***N*-Chloro-*N*-methylurethane with Sodium Methoxide.** A solution of sodium methoxide (14.5 mmol) in methanol (10 ml) was added during 15 min to a solution of *N*-chloro-*N*-methylurethane (2 g, 14.5 mmol) in methanol (20 ml) at 0°. The mixture was stirred at 0° for 1 hr; volume changes were monitored with a gas buret. The sodium chloride was filtered off, and an aliquot of the filtrate was titrated for positive chlorine. Finally the filtrate was analyzed by glpc (column 1).

N,N-Dichlorobenzylamine. A solution of benzylamine (10 g, 93 mmol) in water (55 ml) containing concentrated hydrochloric acid (34 ml) was added during 30 min to an ice-cold suspension of calcium hypochlorite (70%, 38 g, 186 mmol) in water (150 ml). After the viscous yellow-green suspension was stirred for another 10 min, the layers were separated. The crude yellow oil (bottom layer) weighed 11 g (67%): ir (neat) 1456, 755, and 702 cm^{-1}.

Anal. (iodometric titration). Calcd for $C_7H_7NCl_2$: Cl, 40.3. Found: Cl, 39.3.

Ethyl Methyl Carbonate. The ester was obtained according to a published procedure.[10]

Methyl Phenethyl Carbonate. A solution of methyl chloroformate (9.5 g, 0.1 mol) in ether (20 ml) was added slowly to a solution of phenethyl alcohol (12.2 g, 0.1 mol) and pyridine (7.9 g, 0.1 mol) in ether (50 ml). The resulting mixture was heated under reflux for 2 hr. Dilute hydrochloric acid was added, and the layers were separated. The organic layer was washed with water and dried with magnesium sulfate. Removal of solvent and distillation through a short Vigreux column provides 10.8 g (60%) of ester: bp 90–92° (0.35 mm), $n^{20}D$ 1.4962 [lit.[33] bp 85° (0.6 mm), $n^{20}D$ 1.4952]; ir (neat) 1736 (C=O), 1263 (CO), 986, 965, 934, 851, 794, 750, and 700 cm^{-1}; nmr (CCl_4) δ 2.90 (t, 2 H, $PhCH_2$), 3.63 (s, 3 H, OCH_3), 4.23 (t, 2 H, OCH_2), and 7.18 (s, 5 H, C_6H_5).

***tert*-Butyl Methyl Carbonate.** The procedure of Pozdnev and Chaman[34] gave a mixture of carbonates in low yield. The desired ester was isolated in pure form by preparative glpc (column 1): ir (neat) 1748 (C=O), 1397, 1370, 1282 (CO), 1258, 1161 (CO), 1104, 943, 867, 796, and 767 cm^{-1}; nmr (CCl_4) δ 1.45 (s, 9 H, $C(CH_3)_3$) and 3.63 (s, 3 H, OCH_3).

Acknowledgment. We are grateful to the National Science Foundation for support and to Dr. E. A. Hill for helpful discussions.

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Stable Acylpalladium(II) Complexes from Carbon Monoxide Insertion into Alkylpalladium(II) Complexes

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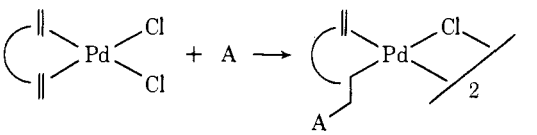
Abstract: Treatment of the unstable σ-alkylpalladium(II) complexes (**1**) resulting from nucleophilic attack of diethylamine on the palladium(II) chloride complexes of ethene, propene, and 1-butene (eq 4) with carbon monoxide results in the formation of stable acylpalladium(II) complexes (**2a–c**). These complexes are isolated in good yield and are well characterized. Treatment with Tl(AcAc) converts them to the corresponding acylpalladium(II) acetylacetonate complexes (**3a–c**).

Olefin palladium(II) complexes undergo facile nucleophilic attack upon the metal-complexed olefin, producing σ-alkylpalladium(II) complexes. With chelating diolefin complexes, the resulting σ-alkyl complexes (eq 1) are stable. Both the mechanism and stereochemistry of this reaction, as well as the physical and chemical properties of the σ-alkyl complexes, have been the subject of much study. Olefin-palladium(II) complexes in which the olefin is part

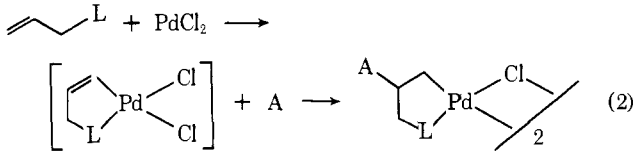


(1)

$A = MeO^-$,[1] R_2NH,[2] $\bar{C}H(COOR)$[3]

of a chelating system containing another ligand such as an

amine[4] or a phosphine[5] undergo similar reactions with nucleophiles to produce stable σ-alkylpalladium(II) complexes (eq 2). In contrast, olefin-palladium(II) complexes *not* sta-

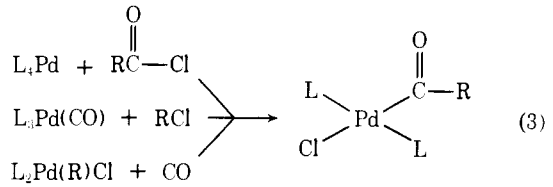


(2)

L = NMe_2, PPh_2

bilized by chelation do not form isolable σ-alkyl complexes upon reaction with nucleophiles but rather spontaneously decompose to Pd metal and organic products.[6,7]

The reactions of the above types of σ-alkylpalladium(II) complexes with carbon monoxide have also been studied in detail. The σ-alkyl complexes resulting from methoxypalladation of chelating diolefin complexes (eq 1, A = MeO^-) react with CO to produce unstable and uncharacterized acylpalladium carbonyl complexes, which react further with solvent or added substrate to produce carbonylated organic products and palladium metal.[8,9] Similarly the σ-alkyl complexes resulting from methoxypalladation of allylamines (eq 2, L = $N(Me)_2$, A = MeO^-) react with CO to produce β-methoxybutyric esters *via* unstable acylpalladium carbonyl complexes.[10] In contrast σ-phenyl complexes from ortho palladation of aromatic oximes react with CO to produce stable σ-phenylpalladium carbonyl complexes, with no evidence for insertion of carbon monoxide into the Pd-C bond.[11] Simple monoolefins react with Pd(II) salts and CO in alcohol solvents to produce diesters[12] or β-methoxy esters,[13] presumably *via* unstable σ-alkyl- and σ-acylpalladium(II) complexes. The stereochemistry of methoxypalladation of 2-butenes has recently been studied by treating the unstable σ-alkylpalladium complex with CO and examining the stereochemistry of the resulting methyl 3-methoxy-2-butanecarboxylate.[13] *Stable* acylpalladium(II) complexes have been prepared by the reaction of phosphinepalladium(0) complexes with acid halides,[14] the reaction of phosphine(carbonyl)palladium(0) complexes with alkyl halides,[15] and the insertion of CO into stable σ-alkylpalladium(II) complexes (eq 3).[16] We report herein the isolation and characterization of a series of stable acylpalladium(II) complexes resulting from the palladium assisted amination of simple monoolefins followed by CO insertion.

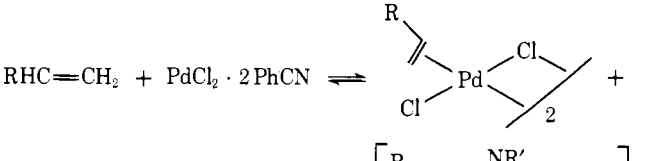


(3)

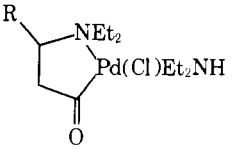
ν_{CO} = 1660–1690 cm^{-1}

Results and Discussion

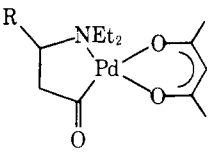
The details of the reaction between secondary amines and monoolefin palladium(II) complexes (eq 4) have recently been reported. The reaction involves nucleophilic attack of the amine on the metal complexed olefin and is thought to proceed through the very unstable and unisolable σ-alkylpalladium(II) complex **1**. *In situ* hydrogenolysis or hydride reduction of **1** produces excellent yields of tertiary amines.[17] Treatment of THF solutions of complex **1**, produced from ethene and diethylamine, with carbon monoxide (30 psi) results in the isolation of the *remarkably stable* acylpalladium(II) complex of structure **2a**. This complex is



(4)



2a, R = H
b, R = CH_3
c, R = C_2H_5



3a, R = H
b, R = CH_3
c, R = C_2H_5

a pale yellow crystalline solid (mp ~120° dec), stable to air and moderate temperatures and readily recrystallizes from petroleum ether–methanol mixtures. The proposed structure is supported by the following data. The infrared spectrum (KBr) has a sharp band at 3420 cm^{-1} due to the N–H of *coordinated* diethylamine[18] and a very intense band at 1670 cm^{-1}, the region characteristic for the carbonyl absorption of acylpalladium(II) complexes.[14–16] There is no absorption in the 2100–1900 cm^{-1} region of the spectrum, indicating the absence of terminal palladium carbonyl groups.[11] The nmr spectrum (Table I) clearly shows the presence of two slightly different diethylamino groups, the coordinated diethylamine and the coordinated diethylalkylamine. That *both* amino groups are coordinated to the palladium is indicated by the downfield shift of the signals due to the ethyl groups relative to the corresponding signals in free diethyl- and triethylamine (Table I). The $-CH_2CH_2-$ group appears as a set of triplets at δ 2.60 and 2.62. The complex has acceptable elemental analyses for five of the six elements present (Table II). The geometry of the complex is unassignable from the available spectral data.

Similar complexes result using propene **2b** or 1-butene **2c** as the olefin component in eq 4. The ir and nmr spectra of these complexes are analogous to those of complex **2a**, and the complexes have elemental analyses consistent with the proposed structures. The single set of peaks for the alkyl substituent (R) in the nmr spectra of **2b** and **2c** suggests that a single positional isomer is isolated. Assignment of the position of the alkyl group (R) as α to the amino group rather than α to the carbonyl group is based on the observed[17] preference for amination at the secondary carbon of terminal olefins and the exclusive attack of methoxide at the secondary carbon of palladium(II) coordinated allylamines.[4] Complexes **2a–c** appear inert to Ph_3P under moderate conditions (benzene, 25°) while forcing conditions (60°) lead to precipitation of palladium metal. Bis(diphenylphosphino)ethane (diphos) reacts with **2a** to initially form an orange solution, which slowly deposits a colorless insoluble uncharacterized solid. In contrast, treatment of complexes **2a–c** with thallium(I) acetylacetonate produces the corresponding acylpalladium(II) acetylacetonate complexes **3a–c**

Table I. Nmr Spectra of Complexes **2a–c** and **3a–c**[a–c]

Groups and complexes	$(CH_3CH_2)_2N$-	$(CH_3CH_2)_2NH$	$(CH_3CH_2)_2N$-	$(CH_3CH_2)_2NH$	R | >N–CH-	R | CH_3CH_2	CH_3CH_2	O || $-CH_2C-$	$(CH_3CO)_2CH$	$(CH_3CO)_2CH$
2a	1.53 (t) 6 H, J = 6 Hz	1.45 (t) 6 H, J = 6 Hz	3.50 (m)	3.08 (m)	R = H 2.62 (t) 2 H, J = 4 Hz			2.60 (t) 2 H, J = 4 Hz		
2b	1.61 (t) and 1.62 (t) 6 H, J = 7 Hz	1.42 (t) 6 H, J = 7 Hz	3.15 (m)	2.60 (m)	3.61 (m) 1 H	1.23 (d) 3 H, J = 7 Hz		2.65 (d) J = 8 Hz		
2c	1.60 (t) and 1.65 (t) 6 H, J = 7 Hz	1.40 (t) 6 H, J = 7 Hz	3.10 (m)	2.65 (m)	3.75 (m) 1 H	0.95 (t) 3 H, J = 7 Hz	1.75 (m)	2.75 (d) J = 6 Hz		
3a	1.48 (t) 6 H, J = 7 Hz		3.10 (m)		2.66 (t) J = 4 Hz			2.65 (t) J = 4 Hz	1.86 (s) and 2.05 (s)	5.24 (s)
3b	1.52 (t) and 1.54 (t) 6 H, J = 8 Hz		2.55 (m) and 3.10 (m)		3.45 (m) 1 H	1.23 (d) 3 H, J = 7 Hz		2.70 (d) J = 7 Hz	1.88 (s) and 2.04 (s)	5.31 (s)
3c	1.56 (t) and 1.58 (t) 6 H, J = 8 Hz		2.60 (m) and 3.15 (m)		3.56 (m) 1 H	0.98 (t) 3 H, J = 7 Hz	1.75 (m)	2.80 (d) J = 7 Hz	1.88 (s) 2.05 (s)	5.30 (s)
$PdCl_2(Et_3N)_2$	1.42 (t)		2.82 (q)							
$PdCl_2(Et_2NH)_2$		1.45 (t)		3.02 (q)						
Et_3N	1.02 (t)		2.52 (q)							
Et_2NH		1.04 (t)		2.63 (q)						

[a] Spectra run on a JEOL 100-MHz instrument in $CDCl_3$ solvent with internal TMS standard. [b] See D. Hollings, M. Green, and D. V. Claridge, *J. Organometal. Chem.*, **54**, 399 (1973), for complete nmr spectra of closely related platinum complexes. [c] Assignments made by complete spin decoupling experiments.

in good yields. The ir spectra (KBr) of these complexes show the loss of the coordinated diethylamine (no band at 3240 cm^{-1}), the retention of the acylpalladium group (ν_{CO} 1700 cm^{-1}), and the presence of the acetylacetone group (ν_{CO} 1590, 1520 cm^{-1}). The nmr spectrum similarly confirms the loss of the coordinated diethylamine, the retention of the diethylamino-acyl ligand, and the addition of the acetylacetonate group, bonded in bidentate fashion[19] as proposed. The pale yellow stable crystalline complexes **3a–c** have acceptable elemental analysis for the proposed structures. Both complexes **2a** and **3a** react with sodium methoxide in methanol to precipitate palladium metal. However, only low yields of methyl 2-diethylaminopropionate are obtained. Optimization of this reaction for the difunctionalization of olefins is under current investigation.

The unusual stability of the acylpalladium(II) complexes **2** and **3** (Table III) is likely due both to the chelating ability of the acyl–amino ligand and the favorability of the five-membered metallocycle thus formed. The role of chelation is suggested by the observation[13] that complexes corresponding to **1** and **2**, in which the R_2N- group has been replaced by the more weakly coordinating RO- group, are too unstable to allow isolation. The importance of chelate ring size is suggested by the instability of σ-alkyl complex **1**, a four-membered metallocycle, relative to acyl complex **2**, a five-membered system, in spite of chelation in both cases. Similarly the σ-alkyl complex resulting from methoxy palladation of *N*,*N*-dimethylallylamine (eq 2, L = NMe_2, A = MeO^-),[4] a five-membered metallocycle, is quite stable. Treatment with CO presumably produces the corresponding acyl complex, a six-membered metallocycle, which is too unstable to isolate but decomposes to palladium metal and 3-aminobutyric ester.[10]

Experimental Section

General. Melting points are uncorrected. Infrared (ir) spectra were measured with a Perkin-Elmer Model 267 or a Beckman Model 1200 spectrophotometer in KBr disks. Nuclear magnetic resonance (nmr) spectra were measured with a Varian Associates Model A-60A or with a JEOL Model JNM H100 spectrometer in deuteriochloroform with TMS internal standard. Layer chromatography was performed using Brinkmann silica gel F254 analytical plates, visualized by uv light, iodine, or Dragendorff's reagent[20] for amine-containing compounds. Microanalyses were performed by Midwest Microanalytical Laboratory, Indianapolis, Ind. All manipulations of palladium–olefin complexes were carried out under argon.

Materials. THF was freshly distilled from $LiAlH_4$ and stored under an argon atmosphere. Petroleum ether (tech grade) was distilled prior to use. Methanol, chloroform, and benzene (Fisher, reagent grade) were used without further purification. Ethene, propene, butene, and carbon monoxide were purchased from Matheson. Diethylamine (Baker Reagent) was used without further purification. Dichlorobis(benzonitrile)palladium(II) was prepared by the method of Kharasch.[21] Thallium acetylacetonate was prepared by the method of Taylor.[22] Palladium chloride was purchased from Englehard.

Preparation of Chloro(3-diethylaminopropionyl)(diethylamine)-palladium(II) (2a). The $PdCl_2$·2PhCN (0.38 g, 1.0 mmol) was placed in a 4-oz Fischer-Porter aerosol compatibility vessel capped with a stainless steel pressure head consisting of a ball valve for liquid additions, a needle valve gas inlet, a pressure gauge, and a safety valve rated at 100 psi and containing a stirring bar. The system was flushed with argon, and the complex was dissolved in 10 ml of argon-saturated THF. The resulting deep red-brown solution was cooled to 0°, and ethene (90 psi) was added. After precipitation of the yellow ethene–palladium chloride complex (10 min), the mixture was cooled to −50° (Dry Ice–CH_3CN). Ethene pressure was released, and diethylamine was added dropwise through the ball valve *via* a syringe to the reaction mixture over a period of 5 min. The resulting grayish-green mixture was stirred for an additional 45 min at −50°, then pressured to 25 psi with carbon monoxide,

Table II. Elemental Analyses for Complexes **2** and **3**[a]

Complex	% C	% H	% Cl	% N	% Pd[b]
2a	38.39 (38.46)	7.22 (7.34)	10.38 (10.32)	8.04 (8.15)	31.80 (30.98)
2b	40.13 (40.32)	7.82 (7.61)	10.05 (9.92)	7.63 (7.83)	29.73 (29.85)
2c	41.89 (42.02)	7.57 (7.87)	9.74 (9.54)	7.55 (7.54)	28.12 (28.72)
3a	43.03 (43.22)	6.30 (6.30)		4.18 (4.20)	31.47 (31.91)
3b	44.70 (44.86)	6.32 (6.66)		3.65 (4.02)	29.41 (30.57)
3c	46.13 (46.44)	6.88 (6.96)		3.44 (3.86)	28.09 (29.38)

[a] Calculated values follow found values in parentheses. [b] Calculated assuming noncombustible residue is Pd metal.

Table III. Properties of Acylpalladium(II) Complexes **2** and **3**

Complex	Yield, %	Mp (dec), °C	ν_{N-H}, cm^{-1}	ν_{CO}, cm^{-1}
2a	73	120–130	3240	1665
2b	72	135–140	3230	1670
2c	58	120–130	3240	1668
3a	95	105–110		1705
3b	58	130–135		1700
3c	64	120–125		1703

and removed from cooling bath. After the mixture was stirred under carbon monoxide pressure overnight, precipitated metallic palladium was removed by filtration and washed on the filter with THF. The solvent was removed under vacuum leaving a dark orange semisolid. This material was washed with petroleum ether twice (10 ml/mmol of complex) to remove benzonitrile, and the collected yellow crystals of **2a** (251 mg, 73%) were dried under vacuum. Recrystallization from petroleum ether–methanol or *n*-hexane–chloroform gave yellow transparent prisms: mp 120–130° dec; ir (KBr) 3240 (s, N-H), 2980 (s), 2940 (s, CH), 1665 (vs, C=O), 1470 (s), 1445 (m, CH), 1380 (s), 1215 (m, C=O), 1152 (m), 1140 (m), 1078 (m), 1045 (m), 1025 (s), 830 (w), 566 (m, Pd-N), 366 (w), 245 (s, Pd-Cl) cm^{-1}; nmr, Table I; analysis, Table II.

Preparation of Chloro(3-diethylaminobutyryl)(diethylamine)palladium(II) (2b). The reaction was run as before, using 959 mg (2.5 mmol) of $PdCl_2$·2PhCN complex, propene pressure of 90 psi, and 913 mg (12.5 mmol) of diethylamine. The resulting complex **2b** (644 mg, 72%) was recrystallized from petroleum ether–methanol giving light yellow transparent needles: mp 135–140° dec; ir (KBr) 3230 (m, N-H), 2980 (vs), 2940 (s), 2895 (s, CH), 1670 (vs, C=O), 1465 (s), 1446 (s, CH), 1395 (m), 1382 (s), 1370 (m), 1212 (m, C=O), 1180 (w), 1152 (s), 1108 (m), 1070 (s), 1055 (vs), 1040 (vs), 1005 (s), 832 (m), 735 (m), 610 (m, Pd-N), 243 (m, Pd-Cl) cm^{-1}; nmr, Table I; analysis, Table II.

Preparation of Chloro(3-diethylaminopentanoyl)(diethylamine)palladium(II) (2c). The reaction was run as before, using 959 mg (2.5 mmol) of $PdCl_2$·2PhCN complex, butene pressure 10 psi, and 913 mg (12.5 mmol) of diethylamine. The resulting complex **2c** (542 mg, 58%) was recrystallized from petroleum ether–methanol giving yellow transparent prisms: mp 120–130° dec; ir (KBr) 3240 (m, N-H), 2980 (vs), 2940 (s), 2910 (s), 2885 (s, CH), 1668 (vs, C=O), 1475 (s), 1447 (s, CH), 1400 (s), 1380 (s), 1369 (m), 1365 (m), 1325 (m), 1214 (s, C=O), 1175 (m), 1152 (s), 1132 (m), 1108 (s), 739 (m), 610 (s, Pd-N), 260 (m), 245 (m, Pd-Cl) cm^{-1}; nmr, Table I; analysis, Table II.

Preparation of Acetylacetonato(3-diethylaminopropionyl)palladium(II) (3a). Complex **2a** (210 mg, 0.61 mmol) was dissolved in 15 ml of benzene, and thallium acetylacetonate (190 mg, 0.61 mmol) was added in small portions, producing an immediate precipitate of white thallium chloride. The mixture was stirred for 2 hr, then filtered, and solvent was removed under vacuum yielding a bright yellow solid (199 mg, 95%). Recrystallization from petroleum ether–methanol gave transparent yellow prisms: mp 105–110° dec; ir (KBr) 2980 (w), 2940 (w), 2800 (w, CH), 1705 (vs, C=O), 1590 (vs, br, C=O acac), 1520 (vs, br, C=O acac), 1470 (s), 1405 (vs, br CH), 1260 (m), 1210 (w), 1200 (w), 1030 (s, br), 930 (m), 765 (m), 745 (w), 595 (w), 430 (m, Pd-N), 250 (m) cm^{-1}.

Preparation of Acetylacetonato(3-diethylaminobutyryl)palladium(II) (3b). The reaction was run as before, using complex **2b** (200 mg, 0.55 mmol) in 15 ml of benzene and thallium acetylacetonate (165 mg, 0.55 mmol). The resulting complex **3b** (204 mg, 58%) was obtained as a bright yellow solid. Recrystallization from petroleum ether–methanol or *n*-hexane–chloroform gave transparent yellow prisms: mp 130–135° dec; ir (KBr) 2990 (s), 2950 (s), 2940 (s), 2910 (s CH), 1700 (vs, C=O), 1590 (vs, br, C=O acac), 1520 (vs, br, C=O acac), 1460 (s), 1410 (vs, br CH), 1260 (s), 1200 (m, C=O), 955 (m), 765 (s), 735 (m), 605 (s), 600 (s), 425 (s, Pd-N), 400 (m) cm^{-1}; nmr, Table I; analysis, Table II.

Preparation of Acetylacetonato(3-diethylaminopentanoyl)palladium(II) (3c). The reaction was run as before, using complex **2c** (220 mg, 0.59 mmol) in 15 ml of benzene and thallium acetylacetonate (170 mg, 0.59 mmol). The resulting complex **3c** (230 mg, 64%) was obtained as a yellow oil. Recrystallization from petroleum ether–methanol or *n*-hexane–chloroform gave transparent yellow rectangular crystals: mp 120–125° dec; ir (KBr) 2980 (s), 2945 (s), 2895 (s, CH), 1703 (vs, C=O), 1590 (vs, br, C=O acac), 1520 (vs, br, C=O acac), 1465 (s), 1405 (vs, br, CH), 1360 (s), 1262 (s), 1202 (m, C=O), 1175 (m), 1140 (w), 1100 (m), 1060 (m), 1040 (s), 1025, 930 (m), 767 (s), 736 (m), 595 (s), 430 (s, Pd-N), 345 (w), 265 (w) cm^{-1}; nmr, Table I; analysis, Table II.

Analytical Thin-Layer Chromatography. All complexes were spotted on silica gel plates and developed with 10:1 benzene–methanol.

Complex:	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**
R_f:	0.25	0.30	0.36	0.32	0.37	0.39

Acknowledgment. This work was supported by the Research Corporation and the National Science Foundation under Grant GP-43626. K.S.-H. acknowledges the Swedish Natural Science Research Council and the American Scandinavian Foundation for support in the form of fellowships. K. C. Van Horne is acknowledged for technical assistance.

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Reactions of Triarylsulfonium Salts with Sodium Alkoxides

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Abstract: The reaction of a triarylsulfonium halide with a sodium alkoxide in a solution in the corresponding alcohol at an elevated temperature produces a mixture of aromatic hydrocarbon, alkyl aryl ether, diaryl sulfide, and aldol resin (or a ketone if the alkoxide is derived from a secondary alcohol). We have now uncovered evidence which clearly indicates that the aromatic hydrocarbon and carbonyl compound are the products of a free radical chain reaction, whereas the alkyl aryl ether is the product of an aromatic nucleophilic displacement reaction.

We have recently presented evidence in the form of a preliminary communication[2] that triarylsulfonium salts undergo competing radical and ionic reactions with sodium alkoxides, aromatic hydrocarbons and aldehydes (which subsequently form aldol resins) or ketones arising by radical chain reactions, and alkyl aryl ethers arising by bimolecular aromatic nucleophilic displacement reactions; diaryl sulfides are formed in both types of reaction. We have also shown that, when all possible sources of radical chain inhibitors are excluded from the reaction mixtures, the aromatic hydrocarbons are usually the major products. On the other hand, the deliberate addition of an inhibitor, such as 1,1-diphenylethylene or diphenylpicrylhydrazyl, to the reaction mixtures causes the products of the aromatic SN reactions to become the major ones. The presumed initiation and propagation steps for the radical chain reaction, as illustrated for the reaction of a triphenylsulfonium halide with sodium ethoxide, are shown in Scheme I.

Scheme I

(1) Initiation

$$(C_6H_5)_3S^+ + CH_3CH_2O^- \rightleftharpoons (C_6H_5)_3S{-}O{-}CH_2CH_3 \rightleftharpoons$$

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$$(C_6H_5)_2\dot{S}{-}O{-}CH_2CH_3,\ C_6H_5\cdot) \rightleftharpoons$$

$$(C_6H_5)_2\dot{S}{-}O{-}CH_2CH_3 + C_6H_5\cdot\ ^{*a}$$

(2) Propagation

$$(C_6H_5)_3S{-}O{-}CH_2CH_3 + C_6H_5\cdot \longrightarrow (C_6H_5)_3S{-}O{-}\dot{C}HCH_3 + C_6H_6$$

$$(C_6H_5)_3S{-}O{-}\dot{C}HCH_3 \longrightarrow (C_6H_5)_3S\cdot + CH_3CHO$$

$$(C_6H_5)_3\dot{S} \longrightarrow C_6H_5SC_6H_5 + C_6H_5\cdot$$

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[a]* Alternatively, $(C_6H_5)_3S\cdot + CH_3CH_2O\cdot$ may be formed.

We have now extended the previously reported studies[2,3] to include: (1) the use of sodium alkoxides other than sodium ethoxide; (2) the use of diphenyl-*p*-tolylsulfonium and tris(*p*-tolyl)sulfonium salts; (3) an evaluation of the effects of numerous additives; and (4) an evaluation of the effects of changes in solvent polarity. The new data are summarized in Tables I–VII.

The essence of the evidence for the competing radical and ionic pathways, as applied to the reaction of diphenyl-*p*-tolylsulfonium iodide with sodium ethoxide in ethanol solution, is as follows: (1) The reaction of 0.001 mol of the sulfonium iodide with 0.003 mol of sodium ethoxide in 3.00 ml of absolute ethanol in a sealed tube at 80° for 24 hr affords benzene (41.4% yield), toluene (14.1%), phenetole (22.1%), diphenyl sulfide (19.3%), and phenyl *p*-tolyl sulfide (84.0%) as the major products when no effort is made to remove oxygen of the air from the system. (The ratio of hydrocarbons to ethers is greater when an argon atmosphere is provided.) These and additional data are shown in Tables I and II. (2) When the same reaction is carried out in the presence of 0.001 mol of 1,1-diphenylethylene, the major products and yields are benzene (8.0%), toluene (2.3%), phenetole (75.5%), *p*-methylphenetole (2.1%), diphenyl sulfide (8.2%) and phenyl *p*-tolyl sulfide (92.5%); 1,1-diphenylethylene is recovered unchanged in 87.5% yield. Thus, in relatively high concentration, 1,1-diphenylethylene is effectively inhibiting the radical chain reaction leading to the formation of aromatic hydrocarbons, presumably by capturing aryl radicals.[4a] It is also of interest that the efficiency of the hydrocarbon additives as inhibitors of the radical chain reaction follows the order 1,1-diphenylethylene > styrene > *trans*-stilbene, and this parallels the data on "methyl affinities" compiled by Szwarc and Binks,[4b] which, in turn, parallels the relative rates of addition of phenyl radicals to unsaturated systems.[4a]

The effects of such well-known radical traps as galvinoxyl and diphenylpicrylhydrazyl on the system under consideration are of interest but subject to some ambiguity in interpretation owing to the fact that these radicals can undergo reactions with strong bases. When 5×10^{-5} mole of diphenylpicrylhydrazyl is added to the reaction mixture described above, without exclusion of oxygen, the major products are benzene (54.1%), toluene (16.5%), phenetole (18.9%), diphenyl sulfide (18.8%), and phenyl *p*-tolyl sulfide (77.0%). With the same amount of diphenylpicrylhydrazyl present, but with exclusion of oxygen (argon atmo-