kis(triethyl phosphite)Ni(0), **2a**. To our knowledge this

$(R_3P)_4Ni$
2a, $R = OC_2H_5$
b, $R = C_6H_5$
c, $R = C_2H_5$

$ArNi(PR_3)_2I$
3a, $R = OC_2H_5$
b, $R = C_6H_5$
c, $R = C_2H_5$

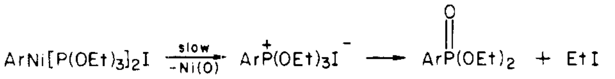
is the first example of a direct reduction of Ni(+II) to Ni(0) by phosphite in the absence of other reducing agents or amines. More to the point, **2a** is an effective catalyst for the conversion of iodobenzene to 1. No induction period is observed with **2a** as a catalyst.

A minimum temperature of ca. 130–140 °C is required for this reaction. Below 140 °C the reaction is sporadic and below 130 °C no reaction is observed. Significantly, this is found for either $NiCl_2$ or **2a**. No reaction is found after 17 h on heating a solution of iodobenzene, triethyl phosphite, and **2a** at 98 °C.

A competitive kinetic study of three para-substituted iodobenzenes has been carried out. The relative rates for 4-iodotoluene, iodobenzene, and methyl 4-iodobenzoate are 1.5, 1.0, and 0.6, respectively. These data indicate increased positive charge character in the slow step of this transformation.

Aryl halides are known to oxidatively add to Ni(0) complexes. For example,[5,6] aryl iodides add to **2b** and **2c** to give **3b** and **3c**. Recent kinetic studies by Kochi[5] have shown the oxidative-addition of aryl iodides to **2c** follows a reaction course defined by a $\rho = 2.0$. Cassar[7] found that in the presence of excess triphenylphosphine, **3b** reacts further to give aryltriphenylphosphonium iodides. Electron-withdrawing groups on the aryl ring were found to retard the rate of formation of the phosphonium iodides.

Based on our data and the above literature precedents, a plausible working hypothesis for the formation of aryl phosphonates is a rapid oxidative addition of the aryl iodide to **2a** to give **3a** followed by slow formation of **4** with regeneration of Ni(0). Decomposition of **4** gives the arylphosphonate and ethyl iodide.[8]



$$\mathrm{ArNi[P(OEt)_3]_2I} \xrightarrow[-\mathrm{Ni(0)}]{\text{slow}} \mathrm{Ar\overset{+}{P}(OEt)_3I^-} \longrightarrow \mathrm{Ar\overset{\overset{O}{\|}}{P}(OEt)_2} + \mathrm{EtI}$$

3a 4

While this hypothesis is consistent with the data, several tenuous assumptions have been made. Most significant is, does the oxidative addition of aryl halides to Ni(0) phosphine complexes always proceed via a path defined by a positive ρ? Cassar[6] has found that for oxidative addition of substituted chlorobenzenes to **2b**, a plot of log k_{rel} vs. σ shows a dramatic break at $\sigma = 0.2$ (for $\sigma > 0.2$, $\rho = 8.8$; $\sigma < 0.2$, $\rho \simeq 0$), indicative of a change in mechanism. Changing from phosphine to phosphite ligands on nickel might also have a radical effect on the mechanism.[9] No reports of oxidative additions with **2a** are currently available.

We have shown that **2a** is involved in the conversion of aryl iodides to arylphosphonates. We suggest that until more data is available on the chemistry of **2a** and **3a**, the mechanism proposed above should be viewed with suspicion. These studies are underway in our laboratory.

Experimental Section

General. All manipulations were carried out under a nitrogen or argon atmosphere. Samples of diethyl phenyl-, diethyl 4-(methylphenyl)- and diethyl 4-[(carbomethoxy)phenyl]-phosphonate were prepared by literature methods.[10]

Tetrakis(triethyl phosphite)nickel(0). A stirred mixture of $NiCl_2$ (5 g, 38.5 mmol) in $(EtO)_3P$ (60 mL) was slowly heated to reflux. At ambient temperature the mixture was light yellow and heterogeneous. At 80 °C, a heterogeneous black mixture resulted. A clear homogeneous solution was found at 150 °C. After 1 h at reflux, the solution was cooled and excess phosphite removed to give a white solid. The solid was triturated with acetonitrile, collected, and washed with cold methanol to give 4.6 g of **2a**, mp 106–109 °C (lit.[11] mp 108 °C). This material is identical by ^1H and ^{31}P NMR with an authentic sample prepared by the method of Vinal and Reynolds.[11]

Diethyl Phenylphosphonate. To a hot (160 °C) stirred solution of **2a** (10 mg) in iodobenzene (10 g, 49.0 mmol) was slowly added $(EtO)_3P$ (9.37 g, 56.4 mmol) in small portions (ca. 5 drops). The solution became deep red upon each addition of phosphite. The color rapidly faded to yellow, ethyl iodide was distilled into a cold trap, and an exotherm was observed. After complete addition, GLC assay indicated <1% iodobenzene remained. Distillation [bp 94–101 °C (0.1 mm); lit.[10] bp 97 °C (0.1 mm)] gave 9.88 g (46.1 mmol, 94%) of diethyl phenylphosphonate identical (GLC, ^1H NMR) with an authentic sample.[10]

Competitive Kinetics. A mixture of 1 equiv each of two aryl iodides and 5 mol % $[(EtO)_3P]_4Ni$ was heated to 160 °C. Triethyl phosphite, 1 equiv, was added in small portions. After the mixture was cooled, the relative concentrations of aryl iodides and arylphosphonates were determined by GLC assay and checked versus NMR peak areas.

Acknowledgment. We thank Dr. S. Tremont (Monsanto) for helpful discussions.

Registry No. 1, 1754-49-0; **2a**, 14839-39-5; **3a**, 75507-28-7; **4**, 75556-05-7; 4-iodotoluene, 624-31-7; iodobenzene, 591-50-4; methyl 4-iodobenzoate, 619-44-3; $NiCl_2$, 7718-54-9; $(EtO)_3P$, 122-52-1.

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(5) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 101, 6319 (1979).

(6) M. Foa and L. Cassar, *J. Chem. Soc., Dalton Trans.*, 2572 (1975).

(7) L. Cassar and M. Foa, *J. Organomet. Chem.*, 74, 75 (1974).

(8) (a) If an oxidative addition mechanism is operative, the reactive nickel species is probably coordinatively unsaturated, i.e., $[(EtO)_3P]_3Ni$. See ref 5. (b) The phosphite that becomes **4** may be externally or internally derived.

(9) An example of the significant dissimilarity of **2a** and **2b** is the K_{eq} for $P_4Ni \rightleftharpoons P_3Ni + P$ (P = triphenylphosphine or triethyl phosphite). For **2b** the compound is extensively dissociated in solution; for **2a** $K_{eq} \leq 3 \times 10^{-7}$M: C. A. Tolman, *J. Am. Chem. Soc.*, 92, 2956 (1970).

(10) G. M. Kosolapoff and L. Maier, Eds., "Organic Phosphorus Compounds", Vol. 7, Wiley-Interscience, New York, 1976, Chapter 18, and references therein.

(11) R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, 3, 1062 (1964).

Reaction of *o*-Diiodobenzene with Alkynes and Nickel Carbonyl. Synthesis of Substituted Indenones

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Nickel carbonyl reacts with iodobenzene to produce a benzoylnickel complex (1, Scheme I) which decomposes to benzil in aprotic solvents (THF) or undergoes alcoholysis to methyl benzoate in methanol.[1] However, in the presence of an alkyne, the benzoylnickel intermediate is trapped, undergoing insertion of the alkyne followed by an insertion of CO to yield nickel complex 2 which then decomposes to organic products.[2]

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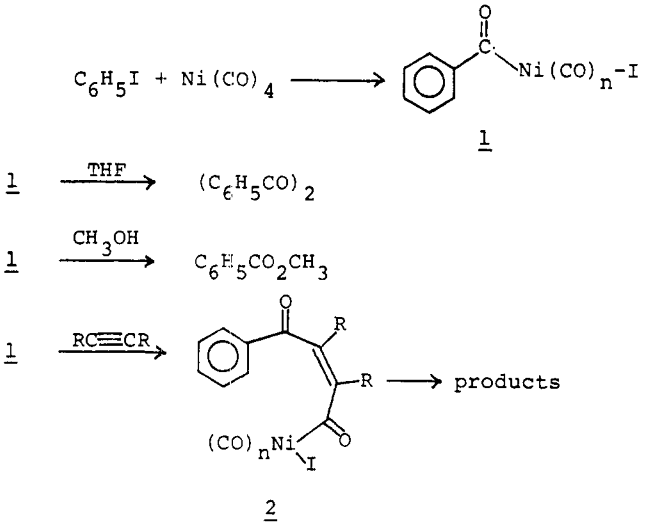
(1) N. L. Bauld, *Tetrahedron Lett.*, 1841 (1963).

(2) P. W. Jolly and G. Wilke "The Organic Chemistry of Nickel", Vol. II, Academic Press, New York, 1975, p 358.

Scheme I



Scheme II

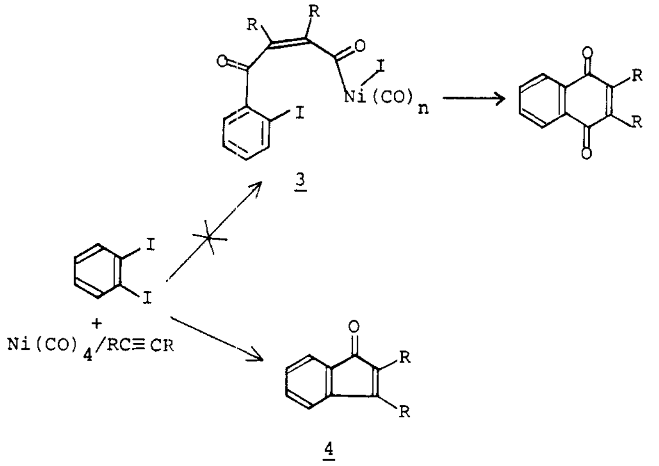


Table I. Indenones[a]

entry	alkyne	product	% yield[b]
1	EtC≡CEt	2,3-diethylindenone[c]	89
2	MeC≡CMe	2,3-dimethylindenone[d]	77
3	PhC≡CPh	2,3-diphenylindenone[e]	51
4	MeC≡CEt	2-methyl-3-ethylindenone[f]	39
		2-ethyl-3-methylindenone	39
5	MeC≡C-*n*-Pr	2-methyl-3-*n*-propylindenone	42
		2-*n*-propyl-3-methylindenone	42
6	MeC≡C-*t*-Bu	2-methyl-3-*tert*-butylindenone	13
		2-*tert*-butyl-3-methylindenone	49
7	MeC≡CPh	2-methyl-3-phenylindenone[g]	37
		2-phenyl-3-methylindenone[h]	30
8	HC≡C-*n*-Bu	2-*n*-butylindenone[i]	52
9	HC≡C-*t*-Bu	2-*tert*-butylindenone	53
10	HC≡C-c-Hx	2-cyclohexylindenone	50

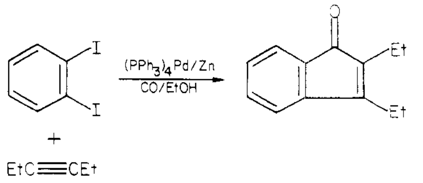
[a] All reactions were run in cyclohexane at 120 °C in a sealed tube for 6 h with *o*-diiodobenzene (1.0 equiv), $Ni(CO)_4$ (1.5 equiv), and alkyne (1.5 equiv). [b] Yields refer to isolated compounds purified by chromatography. [c] Reference 3. [d] Reference 16. [e] Reference 17. [f] Reference 12. [g] References 7 and 18. [h] References 7 and 19. [i] Reference 8.

In an extention of the latter reaction we envisaged reacting *o*-dihalo aromatics with nickel carbonyl in the presence of an alkyne as a potentially mild and convergent route to naphthoquinonoid molecules proceeding through organometallic intermediate **3** (Scheme II). We were somewhat surprised, however, to find that such a reaction produced substituted indenones **4** under mild conditions and in good yields, and we now report our results.

Our investigation began with the reaction of 1 equiv of *o*-diiodobenzene and 2 equiv each of nickel carbonyl (**Caution**: extremely toxic) and 3-hexyne. Upon immersion of a sealed tube cyclohexane solution of the reactants in an oil bath at 80 °C, gas evolution occurred, and the initially pale yellow solution became dark brown and heterogeneous. Workup after 18 h followed by chromatography afforded a yellow homogeneous oil identified as 2,3-diethylindenone (63% yield based on *o*-diiodobenzene).[3] Extensive variation of solvents did not produce results superior to cyclohexane,[4] so we attempted to optimize 2,3-diethylindenone formation by changing our other reaction parameters. By conducting the reaction in an oil bath maintained at 120 °C and using the same relative quantities of reactants, we obtained a 97% yield[5] of 2,3-diethylindenone after only 5 h. Surprisingly, a high yield of product (85%) could also be obtained by decreasing the quantity of $Ni(CO)_4$ to 1.2 equiv and of 3-hexyne to 1.1 equiv (relative to *o*-diiodobenzene) even though alkynes are oligomerized by nickel tetracarbonyl.[6] *o*-Dibromobenzene did show slight reactivity after 18 h at 120 °C; however, *o*-dichlorobenzene was inert.

In order to explore the generality of this indenone synthesis, we reacted *o*-diiodobenzene with a variety of alkynes (1.5 equiv) and nickel carbonyl (1.5 equiv) in cyclohexane at 120 °C for 6 h in a sealed tube. Our results are listed in Table I. Unsymmetrical disubstituted alkynes (entries 4–7) produce both possible isomeric 2,3-disubstituted indenones. Although the reaction is not regiospecific, there appears to be a tendency toward regioselectivity when there is a large steric bulk difference between the alkyne substituents. This is apparent for 2,2-dimethyl-3-pentyne (entry 6) where 2-*tert*-butyl-3-methylindenone predominates over 2-methyl-3-*tert*-butylindenone in the product mixture. This result seems to indicate that the major isomer is that in which the bulkier alkyne substituent ends up at the 2-position of the indenone. This effect becomes dominant with terminal alkynes (entries 8–10) which yield only 2-substituted indenones. Electron-deficient alkynes ($CH_3C{\equiv}CCOOEt$, $EtO_2CC{\equiv}CCO_2Et$) did not yield any indenones under the reaction conditions. Reactions under a CO atmosphere up to 400 psi of CO with 3-hexyne did not induce any 2,3-diethylnaphthoquinone formation.

We have also established a palladium-catalyzed variant of the indenone synthesis with zinc dust as the terminal reductant. Reaction of *o*-diiodobenzene with 3-hexyne (2 equiv) in the presence of $(PPh_3)_4Pd$ (6 mol %) with 1.1 equiv Zn in EtOH under 88 psi of CO gave 63% 2,3-diethylindenone after 4 h at 120 °C (eq 1).



(1)

To establish the substitution pattern for the unknown indenone isomers, we resorted to NMR. A methyl group

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(3) H. Martens and G. Hoornaert, *Tetrahedron Lett.*, 1821 (1970).

(4) Other solvents that were tried were THF, benzene, acetone, DMF, acetonitrile, *N*,*N*-dimethylacetamide, Et_2O, and CH_3OH.

(5) This yield was determined by gas–liquid chromatography using an internal standard.

(6) P. W Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. II, Academic Press, New York, 1975, Chapter 2.

in the 2-position of an indenone is more shielded than that in the 3-position,[7] and as such we have been able to assign the substitution pattern for the isomeric 2,3-disubstituted indenones in Table I. The products resulting from terminal acetylene reactions were determined to be 2-substituted indenones. 1-Hexyne produced 2-*n*-butylindenone as verified by comparison with literature data on the product,[8] and 2-*tert*-butyl and 2-cyclohexylindenone were distinguished from the isomeric 3-substituted products by the absence of a vinyl H absorbance in the region of δ 6.0 which would be expected for 3-substituted indenones.[9]

Versatile syntheses of substituted indenones have historically relied on Friedel–Crafts ring closures of cinnamic acid derivatives or related procedures,[8,10,11] although a number of other methods have been reported.[12-14] The chemistry described herein is unique in that three carbon–carbon bonds can be formed mildly and selectively under neutral conditions and in one pot lead directly to substituted indenones; however, the real potential of this type of chemistry lies in the possibility of using organotransition-metal reactions in convergent syntheses of carbocyclic molecules in general. We are currently investigating other applications of such metal carbonyl based methodologies.[15]

Experimental Section

General Methods. All melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 137 spectrometer and absorptions are reported in wavenumbers. NMR spectra were taken on a JEOL C-60HL or a Varian Associates Model A-60 spectrometer, and absorptions are expressed in parts per million (δ) with Me_4Si as an internal standard. Gas–liquid chromatograms were obtained by using a Varian 3700 instrument equipped with a 6 ft × 0.125 in. stainless-steel column packed with 3% OV-101 on 80/100-mesh Chrom W-HP. Preparative-scale separations were effected on Merck 20 cm × 20 cm × 2 mm silica gel plates or by medium-pressure column chromatography using Merck Lobar prepacked columns. Elemental analyses were performed by Gailbraith Laboratories. The abbreviation DNP used throughout the Experimental Section refers to the dinitrophenylhydrazone derivative of the indenone.

Materials. All solvents, except THF, were purified by passage through a small quantity of Merck activity I alumina and then saturated with dry nitrogen. THF was distilled from sodium benzophenone ketyl. Nickel carbonyl was purchased from Strem chemicals in a 100-g cylinder. *o*-Diiodobenzene was purchased from Eastman Organic Chemicals. All alkynes were purchased from Farchan Division of Chemical Samples Co. Commercially available reagents were used as received. All reactions were performed in heavy-walled glass reactions tubes sealed by means of a two-piece threaded aluminum coupling and an internal Teflon sealing disk, which were purchased from Regis Chemical Co.

General Procedure. Indenone Preparation. All operations concerning $Ni(CO)_4$ and the subsequent workup of the reactions were performed near the back of a very good hood. The reaction tube was equipped with a tiny magnetic stirring bar and flushed with nitrogen. *o*-Diiodobenzene (0.432 g, 1.31 mmol), the alkyne (1.96 mmol, via syringe), and cyclohexane (1.50 mL) were transferred to the reaction vessel. A quantity of nickel carbonyl was removed from the cylinder by inverting the cylinder over an Erlenmeyer flask near the back of a good hood and carefully opening the valve. The desired quantity of $Ni(CO)_4$ (0.336 g, 254 μL, 1.96 mmol) was then removed by syringe and transferred to the reaction tube under a flow of nitrogen. Excess $Ni(CO)_4$ was destroyed with a solution of iodine in acetone. The reaction tube was immediately sealed, immersed in a oil-bath maintained at 120 °C, and magnetically stirred for 6 h. There was a rapid, initial gas evolution, and the homogeneous yellow solution turned dark brown and heterogeneous. After 6 h the reaction vessel was removed from the oil bath, cooled in a dry ice/acetone bath, opened, removed from the low temperature bath, and allowed to warm to room temperature near the back of the hood. With the aid of additional cyclohexane, the reaction mixture was transferred to a round-bottomed flask, and the volatiles were then removed by use of an aspirator in the hood, followed by a vacuum pump (1 mmHg) set up in the hood and equipped with a dry ice/acetone trap. The trapped volatiles were treated with iodine in acetone to destroy any nickel carbonyl which may have remained after the reaction. The reaction residue was triturated with cyclohexane and filtered to remove NiI_2, leaving a yellow to orange solution which was condensed on a rotary evaporator. The resulting residue was dissolved in a small quantity of CH_2Cl_2 and filtered through a small column of silica to remove polar impurities. The eluate was then condensed on a rotary evaporator and the residue was chromatographed on either Merck 20 cm × 20 cm × 2 mm silica gel plates or on Merck Lobar prepacked silica gel columns under medium pressure by eluting with methylene chloride–hexane mixtures.

Palladium-Catalyzed Indenone Synthesis. A heavy-walled glass reaction tube as described above was modified so as to be chargable with a CO atmosphere. To the vessel containing a small magnetic stirring bar was added *o*-diiodobenzene (100 μL, 0.77 mmol), 3-hexyne (175 μL, 1.54 mmol), zinc dust (55 mg, 0.85 mmol), $Pd(PPh_3)_4$ (53 mg, 6 mol %), and 0.4 mL of ethanol. After being flushed with nitrogen, the vessel was charged with 88 psi of carbon monoxide, sealed, and immersed in an oil bath maintained at 120 °C. After the mixture was stirred for 4 h, the reaction vessel was brought to atmospheric pressure, and the reaction mixture was filtered, evaporated under reduced pressure to a crude residue, and then chromatographed by medium-pressure LC (Merck Lobar prepacked silica gel column, 3:2 hexane–CH_2Cl_2) to yield 0.11 g (63%) of 2,3-diethylindenone.

Spectral and Analytical Data. 2,3-Diethylindenone (entry 1):[3] yellow liquid; IR (neat) 2930, 1705, 1615 cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.5 (m, 4 H), 2.60 (q, J = 8 Hz, 2 H), 2.33 (q, J = 8 Hz, 2 H), 1.23 (t, J = 8 Hz, 3 H), 1.11 (t, J = 8 Hz, 3 H); mass spectrum, m/e 186 (molecular ion); DNP, mp 244–246 °C (from chloroform–methanol).

Anal. Calcd for $C_{19}H_{18}N_4O_4$ (DNP): C, 62.28; H, 4.95. Found: C, 62.13; H, 5.11.

2,3-Dimethylindenone (entry 2):[16] yellow solid; mp 77–78 °C (from petroleum ether) (lit.[16] mp 80 °C); IR ($CHCl_3$) 2930, 1705, 1625, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.4 (m, 4 H), 2.0 (s, 3 H, C-3 methyl), 1.75 (s, 3 H, C-2 methyl).

2,3-Diphenylindenone (entry 3): red solid; mp 152–153 °C (from ethanol); identical with a sample obtained commercially from Aldrich Chemical Co.

2-Methyl-3-ethylindenone (entry 4):[12] yellow liquid; IR (neat) 2950, 1705, 1625, 1604, 1585 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 4 H), 2.53 (q, J = 8 H, 2 H), 1.78 (s, 3 H, C-2 methyl), 1.18 (t, J = 8 Hz, 3 H).

2-Ethyl-3-methylindenone (entry 4): yellow liquid; IR (neat) 2950, 1705, 1625, 1604 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.4 (m, 4 H), 2.27 (q, J = 7 Hz, 2 H), 2.09 (s, 3 H, C-3 methyl), 1.06 (t, J = 7 Hz, 3 H); DNP, mp 268.5–270 °C (from chloroform–methanol).

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(7) S. L. Spassov, D. M. Mondeshka, and C. P. Ivanov, *Dokl. Bolg. Acad. Nauk*, 21(4), 351 (1968).

(8) M. B. Floyd and G. R. Allen, Jr., *J. Org. Chem.*, 35, 2647 (1970).

(9) The parent compound, indenone, shows two single proton doublets (J = 5.5 Hz) at δ 7.52 and 5.83 which are ascribed to the vinyl hydrogens at C-3 and C-2, respectively. A 3-substituted indenone would show a C-2 vinyl hydrogen resonance near δ 6.0. See ref. 8.

(10) R. L. Frank, H. Eklund, J. W. Richter, C. R. Vanneman, and A. N. Wennerberg, *J. Am. Chem. Soc.*, 66, 1 (1944).

(11) H. Martens and G. Hoornaert, *Synth. Commun.*, 2, 147 (1972).

(12) W. Munzenmaier and H. Straub, *Synthesis*, 49 (1976).

(13) A. Monahan, P. Campbell, S. Cheh, J. Fong, S. Grossman, J. Miller, P. Rankin, J. Vallee, *Synth. Commun.*, 7, 553 (1977).

(14) E. D. Bergmann, A. Heller, and H. Weiler-Feilchenfeld, *Bull. Soc. Chim. Fr.*, 635 (1959).

(15) In order to make this chemistry more palatable to the synthetic organic chemist, we have recently investigated the use of nonvolatile, air-stable dicarbonylbis(triphenylphosphine)nickel as an alternative to nickel carbonyl. Preliminary results indicate that it is of comparable reactivity in the chemistry described herein.

(16) H. Burton and C. W. Shoppe, *J. Chem. Soc.*, 1156 (1935).

(17) 2,3-Diphenylindenone is commercially available from Aldrich Chemical Co., and our synthetic material was identical with a commercial sample.

Anal. Calcd for $C_{18}H_{16}N_4O_4$ (DNP): C, 61.36; H, 4.58. Found: C, 61.15; H, 4.68.

2-Methyl-3-*n*-propylindenone (entry 5): yellow liquid; IR (neat) 2900, 1705, 1625, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 4 H), 2.5 (t, J = 7 Hz), 1.80 (s, 3 H, C-2 methyl), 1.4–1.9 (m, 2 H), 1.0 (t, J = 7 Hz, 3 H); DNP, mp 230–231 °C (from chloroform–methanol).

Anal. Calcd for $C_{19}H_{18}N_4O_4$ (DNP): C, 62.28; H, 4.95. Found: C, 62.20; H, 5.00.

2-*n*-Propyl-3-methylindenone (entry 5): yellow liquid; IR (neat) 2900, 1705, 1625, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 4 H), 2.26 (t, J = 7 Hz, 2 H), 2.11 (s, 3 H, C-3 methyl), 1.2–1.7 (m, 2 H), 0.93 (t, J = 7 Hz, 3 H); DNP, mp 195.5–197 °C (from chloroform–methanol).

Anal. Calcd for $C_{19}H_{18}N_4O_4$ (DNP): C, 62.28; H, 4.95. Found: C, 62.20; H, 5.09.

2-Methyl-3-*tert*-butylindenone (entry 6): yellow solid; mp 33–34.5 °C (from petroleum ether); IR ($CHCl_3$) 2910, 1705, 1605, 1580, 1565 cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.4 (m, 4 H), 2.0 (s, 3 H, C-2 methyl), 1.46 (s, 9 H); DNP, mp 239–240 °C (from chloroform–methanol).

Anal. Calcd for $C_{20}H_{20}N_4O_4$ (DNP): C, 63.15; H, 5.30. Found: C, 62.05; H, 5.24.

Satisfactory analytical data could not be obtained for this compound; however, all spectral data are consistent with the assigned structure.

2-*tert*-Butyl-3-methylindenone (entry 6): yellow solid; mp 58–59 °C (from petroleum ether); IR ($CHCl_3$) 2925, 1705, 1605, 1580 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.4 (m, 4 H), 2.25 (s, 3 H, C-3 methyl), 1.36 (s, 9 H).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.19; H, 8.15.

2-Methyl-3-phenylindenone (entry 7):[18] orange solid; mp 83–84 °C (from ethanol) (lit.[18] mp 83.5–85 °C); IR ($CHCl_3$) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.4 (m, 4 H), 7.46 (s, 5 H), 1.90 (s, 3 H, C-2 methyl).

2-Phenyl-3-methylindenone (entry 7):[19] orange solid; mp 69–70 °C (from ethanol) (lit.[19] mp 69–70 °C); IR ($CHCl_3$) 2990, 1705, 1598 cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.5 (m, 4 H), 7.36 (s, 5 H), 2.26 (s, 3 H, C-3 methyl).

2-*n*-Butylindenone (entry 8):[8] yellow solid; mp 32.5–33 °C (from petroleum ether) (lit.[8] mp 35–36 °C); IR ($CHCl_3$) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 5 H), 2.1–2.3 (m, 2 H), 1.1–1.7 (m, 4 H), 0.95 (t, 3 H).

2-*tert*-Butylindenone (entry 9): yellow liquid; IR (neat) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.5 (m, 5 H), 1.25 (s, 9 H); DNP, mp 272.5–273.5 °C (from chloroform–methanol).

Anal. Calcd for $C_{19}H_{18}N_4O_4$ (DNP): C, 62.28; H, 4.95. Found: C, 61.97; H, 5.07.

2-Cyclohexylindenone (entry 10): yellow solid; mp 48–49 °C (from petroleum ether); IR ($CHCl_3$) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 5 H), 2.2–2.5 (m, 1 H), 1.2–2.1 (m, 10 H); DNP, mp 225.5–227 °C (from chloroform–methanol).

Anal. Calcd for $C_{21}H_{20}N_4O_4$ (DNP): C, 64.27; H, 5.14. Found: C, 64.02; H, 5.25.

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Registry No. 3-Hexyne, 928-49-4; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; 2-pentyne, 627-21-4; 2-hexyne, 764-35-2; 4,4-dimethyl-2-pentyne, 999-78-0; (1-propynyl)benzene, 673-32-5; 1-hexyne, 693-02-7; 3,3-dimethyl-1-butyne, 917-92-0; ethynylcyclohexane, 931-48-6; 2,3-diethylindenone, 75421-58-8; 2,3-dimethylindenone, 2887-89-0; 2,3-diphenylindenone, 1801-42-9; 2-methyl-3-ethylindenone, 59046-71-8; 2-ethyl-3-methylindenone, 75421-59-9; 2-methyl-3-*n*-propylindenone, 75421-60-2; 2-*n*-propyl-3-methylindenone, 75421-61-3; 2-methyl-3-*tert*-butylindenone, 75421-62-4; 2-*tert*-butyl-3-methylindenone, 75421-63-5; 2-methyl-3-phenylindenone, 13304-52-4; 2-phenyl-3-methylindenone, 10408-73-8; 2-*n*-butylindenone, 24741-71-7; 2-*tert*-butylindenone, 75421-64-6; 2-cyclohexylindenone, 75421-65-7; 2,3-diethylindenone DNP, 75421-66-8; 2-ethyl-3-methylindenone DNP, 75421-67-9; 2-methyl-3-*n*-propylindenone DNP, 75421-68-0; 2-*n*-propyl-3-methylindenone DNP, 75421-69-1; 2-methyl-3-*tert*-butylindenone DNP, 75421-70-4; 2-*tert*-butylindenone DNP, 75421-71-5; 2-cyclohexylindenone DNP, 75421-72-6; *o*-diiodobenzene, 615-42-9; $Ni(CO)_4$, 13463-39-3; $Pd(PPh_3)_4$, 14221-01-3.

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[18] H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168 (1956).

[19] C. F. Koelsch and R. V. White, *J. Am. Chem. Soc.*, **65**, 1639 (1943).

Communications

Base-Induced Conversions of [8 + 2]π Cycloadducts from Azaheptafulvenes and Monosubstituted Ketenes to (*Z*)-α-Substituted Cinnamamides

Summary: The [8 + 2]π cycloadducts from azaheptafulvenes and monosubstituted ketenes rearrange upon treatment with base to give in good yields the amide derivatives of the (*Z*)-α-substituted cinnamic acids.

Sir: Substituted ketenes and 8-azaheptafulvenes, generated (not isolated) from the corresponding acyl chlorides and 8-azaheptafulvenium fluoroborates by use of triethylamine as a base, react to give [8 + 2] cycloadducts.[1,2] The cycloadducts, tentatively assigned trans (exo) stereochemistry,[1,3] when treated with LDA at 0 °C and warmed (refluxed), rearrange to the corresponding amide of (*Z*)-α-aryl(or alkyl)cinnamic acid in good yields (Scheme I, Table I). The rearrangement presumably proceeds through a norcaradiene intermediate.[4-6]

The *Z* configuration was confirmed by comparison with authentic *N*-(*p*-bromophenyl)-α-methylcinnamamide.[7-9]

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[1] K. Yamamoto, S. Kajigaeshi, and S. Kanemasa, *Chem. Lett.*, 91 (1977).

[2] *N*-Aryl adducts are obtained in 70–80% yield and *N*-alkyl adducts in 40–45% yield.

[3] Treatment of the adduct (R = p-C_7H_7, R′ = C_6H_5) in THF at −78 °C with 1 equiv of LDA followed by quenching at the same temperature resulted in no isomerization. Inspection of models confirms that the trans (exo) isomer is less strained.

[4] W. von E. Doering and D. B. Denney, *J. Am. Chem. Soc.*, 77, 4619 (1955).

[5] W. E. Truce and J. P. Shepherd, *J. Am. Chem. Soc.*, **99**, 6453 (1977).

[6] S. W. Staley, M. A. Fox, and A. Cairncross, *J. Am. Chem. Soc.*, **99**, 4524 (1977).

[7] Y. Kishi and M. R. Johnson, *Tetrahedron Lett.*, 4347 (1979).

[8] R. J. DeFeoand and P. D. Strickler, *J. Org. Chem.*, **28**, 2915 (1963).

[9] L. A. Singer and N. P. Kong, *J. Am. Chem. Soc.*, 88, 5213 (1966).