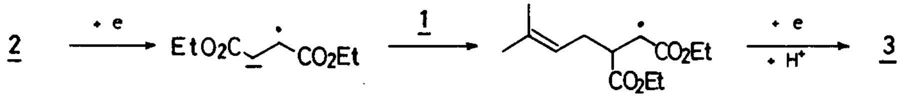
We wish to report on the regioselective additions of allyl groups in substituted allyl halides to α,β-unsaturated esters or acetone by electrolysis. We found that the regioselectivity in the addition of the allyl groups to acetone was controlled by changing conditions of electrolysis.



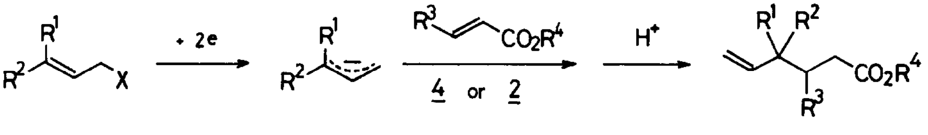
The electrochemical reaction of a substituted allyl chloride, 1-chloro-3-methyl-2-butene (1), with a two-fold excess of diethyl fumarate (2) gave exclusively ethyl 3-(ethoxycarbonyl)-6-methyl-5-heptenoate (3),[6] in which a less heavily substituted carbon terminus of the allyl group was attached to the α,β-unsaturated ester, in a 15% yield (equation i). The electrolysis was conducted in DMF containing 0.2M tetraethylammonium tosylate at a constant current of 25 mA/cm^2. Electricity passed was 2 Faraday per mol of allyl halide 1.

On the other hand, the electrochemical reaction of allyl chloride 1 with methyl crotonate (4) gave methyl 3,4,4-trimethyl-5-hexenoate (5)[6] as a single product, in which a more highly substituted carbon of the allyl group was attached to the α,β-unsaturated ester, in a 22% yield (equation ii). Similarly, electrolysis of an another allyl halide, methyl 4-bromo-2-butenoate (6), with ten-fold excess of diethyl fumarate (2) at -40° gave ethyl 3-(ethoxycarbonyl)-4-(methoxycarbonyl)-5-hexenoate (7)[6] as a single product, in which the allyl group was again combined to the α,β-unsaturated ester with an allylic rearrangement, in a 39% yield (equation iii). The allyl groups were therefore combined to the two different α,β-unsaturated ester 2 and 4 with regioselectivity in different sites.

These regioselectivities can be rationalized in terms of the involvement of the following two different mechanisms. In the electrochemical reaction of allyl chloride 1 with diethyl fumarate (2), preferential reduction of 2[7] generates an anion radical which reacts with a carbon carrying chlorine atom of 1 in an S_N2 fashion to afford the observed product 3 (equation iv). In the reaction of either allyl chloride 1 with α,β-unsaturated ester 4 or allyl bromide 6 with ester 2 , however, two electron reduction of 1 or 6 may take place to generate allylic carbanion which then adds to α,β-unsaturated ester 4 or 2 to afford addition products 5 or 7 (equation v). These explanations can be supported by the results of chemical reactions; several anionic species generated chemically undergo nucleophilic substitution on allyl chloride 1 at the less heavily substituted carbon terminus[8, 1b]; the reactions of allylic organometallic compounds derived from 3,3-dimethylallyl compounds with carbonyl compounds,[2] acyl halides,[9] acetals,[10] and α,β-enones[3] take place almost exclusively at the more highly substituted terminus of the allyl group.



(iv)



(v)

1 : $R^1 = R^2 = CH_3$, X = Cl

6 : $R^1 = H$, $R^2 = CO_2Me$, X = Br

4 : $R^3 = CH_3$, $R^4 = Me$

2 : $R^3 = CO_2Et$, $R^4 = Et$

5 or 7

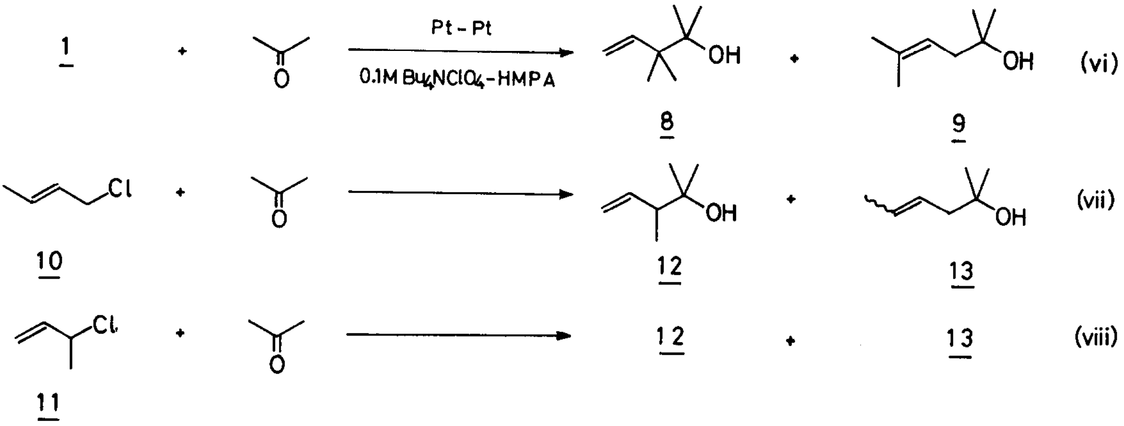


Table 1. Electrochemical addition of allyl chloride 10 or 11 to acetone[a]

Cathode	Current or Potential	10 Yield of products (%)	10 12 : 13	11 Yield of products (%)	11 12 : 13
Zn	25 mA/cm^2 [b]	77	92 : 8	72	90 : 10
Pt	25 [b]	56	71 : 29	81	62 : 38
C	25 [b]	89	60 : 40	82	29 : 71
Hg	25 [b]	15	87 : 13	22	45 : 55
C	-1.6 V *vs* Ag/AgI	63	59 : 41	58	56 : 44
C	-1.3	40	66 : 34	35	43 : 57
C	-1.2	36	69 : 31	10	39 : 61

a) A mixture of 1.0M 10 or 11 and 3.0-5.0M acetone in HMPA was electrolyzed.
b) At a constant current electrolysis, 2.0 F/mol of 10 or 11 was passed.

Few trapping reactions of carbanions generated by electrochemical reduction of alkyl halide by ketone are known.[11] We find, however, that the electrochemical addition of allyl species generated from allyl halide to acetone can be successfully carried out by employing hexamethylphosphoramide (HMPA) as a solvent.[12] From the argument presented above it might be expected that the electrochemical reaction of allyl chloride 1 with acetone will give an addition product with an allylic rearrangement since 1 is reduced more readily than acetone in HMPA. Electrolysis of 1 in HMPA in the presence of five molar excess of acetone, however, led to the formation not of a single product, 2,3,3-trimethyl-4-penten-2-ol (8), but a mixture of 8 and its isomer (9) in a ratio of 78 to 22 (70% yield; equation vi). Although the regioselectivity is appreciably reduced in this case, the formation of 9 is synthetically significant since the addition reaction of allylic organometallics derived from allyl chloride 1 with ketone gives the product having the allyl group attached at the more highly substituted carbon terminus exclusively.[2, 13]

The regioselectivity of the electrochemical addition was further examined by using 1-chloro-2-butene (10) and its isomer, 3-chloro-1-butene (11). Electrolysis of allyl chloride 10 or 11 in the presence of acetone was found always to give a mixture of homoallyl alcohol 12 and its isomer 13 (equations vii and viii). Table 1 shows the combined yields of the two products and the ratio of 12 to 13 obtained under various conditions. When zinc was used as a cathode nearly the same ratio of 12 to 13 was obtained regardless of whether the electrolysis was initiated by allyl chloride 10 or 11. The predominant formation of 12 from either 10 or 11 is parallel with the results of an allylic organometallic reaction. When the electrolysis was carried out by using platinum, carbon, or mercury cathodes, however, the yield of 13 was found to increase appreciably. Moreover, it has been found that the electrolysis at a mercury cathode or at a lower potential of -1.2 to -1.3 V vs Ag/AgI afforded a higher proportion of the product arising from the allylic rearrangement (12 from 10, and 13 from 11). The exact reasons which would explain these results are not clear at the present stage. Some interactions between the electrode surface and allyl halides must play a role in determining the regioselectivity when a mercury or a carbon electrode as a cathode is used and when the electrolysis is conducted at a rather low potential.

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