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THE REACTION OF β-BROMOSTYRENE WITH NICKEL CARBONYL IN THE PRESENCE OF ALKYNES

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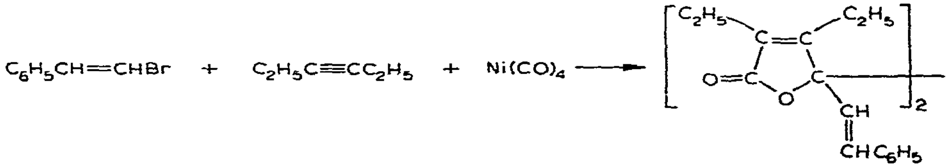
SUMMARY

β-Bromostyrene is reactive towards nickel carbonyl in polar, coordinating solvents and the reaction between β-bromostyrene and nickel carbonyl in *N,N*-dimethylformamide in the presence of several alkynes proceeds smoothly at 60° to yield dimers of γ-but-2-enolactone in moderate yields.

Organic syntheses by using metal carbonyls and organic halides have been extensively studied[1], but the corresponding reactions of alkenyl halides remain almost unexplored, because of the inactiveness towards nucleophilic substitution reaction and also towards metal carbonyls in ordinary organic solvents. However, recently some examples of alkenyl halides with metal carbonyls or their derivatives have been reported: *i.e.* alkoxycarbonylation[2] or carbamoylation[3] of alkenyl halides by using nickel complexes derived from nickel carbonyl, and cinnamoylation of acrylonitrile with nickel carbonyl and β-bromostyrene[4]. Especially the latter, new type of cinnamoylation of olefin prompted us to study the reaction of alkenyl halides with nickel carbonyl in the presence of other olefins, dienes or acetylenes.

Now we wish to report the formation of dimers of γ-butenolactone from the reaction between β-bromostyrene and nickel carbonyl in the presence of several mono- or di-substituted acetylenes.

From nickel carbonyl and β-bromostyrene in the presence of 3-hexyne in *N,N*-dimethylformamide (DMF) as solvent, the dimer of 2,3-diethyl-4-styryl-γ-but-2-enolactone (I) was obtained in 65% yield using the following experimental procedure.



(I)

A mixture of 3-hexyne (3.0 g, 0.036 mole), *trans*-β-bromostyrene (6.6 g, 0.036 mole) and nickel carbonyl (6.2 g, 0.036 mole) in 300 ml of DMF was stirred at 60° for 3 h under nitrogen atmosphere. The color of the mixture changed immediately to pale yellow and finally a dark green solution with powder-like solids was obtained. After a removal of remaining nickel carbonyl and 3-hexyne under reduced pressure at room temperature, the mixture was poured into 200 ml of 2 *N* HCl solution. Precipitated light yellow solids (5.65 g) were recrystallized, after washing with petroleum ether, from benzene/petroleum ether to give colorless crystals; m.p. 230–230.5°. The IR spectrum of the crystals has the lactonic carbonyl band at 1758 cm^{-1}. On the basis of analysis, mass spectrum and NMR spectrum, the product was assumed to be (I), although the position of junction has not yet been established. NMR: τ 9.10 (t, 6 H), 8.98 (t, 6 H), 7.78 (q, 4 H), 7.72 (q, 4 H), 5.58 (m, 2 H), 4.87 (m, 2 H), 2.75 (s, 10 H).

The results of the reactions between some acetylenes and β-bromostyrene or benzyl bromide and the analytical data of the dimers of γ-lactone are summarized in Tables 1 and 2, respectively.

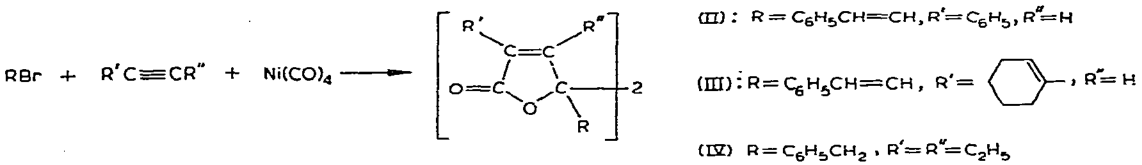


TABLE 1

THE DIMER OF γ-BUT-2-ENOLACTONE

Compound	*Yield* (%)	*M.p.* (°C)	*IR* ν(C=O) cm^{-1}
(I)	65	230~230.1	1758
(II)	45	223	1755
(III)	30	198~199	1755
(IV)	42	235~237	1765

TABLE 2

MASS SPECTRA AND ANALYTICAL DATA OF DIMERS

Compound	*m/e*	*Analyses, found (calcd.)*		
		C (%)	*H* (%)	*Mol. wt.* (*Rast*)
(I)	241, 131, 103	79.42 (79.64)	7.07 (7.10)	473 (482)
(II)	264, 131, 103	83.06 (82.74)	4.93 (5.02)	523 (528)
(III)	264, 162, 131 103, 81	81.18 (81.48)	6.33 (6.46)	
(IV)	458, 229, 91	78.49 (78.57)	7.19 (7.47)	

Various types of reactions of organic halides with metal carbonyls are known but there appear to be only few examples of the reaction between organic halides and metal carbonyls in the presence of acetylenes. Chiusoli reported the reaction between allyl halides and nickel carbonyl in the presence of acetylene to give unsaturated carboxylic acids, their esters, cyclic ketones and lactones but the yield of lactones was not so good[5]. The reaction of benzyl halide with triiron dodecacarbonyl in the presence of phenylacetylene in DMF gave 1,3-diphenylpropane and -propene but no carbonylated products were obtained[6].

However, the present reaction proceeds cleanly and gives the dimer of γ-but-2-enolactone in good yield.

Further application of this reaction to various alkenylhalides is currently continuing.

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