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A CARBON–NICKEL ADDITION TO BENZYNE

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SUMMARY

The thermal decomposition of benzenediazonium-2-carboxylate in the presence of *trans*-(phenylethynyl)(trichlorovinyl)bis(triethylphosphine)nickel(II), (I), in dichloromethane affords [2-(phenylethynyl)phenyl](trichlorovinyl)bis(triethylphosphine)-nickel(II), (III). Also present in the product mixtures was 2-(phenylethynyl)(trichlorovinyl)benzene, (IV), which was shown to be formed from (III) under the reaction conditions employed. Evidence is presented which indicates that (III) is derived from a carbon–nickel addition to benzyne.

INTRODUCTION

Very little is known regarding the behavior of 1,2-dehydrobenzene (benzyne) toward transition metal complexes*. In view of proposals$^{4-8}$ concerning its electronic structure which relate the nature of the "extra" bond to that of an ethylene-like π bond, it is of particular interest to deduce whether its reactions with transition metal complexes simulate those of alkenes and alkynes. We wish to report a carbon–transition metal addition to the aryne, a mode of reaction which has parallels in the chemistry of both alkenes and alkynes.

RESULTS AND DISCUSSION

The transition metal complex employed was *trans*-(phenylethynyl)(trichlorovinyl)bis(triethylphosphine)nickel(II), (I), which was prepared in 99% yield by treatment of *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II), (II), with (phenylethynyl)magnesium bromide in benzene–diethyl ether solution. Compound(I) is a yellow solid, m.p. 102–103° (decompn. 130–150°). Its IR spectrum (KBr) exhibited strong absorptions at 2085 cm^{-1} [C≡C stretching vibration, characteristic of (phenylethynyl)nickel compounds[9]] and 883 cm^{-1} (vinyl C–Cl asymmetric stretching vibration). The PMR spectrum (C_6D_6) consisted of a complex multiplet centered near τ 2.78 ppm (aromatic) and multiplets near τ 8.30 ($P-CH_2-C$) and 8.90 ppm ($P-C-CH_3$),

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* A compound formulated as a benzyne–nickel complex has been reported, see ref.1; Ni–Cl additon to benzyne, see ref. 2; Cyclo-addition of perfluorobenzyne to a cyclopentadienyl ligand in nickelocene, see ref. 3.

the high field resonance appearing as a 1/4/6/4/1 quintet similar to those found in spectra of *trans*-planar bis(triethylphosphine)metal complexes[10-13]. Treatment of an ether solution of (I) with hydrogen chloride gave (II) and a hydrocarbon product with a GLC retention time identical with that of phenylacetylene.

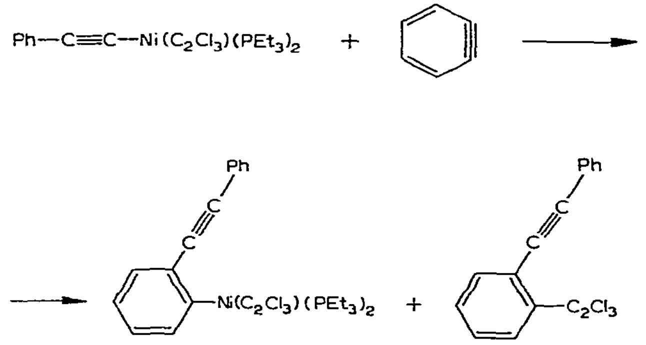
Compound (I) was selected for this study because the nature of its ligands and its planar configuration provide an available apical site for coordination of an aryne reactant. The compound exhibited a resistance to attack by the solvent utilized for the decomposition of the benzyne precursor and was thermally stable in the temperature range required.

Benzenediazonium-2-carboxylate was suspended in a dichloromethane solution of (I) and the mixture was stirred at reflux for 1 h. Chromatography of the product mixture afforded two compounds; a yellow solid, (III), m.p. 134–136° (decompn.), 24 % yield, and a colorless oil, (IV), 56 %. The elemental analyses and mol. wt. of (III) indicated that the elements of C_6H_4 had been incorporated into the organonickel precursor. The most significant feature in the IR spectrum (KBr) of (III) is a weak band at 2210 cm^{-1}, attributable to a C≡C stretching vibration, which may be compared to the strong 2085 cm^{-1} band in (I) and to a peak at 2211 cm^{-1} in the Raman spectrum[14] of diphenylacetylene. The spectrum of (III) also exhibited a strong band at 880 cm^{-1}.

The PMR spectrum (C_6D_6) consisted of complex multiplets centered near τ 2.40 and 3.00 ppm, and overlapping multiplets (Et_3P protons) near τ 8.73 and 8.98 ppm. The alkylaromatic proton ratio as determined by integration of the peak areas was 3.3/1.0.

Compound (III) could be synthesized in very low yield by an independent route. Treatment of (II) with 2-lithiophenylethynylbenzene resulted in a 95 % recovery of (II) and a 2 % yield of (III). Repeated attempts to improve the yield of (III), formed via this general route, were unsuccessful. Similar attempts to synthesize(2,6-dimethylphenyl)(trichlorovinyl)bis(triethylphosphine)nickel(II) through the reaction of (II) with the appropriate organolithium or -magnesium compounds have failed, although the *o*-tolyl derivative could be prepared[12]. The facility with which (II) reacts with arylmetal compounds, not unexpectedly, decreases with increasing size or number of substituents at the *ortho* positions in the aromatic ring.

The IR spectrum of (IV) displayed a band at 2220 cm^{-1} (liquid film), and a strong band at 889 cm^{-1}, and the PMR spectrum exhibited one complex multiplet



(III) (IV)

near τ 2.67 ppm. The mass spectrum, in agreement with structure (IV), indicated an elemental composition of $C_{16}H_9Cl_3$ with a molecular mass, based on ^{35}Cl, of 306. The consecutive loss of three chlorine atoms from the molecular ion was determined by metastable peaks at *m/e* 171, 206 and 240. This multistep fragmentation process was also observed for 2-chloro(trichlorovinyl)benzene[2]. This, coupled with the similarities in peak intensities for the two compounds, implied the existence of a trichlorovinyl group in (IV).

The decomposition of benzenediazonium-2-carboxylate in refluxing dichloromethane containing (I) and an excess of furan afforded a 29% yield of 1,4-dihydronaphthalene-1,4-endoxide, (V), based on moles of diazonium carboxylate employed, but no (III) or (IV) could be detected in the product mixture. Although a 50/1 mole ratio of furan/(I) was employed, the amount of furan used was not large enough to alter the polarity of the solvent medium appreciably (29 ml CH_2Cl_2, 1.2 ml furan).

The evidence indicates that (III) is [2-(phenylethynyl)phenyl](trichlorovinyl)-bis(triethylphosphine)nickel(II), derived from a carbon–nickel addition to benzyne. Support for the latter contention is found in: (1) the demonstration that the thermal decomposition of benzenediazonium-2-carboxylate in aprotic media affords benzyne[15] and (2) the fact that (III) and (IV) are not formed when an excess of furan, an effective benzyne "trapping agent"[16–18], is present in the reaction mixture.

Compound (IV) appears to be derived from the decomposition of (III) under the reaction conditions employed. A 33% yield of (IV) was obtained when a refluxing dichloromethane solution of pure (III) was stirred with a suspension of benzenediazonium-2- carboxylate for 1 h, 35% of (III) being recovered. Compound (III) was recovered unchanged (99%) after it was stirred for 1 h in refluxing dichloromethane. Chromatography of a pure sample of (III) on acid-washed alumina (the method by which it was isolated from reaction mixtures) afforded a 90% recovery of (III), and no (IV) was detected in the eluate. Thus, the formation of (IV) appears to result from a carbon–carbon coupling reaction of (III), induced during the diazonium carboxylate decomposition.

The gross transformation observed in the reaction of benzyne with (I) is formally related to the growth step in certain transition metal-catalyzed alkene and alkyne oligomerization reactions. It has been proposed[19,20], and recent work lends support to the hypothesis[21–27], that this class of reactions involves a carbon–metal addition to coordinated alkene or alkyne. Analogy implies the possible formation of a benzyne–nickel complex which rearranges to (III) in the reaction reported herein.

EXPERIMENTAL

All experiments, including chromatographic separations, were conducted under a nitrogen atmosphere. Solvents were purified by conventional methods and were deoxygenated before use.

Elemental analyses and molecular weight determinations were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Melting points are uncorrected. The IR spectra were recorded on a Beckman IR 12 spectrophotometer, and the PMR spectra were obtained using a Varian A-60 spectrometer, tetramethylsilane being employed as an internal standard. The mass spectrum was recorded by the Morgan–Schaffer Corporation, Montreal, Canada.

Preparation of trans-(phenylethynyl)(trichlorovinyl)bis(triethylphosphine)nickel(II), (I)

A solution of 6.00 g (13.0 mmoles) of *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II)[12] in 60 ml of benzene was added to a solution of phenylethynylmagnesium bromide (prepared from 26.1 mmoles of ethylmagnesium bromide and 26.1 mmoles of phenylacetylene in ether/benzene) over ca. a 5 h period. The reaction mixture was then stirred for 9 h, after which it was treated with 6 ml of 2-propanol, and the solvent was removed *in vacuo*. The residue was triturated with hexane and the hexane-soluble material was chromatographed on a 76 × 3.3 cm column of silica gel prepared in 5/95 benzene/hexane. Elution with 3/7 benzene/hexane afforded 5.64 g (99.4 %) of (I) after recrystallization from hexane, m.p. 102–103° (decompn. 130–150°). (Found: C, 50.38; H, 6.77; mol.wt., 532. $C_{22}H_{35}Cl_3NiP_2$ calcd.: C, 50.19; H, 6.70 %; mol.wt., 527.)

Treatment of a solution of 30 mg of (I) in 10 ml of ether with hydrogen chloride for 7 h afforded 17 mg (63 %) of (II) and a hydrocarbon with a GLC retention time, identical with that of phenylacetylene, on a 5′ × 1/4″ 20 % SE-30 on 60/80 Chromosorb W column.

Chromatography of 0.54 g of (I) on a 18 × 2.2 cm column of Baker aluminum oxide ("Analytical Reagent for Chromatography", pH 3.8), which contains the elements of HCl, afforded 0.099 g (18 %) of recovered (I) on elution with 3/7 benzene/hexane. Elution with 3/7 ether/hexane afforded 0.377 g (79.6 %) of (II).

Preparation of benzenediazonium-2-carboxylate

The compound was prepared by the general method of Friedman and Logullo[28]. The reactions were conducted and the product was isolated using a procedure communicated to us by Stiles[29].

To a solution of 2.74 g (0.02 mole) of anthranilic acid in 20 ml of absolute ethanol and 8 ml of water, at 5°, were added 5 ml of cold isopentyl nitrite. After standing at 0° for 1.5 h, the red solution was poured into 100 ml of cold ether/ethanol (1/1). After adding 170 ml of cold ether, the mixture was allowed to stand for 25 min at − 10°. The off-white crystals were then filtered, washed with cold ether, and allowed to dry. Yield: 2.64 g (89.2 %). As reported earlier[15,17,30] the compound detonates when exposed to heat or shock, and must be handled with caution.

Decomposition of benzenediazonium-2-carboxylate in the presence of trans-(phenylethynyl)(trichlorovinyl)bis(triethylphosphine)nickel(II), (I)

To a suspension of 1.07 g (7.23 mmoles) of freshly prepared benzenediazonium-2-carboxylate in 75 ml of dichloromethane was added a solution of 0.54 g (1.03 mmoles) of (I) in 25 ml of dichloromethane. The mixture was stirred at reflux for 1 h after which the solvent was removed *in vacuo* and the residue was triturated with hexane. The hexane-soluble material was chromatographed on a 18 × 2.2 cm column of Baker acid-washed alumina. Elution with 3/7 benzene/hexane afforded 130 mg (56.4 %) of 2-(phenylethynyl)(trichlorovinyl)benzene as a colorless oil. A sample was prepared for mass spectral analysis by molecular distillation. Elution with 1/1 benzene/hexane gave 147 mg (23.6 %) of [2-(phenylethynyl)phenyl](trichlorovinyl)bis(triethylphosphine)nickel(II), (III), m.p. 134–136° decompn. after recrystallization from hexane. (Found: C, 56.01; H, 6.58; mol.wt., 610. $C_{28}H_{39}Cl_3NiP_2$ calcd.: C, 55.81; H, 6.52 %; mol.wt., 603.) Elution with 1/1 ether/hexane afforded 13 mg (2.7 %) of (II).

Chromatography of 42 mg of (III) on a 17.5 × 1.6 cm column of Baker acid-washed alumina afforded 38 mg (90%) of recovered (III) on elution with 3/7 benzene/hexane.

A solution of 41 mg of (III) in 8 ml of dichloromethane was refluxed for 1 h and then concentrated to dryness. Forty mg of (III) was recovered.

Synthesis of (III) from trans-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II) and 2-lithio(phenylethynyl)benzene

To 1.00 g (2.17 mmoles) of *trans*-chloro(trichlorovinyl)bis(triethylphosphine)-nickel(II) in 20 ml of ether at 0° was added 4.46 ml of an ether solution of 2-lithio-(phenylethynyl)benzene (2.17 mmoles) (prepared by the method of Mulvaney and Carr[31]). The mixture was stirred at 0° for 5 min, then allowed to warm to room temperature where it was stirred for 10 min, and then the solvent was removed. The hexane-soluble products were chromatographed on a 52 × 2.2 cm column of Baker acid-washed alumina. Elution with 3/7 benzene/hexane afforded yellow crystals, 22 mg (1.7%) after recrystallization from hexane. Mixed m.p. with an authentic sample of (III) was undepressed and the IR spectrum was identical with that of (III). Elution with 1/3 ether/hexane afforded 0.95 g (95%) of (II).

Decomposition of benzenediazonium-2-carboxylate in the presence of (I) and furan

To a suspension of 340 mg (2.30 mmoles) of freshly prepared benzenediazonium-2-carboxylate in 15 ml of dichloromethane was added a solution of 172 mg (0.328 mmole) of (I) in 14 ml of dichloromethane and 1.19 ml (16.4 mmoles) of furan. The mixture was stirred at reflux for 1 h after which the solvent was removed and the 1,4-dihydronaphthalene-1,4-endoxide was sublimed from the residue at 25°/0.3 mm. Yield: 95 mg (29%), m.p. 51–53°. The IR spectrum was identical with that of an authentic sample of (V). The residue from the sublimation was triturated with hexane and the hexane-soluble material was chromatographed on a 12 × 1.8 cm column of Baker acid-washed alumina. Elution with 1/4 ether/hexane afforded 50 mg (33%) of (II). No (III) or (IV) were detected in the product mixture.

Decomposition of benzenediazonium-2-carboxylate in the presence of (III)

A solution of 200 mg (0.332 mmole) of (III) in 10 ml of dichloromethane was added to a suspension of 123 mg (0.830 mmole) of freshly prepared benzenediazonium-2-carboxylate in 2.5 ml of dichloromethane. The mixture was stirred at reflux temperature for 1 h, after which, the solvent was removed *in vacuo*, and the residue was triturated with hexane. The hexane-soluble material was chromatographed on a 12 × 1.8 cm column of Baker acid-washed alumina. Elution with 1/9 benzene/hexane afforded 34 mg of (IV) (33%). Elution with 3/7 benzene/hexane afforded 70 mg (35%) of recovered (III).

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