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NOVEL NICKEL CATALYZED CONVERSION OF 2-BROMO-1-PHENYL-1,3-BUTADIENE TO AN α KETO LACTONE. AN EXAMPLE OF DOUBLE CARBONYLATION OF A HALODIENE

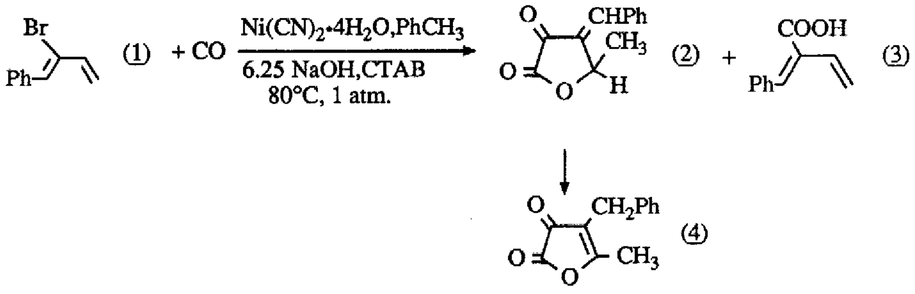
Howard Alper*
Department of Chemistry, University of Ottawa
Ottawa, Ontario, Canada K1N 6N5

Giuseppe Vasapollo
Centro M.I.S.O. del CNR, Department of Chemistry
University of Bari, 70126 Bari, Italy

Summary: Nickel cyanide and phase transfer catalyzed carbonylation of 2-bromo-1-phenyl-1,3-butadiene affords an methylene-α-keto lactone in good yield; isomerization to a ketobutenolide occurs on silica gel.

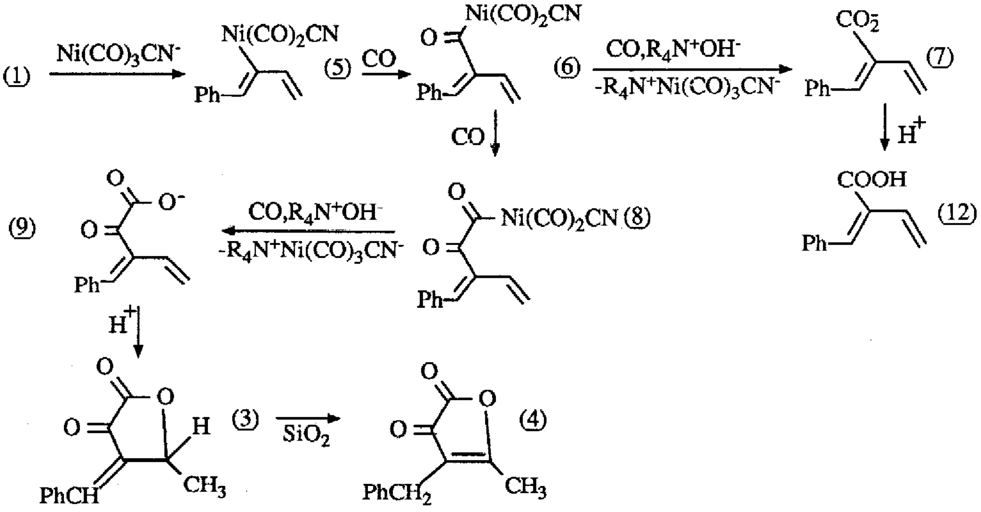
A simple, stereospecific method for the carbonylation of vinyl bromides and chlorides to α-β-unsaturated acids using catalytic quantities of nickel cyanide is described in the accompanying communication.[1] It was anticipated that a halodiene would react in an analogous manner affording the dienoic acid. 2-Bromo-1-phenyl-1,3-butadiene (1, readily obtained from α-bromocinnamaldehyde) was chosen as a representative diene for the carbonylation reaction and, while the dienoic acid is formed, it is the minor product, the major one arising from a double carbonylation reaction. Double carbonylation reactions have attracted considerable interest in recent years.[2-6] This communication describes the first example of the double carbonylation of a halodiene resulting in a novel synthesis of an α-keto lactone.

The catalytically active nickel species[1] was generated by treatment of $Ni(CN)_2{\bullet}4H_2O$ [1.0mmol] and cetyltrimethylammonium bromide [CTAB -0.08 g] in 6.25 N NaOH [10 mL] and toluene [10 mL] with carbon monoxide for 40 minutes at 80°C. Drop-by-drop addition of 10 mmol of 1 to the stirred mixture, followed by reaction for four hours at 80°C and then work-up with 10% HCl gave the α-keto lactone 2 in 60% yield and the dienoic acid 3 in 15% yield. The structure assigned to 2 is supported by the following spectral data: ir[ν(CO)]1770,1710cm^{-1};H-1NMR(CDC_3)δ1.55(d,3H,CH_3),3.85 (q,1H,CH),7.05(s,1H,CHPh), 7.35(m,5H,Ph);C-13 NMR($CDCl_3$) δ16.8(CH_3), 44.5(CH), 128.74, 129.02, 129.20, 131.27(Ph carbons), 135.65(C=), 140.50(CH=), 172.90 (CO),180.20(CO); [7] mass spec (m/e)202[M]$^+$. The ir[ν(CO)1702 cm^{-1}] and H-1NMR[($CDCl_3$)δ5.45,5.88,6.38,(m,3H,CH=CH_2),7.30(m,5H,Ph),7.70 (s,1H,PhCH)] data are in accord with the structure for 3.



When the methylene-α-keto lactone 2 was subjected to column chromatography on silica gel, isomerization occurred to give 4. The base and molecular ion peak occurred in the mass-spectrum of 4 at m/e 202. The H-1 NMR spectrum was very simple, showing singlets at δ 2.04(s,3H,CH_3) and at 3.77(s,2H,CH_2), and a multiplet centered at δ 7.30 for the aromatic protons. The carbonyl carbons of 3 [δ 172.0,179.9] were at similar chemical shifts to those of 2. A possible mechanism for the conversion of 1 to 2 and 3 is outlined in Scheme 1. Reaction of 1 with the in situ generated $Ni(CO)_3CN^-$ may give the σ-dienylnickel complex (5). Carbonylation (via ligand migration) would afford 6 which can undergo either C-Ni bond cleavage by base to give 7 (and then 2 on acidification), or insertion of a second carbon monoxide would generate the α-dicarbonylnickel complex 8. The quaternary ammonium hydroxide may then, under CO, convert 8 to 9 with regeneration of the catalytic nickel

SCHEME 1



species. Acidification of 9 would give the a-keto lactone 3 on cyclization.

Acknowledgement

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7. NMR assignments were corroborated by COSY and HETCOR techniques.

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