TABLE I

PHYSICAL PROPERTIES AND YIELDS OF 2-BROMO-4′-HYDROXY-3′,5′-DI-*t*-BUTYLACETOPHENONES (1)

			Found, %			Calcd, %			Nmr,[a] δ				
R, R′	% yield	Mp, °C	C	H	Br	C	H	Br	2′,6′-ArH	3′,5′-*t*-Bu	4′-OH	R	R′
H, CH_3	57	133–134	59.85	7.37	23.54	59.83	7.38	23.41	8.00	1.50	5.86	5.33 (q)[b]	1.89 (d)[b]
H, C_2H_5	80	126–127	60.84	7.63	22.49	60.85	7.66	22.49	7.99	1.50	5.86	5.10 (t)[b]	2.22 (p)[b] (CH_2) 1.08 (t)[b] (CH_3)
H, C_6H_5	83	119–120	65.37	6.79	19.94	65.51	6.75	19.81	7.94	1.43	5.80	6.40	7.24–7.74 (m)
CH_3, CH_3	82	141–142	61.00	7.73	22.48	60.85	7.66	22.49	8.21	1.48	5.76	2.07	2.07

[a] Unless otherwise specified, all absorptions are singlets: d, doublet; t, triplet; q, quartet; p, quintet; m, multiplet. In each case, integration was consistent with the proposed assignment. [b] $J = 7$ cps.

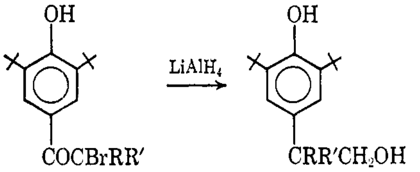
TABLE II

CHARACTERIZATION OF 2-SUBSTITUTED 2-(4-HYDROXY-3,5-DI-*t*-BUTYLPHENYL)ETHANOLS (4)

		Found, %		Calcd, %		Nmr,[a,b] δ							
R, R′	Mp, °C	C	H	C	H	ArH	*t*-Bu	ArOH	CH_2	ROH	ROH[c]	R	R′
H, CH_3	93.2–94.5	77.11	10.80	77.23	10.67	7.06	1.45	5.13	3.66 (d)[d]	1.62	4.54 (t)[e]	2.85 (s)[d]	1.28 (d)[d]
H, C_2H_5	86.0–86.5	77.73	10.92	77.65	10.86	7.01	1.45	5.11	3.71 (d)[d]	1.52	4.46 (t)[e]	2.59 (p)[d]	1.76 (m) (CH_2) 0.85 (t)[d] (CH_3)
H, C_6H_5	107–108	80.70	9.13	80.94	9.26	7.10	1.42	5.11	4.11	1.58	4.70 (t)[f]	4.11	7.31
CH_3, CH_3	149.8–150.3	77.85	10.82	77.65	10.86	7.24	1.47	5.14	3.57	1.47	4.54 (t)[e]	1.32	1.32

[a] Unless otherwise specified, all absorptions are singlets: d, doublet; t, triplet; p, quintet; s, sextet; m, multiplet. In each case, integration was consistent with the proposed assignment. [b] For comparison, 2-(4-hydroxy-3,5-di-*t*-butylphenyl)ethanol (R, R′ = H, H) has the following absorptions: 7.05 (ArH), 1.45 (*t*-Bu), 5.11 (ArOH), 1.77 (ROH), 3.82 (t)[d] (CH_2O), 2.78 (t)[d] ($ArCH_2$). [c] Spectrum taken in DMSO-d_6. [d] $J = 7$ cps. [e] $J = 5.5$ cps. [f] $J = 5.0$ cps.

aryl rearrangement pathway (eq 4) and is independent of the substitution at C_2.[11]



1 4 (4)

Experimental Section

Melting points are corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Unless otherwise specified, nmr spectra were determined in $CDCl_3$ solution using a Varian Associates A-60 spectrometer. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane as zero.

2-Bromo-4′-hydroxy-3′,5′-di-*t*-butylacetophenones (1).—The acetophenone (0.29 mol), cupric bromide (0.67 mol) (the preparation of **1b** is best accomplished with 0.58 mol), 330 ml of ethyl acetate, and 220 ml of chloroform were heated at reflux, with stirring, for 1.25 hr (the preparation of **1g** required 1.75-hr heating time). The cooled reaction mixture was filtered and the solvent was removed by evaporation. The dark residue was dissolved in excess $CHCl_3$–hexane and repeatedly treated with charcoal until a light colored solution was obtained. Recrystallization from hexane or $CHCl_3$–hexane yielded the product **1** (Table I).

Reduction with $LiAlH_4$.—To 0.020 mol of the phenacyl bromide (**1**) in 200 ml of anhydrous ether, cooled to 0°, was rapidly added 0.045 mol of powdered $LiAlH_4$ with vigorous stirring. The reaction mixture was heated at reflux for 3 hr with vigorous stirring. Addition of 30 ml of H_2O and 100 ml of 10% H_2SO_4, followed by drying and evaporation of the ether layer, yielded the crude product in essentially quantitative yield. In each case, nmr spectroscopy indicated the crude product to be essentially pure. Crystallization was effected from hexane to yield the pure product **4** (Table II).

Registry No.—Lithium aluminium hydride, 1302-30-3; **1b,** 17055-13-9; **1c,** 17055-14-0; **1f,** 17055-17-3; **1g,** 17055-18-4; **4b,** 19510-15-7; **4c,** 19598-29-9; **4f,** 19598-30-2; **4g,** 19598-31-3.

Acknowledgment.—We thank Mr. Sidney Liebgold for his kind assistance.

The Reaction of Iodobenzene and Nickel Carbonyl in the Presence of Olefins

E. YOSHISATO, M. RYANG, AND S. TSUTSUMI

Department of Chemical Technology, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka, Japan

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In the course of our study of the reactions of organo transition metal complexes with unsaturated compounds, we observed that organo transition metal complexes derived from the reaction of transition metal carbonyls with organolithiums or active halides are reactive toward acetylenes and/or olefins.[1–3]

Bauld[4] reported that nickel carbonyl reacted with iodobenzene at 50–60° to form benzoylnickel carbonylate, $C_6H_5CoNi(CO)_nI$, as an intermediate complex, and its thermal decomposition or alcoholysis gave benzil or esters of benzoic acid, respectively.

On the other hand, acetylene insertion between the acyl and metal carbonyl groups in acyl metal carbonyls

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[11] Preliminary results by R. V. Flor indicate that the substituents at C_3' and C_5' have a profound effect on the course of the reaction.

(1) Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2159 (1968).

(2) S. Fukuoka, M. Ryang, and S. Tsutsumi, *ibid.*, **33**, 2959 (1968).

(3) (a) I. Rhee, M. Ryang, and S. Tsutsumi, *J. Organometal. Chem.*, **9**, 369 (1967); (b) I. Rhee, N. Mizuta, M. Ryang, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **41**, 1417 (1968).

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

has been reported by several groups of workers in recent years,[1,5,6] but examples of olefin insertion into an acyl metal bond are limited only butadiene insertion with acylcobalt carbonyls and intramolecular olefin insertion in ω-alkenoylcobalt carbonyls.[7,8] Benzoylnickel carbonylate is too unstable to be isolated,[4] but seems to be reactive to olefins because of the relatively positive character of the metal atom compared with the case of acylcobalt carbonyls and lithium acylnickel carbonylates. We studied the reaction of iodobenzene with nickel carbonyl in the presence of olefins such as styrene, acrylonitrile, and ethyl acrylate and obtained some interesting results.

The reaction was carried out in tetrahydrofuran or in benzene at 50-60° for 100 hr in an argon atmosphere. Slight evolution of carbon monoxide was observed in the course of the reaction. The products obtained are listed in Table I.

TABLE I

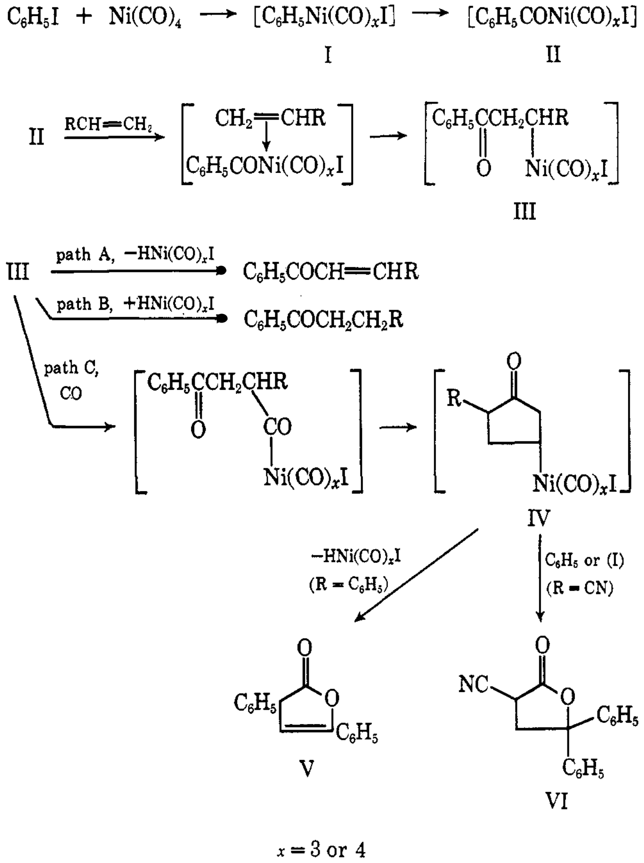
THE REACTION OF IODOBENZENE WITH NICKEL CARBONYL IN THE PRESENCE OF OLEFINS

Olefin	Solvent	Products identified (yield %[a])
$CH_2{=}CHC_6H_5$	THF[b]	$C_6H_5COCH{=}CHC_6H_5$ (5)
		$C_6H_5CH{=}CHC_6H_5$ (4)
		Lactone V (19)
$CH_2{=}CHC_6H_5$	Benzene	$C_6H_5COCH{=}CHC_6H_5$ (1)
		$C_6H_5COCH_2CH_2C_6H_5$ (43)
		Lactone V (25)
$CH_2{=}CHCN$	Benzene	$C_6H_5COCH{=}CHCN$[c] (1)
		$C_6H_5COCH_2CH_2CN$ (29)
		Lactone VI (30)
$CH_2{=}CHCOOC_2H_5$	Benzene	$C_6H_5COCH_2CH_2COOC_2H_5$[d] (24)

[a] Based on iodobenzene consumed. [b] Considerable amounts of benzoic acid esters were formed by the cleavage of the tetrahydrofuran (THF) ring. This kind of side reaction was observed in another system. For example, see E. Yoshisato and S. Tsutsumi, *J. Org. Chem.*, **33**, 869 (1968). [c] See Experimental Section. [d] Identified as 3-benzoylpropionic acid.

The above results can be explained by a stepwise insertion mechanism as shown in Scheme I; herein the coordination number of carbon monoxide is not certain because of the possibility of carbon monoxide exchange reaction in solution.

SCHEME I



As shown in Table I, the reactions of styrene were considerably influenced by the solvent. In tetrahydrofuran solution, the products isolated were all unsaturated compounds but in benzene saturated compounds were obtained mainly. The latter might be produced by the reduction of III by the nickel hydride complex shown by path B. Although there is no certain evidence for a nickel hydride complex, this result suggests that the coordinating ability of the solvent, on which the stability of the eliminated hydride complex depends, plays an important role for the product distribution. This mechanism is in agreement with the fact that, when the reaction (in benzene solution) was carried out in the presence of an appropriate base such as dicyclohexylethylamine, only unsaturated benzalacetophenone was obtained in 19% yield and no saturated benzylacetophenone was detected. In this case the eliminated nickel hydride complex (path A) might be stabilized as a stable salt such as $[BH]^+ [Ni(CO)_xI]^-$ (B = base), which would no longer have the reducing ability of III by path B.

While the final structures of lactones depend on individual olefins, their formation is considered to proceed *via* path C, *i.e.*, insertion of a second carbonyl group in carbon nickel bond in III followed by cyclization to form the complex IV, from which unsaturated or saturated lactone is produced by the elimination of the nickel hydride complex or the cleavage of carbon nickel bond by iodobenzene or I, respectively. Although the formation of lactones from acetylenes and acyl metal carbonyls were reported,[1,5,6] the present results are the first examples of the formation of lactones from olefins. This is, at least in part, due to the high ability of nickel, compared with other metals, to absorb or exchange carbon monoxide in solution.[9] Another carbon monoxide absorbed is considered to occupy the coordinately unsaturated site caused by the insertion of second carbonyl group in III and allows the formation of lactones. In the case of acetylenes, the resulting double bond may take this role forming the relatively stable π-lactenyl metal complexes.[5] Thus lactones can be prepared more easily without absorption of carbon monoxide.

When butadiene or cyclohexene was used as the olefin, these olefins were recovered unreacted. In the case of 1-octene, infrared (ir) spectroscopy showed the

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(5) R. F. Heck, *J. Amer. Chem. Soc.*, **86**, 2819 (1964).

(6) L. Cassar and G. P. Chiusoli, *Tetrahedron Lett.*, 3295 (1965).

(7) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 3381 (1963).

(8) R. F. Heck, *ibid.*, **85**, 3116 (1963).

(9) Thus nickel carbonyl can be prepared from the reaction of carbon monoxide at atmospheric pressure with nickel halide in the presence of a reducing agent and catalysts in aqueous solution. For the rate of exchange reaction of various metal carbonyls with carbon monoxide in solution, see D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959); F. Basalo and A. Wojicki, *J. Amer. Chem. Soc.*, **83**, 520 (1961).

presence of lactones among the products; however, these could not be isolated in pure form owing to the easy rearrangement during the column chromatography and recrystallization. Further investigation concerning the mechanism and application of this reaction is being undertaken.

Experimental Section[10]

Commercially available iodobenzene was treated with concentrated sulfuric acid, washed with water, and then distilled. Nickel carbonyl was prepared by the procedure of Chiusoli and Mondelli.[11] Styrene and ethyl acrylate were distilled under reduced pressure before use. Tetrahydrofuran was refluxed with sodium and benzophenone until the solution turned blue and was then distilled. All solvents were saturated with argon before use.

The Reaction of Iodobenzene with Nickel Carbonyl in the Presence of Styrene. A. In Tetrahydrofuran.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.2 g (0.05 mol) of styrene in 50 ml of tetrahydrofuran was stirred at 50–60° for 100 hr under an atmosphere of argon. The reaction mixture was filtered to remove nickel iodide deposited during the reaction. The filtrate was distilled under reduced pressure to give the following fractions: fraction 1, bp 140–190° (0.5 mm), 2.5 g; fraction 2, bp 190–230° (0.5 mm), 2.3 g; and 1.0 g of polymeric residue. The ir spectrum of fraction 1 showed that this fraction consisted mainly of esters of benzoic acid, which were probably formed from the cleavage of tetrahydrofuran. Chromatography of fraction 1 on silica gel using petroleum benzine (bp 70–80°) as an eluent gave 0.4 g of white crystals and 0.5 g of pale yellow crystals. The former was recrystallized from ethanol to give white needles, mp 124°, and was found to be *trans*-stilbene by mixture melting point with an authentic sample. The latter was also recrystallized from ethanol to give pale yellow needles, mp 56°, and was identified as benzalacetophenone by mixture melting point with an authentic sample. Fraction 2 crystallized on standing and these crystals were recrystallized from ethanol to give 1.5 g of white crystals, mp 109°. This compound was shown to be 2,4-diphenyl-$\Delta^{3,4}$-crotolactone (V) (lit.[12] mp 109–110°) by the following data. The ir spectrum showed a carbonyl band at 1760 cm^{-1} and the nmr spectrum in $CDCl_3$ showed signals at τ 4.10 (one proton) and at 2.2–2.8 (ten aromatic protons and one olefinic proton).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12; mol wt, 236. Found: C, 80.98; H, 5.17; mol wt (in benzene), 240.

B. In Benzene.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.2 g (0.05 mol) of styrene in 50 ml of benzene was treated in a similar manner to that described above. From the reaction mixture 4.8 g of iodobenzene was recovered and vacuum distillation gave two fractions: fraction 1, bp 130–160° (1 mm), 2.7 g; and fraction 2, bp 190–230° (1 mm), 2.5 g. Chromatography of fraction 1 gave a small amount (<0.1 g) of benzalacetophenone and 2.5 of benzylacetophenone, mp 72–73° (lit. mp 73°), and no depression resulted on admixture with an authentic sample. Fraction 2 was triturated in petroleum ether (bp 50–60°) and 1.4 g of 2,4-diphenyl-$\Delta^{3,4}$-crotolactone (V) was obtained.

C. In the Presence of Amine.—An equimolar mixture (0.05 mol) of iodobenzene, nickel carbonyl, styrene, and dicyclohexylethylamine in 50 ml of benzene was treated as described above. Distillation at reduced pressure gave a fraction of bp 130–150° (0.7 mm), 2.4 g. Chromatography of this fraction gave 2.0 g of benzalacetophenone; no benzylacetophenone was detected.

The Reaction of Iodobenzene and Nickel Carbonyl in the Presence of Acrylonitrile.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.3 g (0.1 mol) of acrylonitrile in 50 ml of benzene was treated as described above. Distillation at reduced pressure gave two fractions: fraction 1, bp 135–170° (1 mm), 2.7 g; and fraction 2, bp 185–240° (1 mm), 2.5 g. Fraction 1, which crystallized on standing, was recrystallized from ethanol to give 2.3 g of white needles, mp 70°. This compound was identified as 3-benzoylpropionitrile as follows. The ir spectrum showed a nitrile band at 2270 and a carbonyl band at 1680 cm^{-1}. The nmr spectrum showed a triplet at τ 7.27 (two protons), a triplet at 6.67 (two protons), and a broad band at 2.0–2.8 (five protons).

Anal. Calcd for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80; mol wt, 159. Found: C, 75.71; H, 5.88; N, 8.54; mol wt (in N,N-dimethylformamide), 159.

The ir spectrum of fraction 1 showed also weak bands at 2250, 1675, and 1610 cm^{-1}, indicating the presence of small amounts of unsaturated 3-benzoylacrylonitrile. Fraction 2, which crystallized on standing, was recrystallized from benzene and petroleum benzine (bp 70–80°) to give 1.8 g of white crystals, mp 123–124°. This compound showed in its ir spectrum a nitrile band at 2270 and a carbonyl band at 1742 cm^{-1} but showed no bands characteristic for ester group. The nmr spectrum in $CDCl_3$ showed a doublet at τ 6.70 (two protons), a triplet at 4.15 (one proton), and a broad band at 2.0–3.0 (ten protons).

Anal. Calcd for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32; mol wt, 263. Found: C, 77.84; H, 5.03; N, 5.13; mol wt (in N,N-dimethylformamide), 265.

Thus this material was assigned the structure of 4,4-diphenyl-2-cyanobutylolactone (VI).

The Reaction of Iodobenzene with Nickel Carbonyl in the Presence of Ethyl Acetate.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.0 g (0.05 mol) of ethyl acrylate was treated as described above. The fraction, bp 100–160° (1.5 mm), 3.5 g, was hydrolyzed by KOH in diethylene glycol to give 2.5 g of white leaflets. These crystals, recrystallized from ethanol and water, mp 116°, was identified as 3-benzoylpropionic acid by mixture melting point with an authentic sample.

Registry No.—Iodobenzene, 591-50-4; nickel carbonyl, 13463-39-3; 3-benzoylpropionitrile, 5343-98-6; 4,4-diphenyl-2-cyanobutylolactone, 19598-21-1.

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(10) Nmr spectra were taken with a Model JNM-G-60 spectrometer (Japan Electron Optics Laboratory Co.). Infrared spectra were taken with a Shimazu IR-27C spectrometer. Molecular weights were determined in benzene or in N,N-dimethylformamide by using a Mechrolab vapor pressure osmometer. Melting points and boiling points are uncorrected.

(11) G. P. Chiusoli and G. Mondelli, *Chem. Ind.* (Milan), **43**, 259 (1961).

(12) A. Anshütz and W. F. Montfort, *Ann.*, **284**, 5 (1895).

Preparation and Spectral Characteristics of Some Allyltins. Nature of Allyltin Interactions

KATSUHIKO KAWAKAMI AND HENRY G. KUIVILA

Department of Chemistry,
State University of New York at Albany,
Albany, New York 12203

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In the course of our kinetic study of acid cleavage reaction,[1] we have observed a red shift in the uv spectrum of allyltin compounds compared with that of vinyl derivatives.

A red shift is observed in the spectrum of allylmercuric iodide, too.[2] This suggests an interaction between the allyl group and the metal atom. Spectral data for a series of $R_3M(CH_2)_nCH{=}CH_2$ compounds (in which M = C, Si, Ge, Sn; R = alkyl or halogen, and $n = 1$ or 2) have been reported.[3] The results show that the red shift increases with the atomic weight of M. It was proposed that these shifts result from an interaction between the σ C–M bond and the allylic double bond.

As a means of probing further into the cause of this red shift, we have prepared, and examined some spec-

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(1) H. G. Kuivila and J. A. Verdone, *Tetrahedron Lett.*, 119 (1964).

(2) M. M. Kreevoy, P. J. Steinwand, and T. S. Straub, *J. Org. Chem.*, **31**, 4291 (1966).

(3) V. A. Petukhov, V. F. Mironov, and P. P. Shorygin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2203 (1964).