Stereochemistry of the Bimolecular Metal Reduction of Benzalaniline[1]

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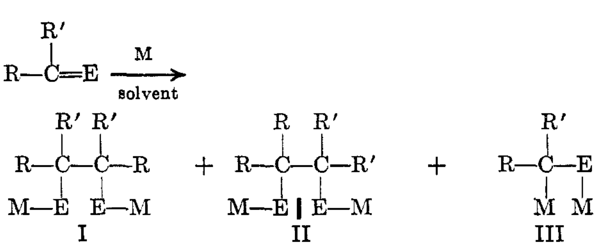
The reduction of benzalaniline by active metals in aprotic solvents was examined as to (a) the competition between monomolecular and bimolecular reduction; (b) the stereoselectivity of bimolecular coupling as reflected in the ratio of *dl* to *meso* product; and (c) the specific solvation effect of the reaction medium. In every case the representative metals, lithium, sodium, magnesium, and barium, yielded 1,2-dianilino-1,2-diphenylethane as the principal reduction product after hydrolytic work-up. Only in the case of aluminum or in metal reductions conducted at elevated temperatures did much monomolecular reduction occur. Preference was shown for bimolecular reduction to *dl*-1,2-dianilino-1,2-diphenylethane; *dl*/*meso* ratios ranged from almost that expected for a random combination of benzalaniline units (1.0) to ratios reflecting a high stereoselectivity in reductive coupling (15.0). The results are interpreted in terms of heterogeneous and homogeneous reactions of radical-anion intermediates.

The reductive dimerization of carbonyl derivatives by means of active metals is a most valuable method for establishing carbon–carbon bonds. Among its principal variants are the pinacol reduction, the acyloin condensation, and the Dimroth reaction.[4,5] In a general fashion, the initial coupling of the carbonyl derivative RR′C=E (where R and R′ = alkyl, hydrogen, or alkoxyl, and E = O, NR, or CHCH=NR) by the metal M can lead to the *meso* form of the dimer I and to the racemic pair (II, *dl* form). In addition, the monomolecular reduction product III can result from the action of 2 equiv. of the metal (eq. 1).

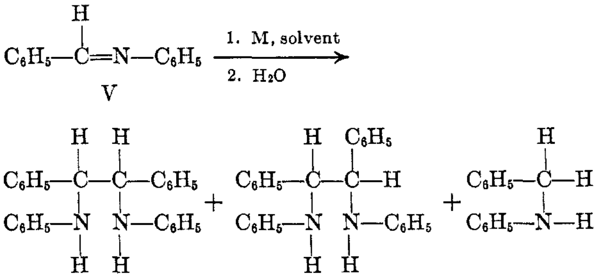


$$\mathrm{R{-}\overset{R'}{\overset{|}{C}}{=}E \xrightarrow[\text{solvent}]{M}}$$

$$\underset{\text{I}}{\mathrm{R{-}\underset{M-E}{\overset{R'}{C}}{-}\underset{E-M}{\overset{R'}{C}}{-}R}} + \underset{\text{II}}{\mathrm{R{-}\underset{M-E}{\overset{R}{C}}{-}\underset{E-M}{\overset{R'}{C}}{-}R'}} + \underset{\text{III}}{\mathrm{R{-}\underset{M}{\overset{R'}{C}}{-}\underset{M}{E}}} \qquad (1)$$

The early chemical investigations of Schlenk and coworkers[6,7] and the more recent physicochemical measurements of Sugden[8] and of Weissman[9] on the alkali metal adducts of benzophenone give much insight into the metal reductions depicted in eq. 1. Not only are 1:1 and 2:1 diamagnetic metal adducts of benzophenone formed (I and III, where R, R′ = C_6H_5), but also the readily formed paramagnetic monomer, $R_2\dot{C}$—E—M (IV), has been detected. Indeed, the dimer I could arise by simple coupling of two radical-anion units (2IV → I) or by nucleophilic attack of III on benzophenone [III + $(C_6H_5)_2C{=}O$ → I]. Presently, opinion favors the origin of I by way of radical-anion coupling. There is much evidence to suggest that dimetallic adducts such as III tend to transfer electrons to unsaturated systems (*e.g.*, benzophenone) to form radical anions (IV), rather than to yield adducts of type I.[10]

The present investigation sought to elucidate the stereochemical characteristics of the bimolecular reduction of carbonyl derivatives. Although such reductions have been key steps in many synthetic studies, no attention appears to have been given to the stereochemistry of the bimolecular coupling as a function of reaction conditions. *A priori*, if the union of the postulated radical-anion intermediates, RR′$\dot{C}$—EM (IV), were completely random, then dimers I and II (eq. 1) should form in equal amounts, but, since the reduction involves the union of polar species (IV), it is reasonable to expect the nature of the metal M and the solvating properties of the medium to influence the stereochemistry of reduction. As the test substrate for this study, benzalaniline (V) was chosen, since the *meso* (VIa) and racemic (VIb) forms of the hydrolyzed bimolecular reduction product, 1,2-dianilino-1,2-diphenylethane, have been separated[11] and their configurations have been established unequivocally[12] (eq. 2).



$$\underset{\text{V}}{\mathrm{C_6H_5{-}\overset{H}{\overset{|}{C}}{=}N{-}C_6H_5}} \xrightarrow[\text{2. } H_2O]{\text{1. M, solvent}}$$

$$\underset{\text{VIa}}{\mathrm{C_6H_5{-}\underset{C_6H_5-NH}{\overset{H}{C}}{-}\underset{NH-C_6H_5}{\overset{H}{C}}{-}C_6H_5}} + \underset{\text{VIb}}{\mathrm{C_6H_5{-}\underset{C_6H_5-NH}{\overset{H}{C}}{-}\underset{NH-C_6H_5}{\overset{C_6H_5}{C}}{-}H}} + \underset{\text{VII}}{\mathrm{C_6H_5{-}\underset{C_6H_5-N-H}{\overset{H}{C}}{-}H}} \qquad (2)$$

As reducing agents, metals were chosen having widely differing ionization potentials and covalent radii. The trios of sodium, magnesium, and aluminum to probe electron-donor ability and of lithium, sodium, and barium to probe covalent size were especially attractive. Aprotic solvents ranging in polarity from hexane to N-methylpyrrolidine and tetrahydrofuran were employed; however, no reaction could be observed in pure hexane. Crucial to this research was finding a reliable analytical method for the reduction products, VIa, VIb, and VII. A convenient procedure

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(1) Part VI of the series, Chemistry of Alkali Metal–Unsaturated Hydrocarbon Adducts. For previous papers, *cf.* J. J. Eisch, *et al.*, *J. Org. Chem.*, **27**, 3745, 4171 (1962); **28**, 707, 2145, 2876 (1963).

(2) National Science Foundation Undergraduate Research Participant, University of Michigan, 1962–1963.

(3) National Science Foundation Undergraduate Research Participant, The Catholic University of America, 1964–1965.

(4) *Cf.*, *inter alia*, H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp. 50–77.

(5) D. Dimroth and R. Heene, *Ber.*, **54**, 2934 (1921).

(6) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *ibid.*, **47**, 473 (1914).

(7) W. Schlenk and E. Bergmann, *Ann.*, **464**, 22 (1928).

(8) F. L. Allen and S. Sugden, *J. Chem. Soc.*, 440 (1936); S. Sugden, *Trans. Faraday Soc.*, **30**, 18 (1934).

(9) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).

(10) *Cf.* the pace-setting work by G. A. Russell, E. G. Janzen, and E. T. Strom [*ibid.*, **86**, 1807 (1964)] on the electron transfer occurring between organic anions and diverse unsaturated electron acceptors.

(11) R. Jaunin, *Helv. Chim. Acta*, **39**, 111 (1956).

(12) W. Stühmer and G. Messwarb, *Arch. Pharm.*, **286**, 221 (1953).

TABLE I

REDUCTION OF BENZALANILINE WITH ACTIVE METALS

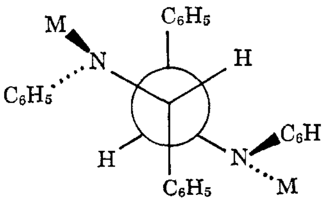
Expt no.	Metal	Solvent	Temp, °C	Time, hr	% recovery (mp range, °C)	Hydrolysis products, %: *meso* dimer	*dl* dimer	*dl*/*meso*	Benzylaniline
1	Na	Benzene	45–50	22	70 (50–120)	41	53	1.3	6
2	Na	Ethyl ether	45–50	22	89 (131–140)	42	53	1.3	5
3	Na	Tetrahydrofuran	45–50	40	99 (130–150)	6	90	15.0	4
4	Na[a]	Tetrahydrofuran	65–70	80	85 (. . .)	10	84	8.4	6
5	Na[b]	N-Methylpyrrolidine	25	70	95 (126–135)	36	55	1.5	9
6	Na[b]	N-Methylpyrrolidine	25 80–85	40 8	. . . (oil)	24	45	1.9	31
7	Li	Tetrahydrofuran	45–50	22	94 (126–136)	41	46	1.1	13
8	Li[b]	Biphenyl–THF	25	96	. . .	30	57	1.9	13
9	Mg (MgI_2)[b]	Benzene	45–50	22	95 (125–130)	43	54	1.3	3
10	Mg (MgI)[b]	Ethyl ether	45–50	22	94 (134–140)	44	56	1.3	0
11	Ba[b]	Tetrahydrofuran	25 65–70	70 6	99 (121–133)	43	51	1.2	6
12	Al (Hg)[b]	Tetrahydrofuran	45–50	22	83 (oil)	24	26	1.1	50

[a] In this reaction, the ratio of sodium to benzalaniline was 1.5:1.0; in all other reactions the ratio was 3.0:1.0. [b] In this case, the unreacted metal was not removed prior to hydrolysis.

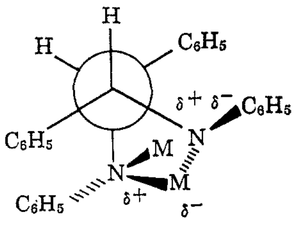
of sufficient accuracy involved treating the crude reaction product with deuterium oxide, in order to remove interfering N–H groups, and then recording the n.m.r. spectrum. The individual benzylic C–H signals for VIa, VIb, and VII were cleanly separated and hence the integrated signals provided a direct measure of the products. The reaction conditions for the metal reduction of benzalaniline and the results of the n.m.r. product analysis are presented in Table I.

Examination of the results leads to the following noteworthy findings. Firstly, *dl*-1,2-dianilino-1,2-diphenylethane (VIb) is the principal bimolecular reduction product in every case studied. Secondly, a wide range of metal activity and covalent size (lithium, sodium, magnesium, barium, and aluminum) produces about the same ratio of *dl* to *meso* dimers (1.1–1.3). Thirdly, however, the use of solvents of greater Lewis basicity (expt 3–6) or the use of an homogeneous medium (expt 7 *vs.* expt 8) causes a pronounced preference (ratio of 1.9 in expt 6 and 8) or, indeed, a striking proclivity (ratio of 15.0 in expt 9) for the racemic dimer VIb. Fourthly, under aprotic conditions monomolecular reduction is a minor side reaction, except with aluminum or at elevated temperatures[13] (expt 6). The large proportion of benzylaniline observed in the run with sodium and N-methylpyrrolidine at 85° (expt 6) suggests that the initially formed dimers, VIa and VIb, have undergone carbon–carbon bond cleavage under the stringent conditions[14] (*cf.* expt 5). A similar bond cleavage may be operative to a small extent in the case of lithium reductions[14] (expt 7 and 8). In the case of aluminum, the predominance of monomolecular reduction can be interpreted in terms of a slower one-electron transfer step for reductive dimerization. Some of the resulting Al^+ might be expected to undergo fast transfer of two electrons[15] to benzalaniline, thus increasing the amount of VII.

The remarkable stereoselectivity of the bimolecular reduction of benzalaniline by sodium in donor solvents deserves further consideration. As noted previously, the random combination of the postulated radical-anion intermediate, here $M^+C_6H_5\dot{C}H\text{–}\bar{N}C_6H_5$ (VIII), should produce equal amounts of the *meso* and *dl* dimers, VIa and VIb, upon hydrolysis. If, however, steric hindrance were decisive in determining the rates with which VIII couples with a like radical anion to form VIa and VIb, respectively, one would expect the *meso* dimer VIa to be the predominant product. This follows from two stereochemical considerations. First, since benzalaniline appears to exist exclusively in the configuration where the phenyl groups are *trans* or *anti*, an approximately *anti* conformation for the radical anion VIII seems reasonable.[16] Secondly, the coupling of the bulky radicals VIII should occur more readily through that transition-state configuration where the largest groups are staggered *trans* with respect to each other[17] (IX). From the results in Table I, it is clear that steric factors alone are not product determining. On the other hand, if attractive forces between two distinct metal–anion pairs (VIII) were significant, the resulting ion clustering might well favor radical coupling to yield the *dl* isomer VIb. As is apparent from structure X, the *dl* configuration would result from the tendency of the C-phenyl groups to be as far removed from each other as possible, while the central carbon–carbon bond is being made. Such



IX



X

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[13] Since benzylaniline (VII) is formed usually in small amounts (<10%), it might be questioned whether this amine is formed in the reaction proper or is generated by the decomposition of the excess metal in the hydrolysis step. However, the amount of VII did not decrease in those cases where the excess metal was removed prior to hydrolysis.

[14] Lithium–biphenyl adducts in THF [J. J. Eisch, *J. Org. Chem.*, **28**, 707 (1963)] and lithium metal itself in THF [H. Gilman and J. J. Dietrich, *J. Am. Chem. Soc.*, **80**, 380 (1958)] have been found to cleave benzylic and benzhydrylic carbon–carbon bonds.

[15] *Cf.* A. W. Davidson and F. Jurik, *ibid.*, **72**, 1700 (1950), for the proposed electrolytic generation of Al^+ species.

[16] E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957).

[17] M. S. Kharasch, H. C. McBay, and W. H. Urry [*J. Org. Chem.*, **10**, 394 (1945)] found that oxidative coupling of dimethyl succinate by acetyl peroxide (apparent union of $CH_3OCOCH_2\dot{C}HCO_2CH_3$ radicals) yields the *meso*-1,2,3,4-tetracarbomethoxybutane and the *dl* ester in a 49:1 ratio.

ion-cluster coupling seems responsible for the predominance of the *dl* dimer.

In such heterogeneous reactions as metal reductions, the radical anions could couple at the metal surface or this reactive species could escape to the solution proper before dimerization occurs. The radical anion VIII, initially formed on the metal surface, should enter the solution with greater ease as the polarity and solvating properties of the solvent are enhanced. Indeed, phenanthridine, formally a closed-ring model of *cis*-benzalaniline, has been observed to form a radical anion when treated with sodium metal in THF solution.[18] In the present study, all of the metals considered, regardless of their activity, were found to cause almost random reductive coupling (ratios 1.1 to 1.3) in certain solvents. This result suggests that coupling of the same intermediate VIII is occurring at the metal surface, with little influence of the solvent. With the most active metal (sodium) and with solvents of higher donor character, the marked increase in the proportion of *dl* isomer VIb suggests that many of the radical anions (VIII) are being solvated at the metal surface and are undergoing coupling in the solution proper. Ion pairing in the manner depicted in X would then lead to predominantly *dl* dimer. Support for this view is seen in the case of lithium (runs 7 and 9). Use of the lithium-biphenyl adduct in THF permits electron transfer to occur in homogeneous solution and hence causes an increase in the amount of *dl* coupling. The striking selectivity observed with sodium and THF, as compared with sodium and N-methylpyrrolidine, is not readily understood in terms of Lewis basicity. Although the amine is clearly the stronger base, possibly the smaller steric requirements of THF as a donor are decisive. Ion alignment of the type proposed for *dl* coupling (X) may be most sensitive to specific solvation. Further exploration of the nature of these specific solvent effects should lead to novel methods of stereoselective synthesis.

Experimental Section[19]

Starting Materials.—Benzalaniline was prepared from freshly distilled benzaldehyde and aniline in accordance with a published procedure.[20] The pale yellow platelets (mp 54.5–55.5°) were stored in a vacuum desiccator.

All the metals employed for the reductions were of greater than 99% purity. The aluminum ingot employed for the turnings was 99.992% pure, the lithium ribbon contained 0.6% sodium, and the magnesium turnings were those recommended for Grignard reactions.

The solvents used for the metal reduction media were of reagent grade. Preliminary drying was accomplished by distilling from metallic sodium. The solvents then were distilled from added lithium aluminum hydride directly into the reaction vessel.

Properties of Reduction Products.—Benzylaniline was prepared from freshly distilled benzyl chloride and aniline according to a published procedure.[21] The colorless granules melted at 37–39° after recrystallization from petroleum ether (bp 90–100°). The infrared spectrum in mineral oil displayed prominent bands at 685, 695, 730–740, 985, 1185, 1280, 1335, 1610, and 3425 cm^{-1}. The nmr spectrum in deuteriochloroform displayed a sharp phenyl (C-phenyl) singlet at δ 7.37 (intensity, 5.0), a typical anilino phenyl pattern between δ 6.58 and 7.35 (5.0), a sharp CH_2 singlet at δ 4.28 (2.0), and a broad NH peak at δ 3.91 (1.0). In another run, a sample of benzylaniline was treated with deuterium oxide (99.9%) and the amine was then extracted into deuteriochloroform. After brief drying over anhydrous calcium sulfate, the nmr spectrum of the solution contained no trace of the NH signal.

The authentic samples of the *dl*- and the *meso*-1,2-dianilino-1,2-diphenylethanes were secured in general accordance with the procedure of Jaunin.[11] A refluxing solution of 18.1 g (0.10 mole) of benzalaniline in 300 ml of anhydrous ether was stirred with 7.5 g (0.32 g-atom) of finely divided sodium for 12 hr. After cooling the reaction mixture, the residual piece of sodium was removed and the ethereal suspension was treated with water. Usual work-up of the organic layer and removal of the solvent gave a residue of the crude reduction products. Digestion with warm methanol yielded 15 g of solid melting over 130°. This was used to prepare the complexes of the diastereoisomers with dimethylformamide (DMF). Decomposition of the individual DMF complexes and recrystallization yielded the pure amines: (a) *meso* compound, colorless needles, mp 169–170°; (b) *dl* compound, pale yellow flat needles, mp 152.5–153.5°. The infrared spectra of these compounds in mineral oil suspension were different: that of the *dl* compound was considerably simpler, but did have a broadened NH band at 3400–3450 cm^{-1}. The infrared spectrum of the *meso* compound exhibited additional bands at 800, 1200, 1280, and 1350 cm^{-1} and a sharp NH band at 3400 cm^{-1}. However, in carbon disulfide solution of both compounds were the same.

The n.m.r. spectra of the isomers proved more useful for qualitative and quantitative analysis. The spectrum of the *meso* compound in deuteriochloroform displayed both C-phenyl and N-phenyl multiplets (δ 6.54–7.38; intensity, 20.0), a broadened CH peak at δ 4.9–5.1 (2.0), and a broadened NH peak at δ 4.45–4.75 (2.0). The spectrum of the *dl* compound exhibited a C-phenyl singlet at δ 7.28 (intensity of 10.0), anilinophenyl multiplets from δ 6.54 to 7.25 (10.0), a sharp singlet at δ 4.64, with a broad shoulder at δ 4.56 (4.0). For quantitative analysis, therefore, deuterium exchange to remove the broad NH absorptions was necessary. Treatment of the isomers with deuterium oxide in the manner described for benzylaniline resulted in the following nmr spectra: (a) *meso*, sharp singlet at δ 5.03 with no residual NH resonance, intensity of aromatic:aliphatic protons = 10:1; (b) *dl*, sharp singlet at δ 4.6 with no shoulder, intensity of aromatic:aliphatic protons = 10:1.

General Procedure for the Metal Reductions of Benzalaniline.—All metal reductions were conducted in a 100-ml, round-bottomed, three-necked flask equipped with reflux condenser, sealed paddle stirrer, and a pressure-equalized addition funnel. By means of a three-way stopcock at the upper end of the condenser, the warm apparatus could be evacuated and refilled with nitrogen. After 50 ml of the appropriate anhydrous solvent was added to the flask, small pieces of the metal (Li, Na, Ba, and Al), subdivided under dry nitrogen, were introduced. In the case of magnesium metal and in certain runs with aluminum metal, the metal was activated by preliminary treatment. Thus, the magnesium suspension in the reaction solvent was treated with iodine, in order to form magnesium iodide, while dry aluminum pieces were heated to 100° with some mercuric chloride before use.

A solution of 9.05 g (0.050 mole) of benzalaniline in 50 ml of the same anhydrous solvent then was introduced onto the metal suspension. The reaction mixture was stirred under a nitrogen atmosphere according to the times and temperatures given in Table I. (In certain cases, the unreacted metal was removed prior to hydrolysis.) The cooled reaction mixtures were hydrolyzed with aqueous ammonium chloride solution. With the aid of additional ether or benzene the organic layer was separated and stored over anhydrous calcium sulfate. Removal of solvent yielded the monomolecular and bimolecular reduction products. Representative samples of the individual reduction runs were treated with deuterium oxide and the nmr spectra of the N-

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[18] J. J. Eisch and R. M. Thompson [*J. Org. Chem.* **27**, 4171 (1962)] have detected the phenanthridine radical anion in THF solution by means of esr spectroscopy.

[19] Reactions between benzalaniline and various metals were conducted in an atmosphere of dry, oxygen-free nitrogen. Matheson prepurified nitrogen (99.997%) was passed over bright copper gauze heated at 400° and then dried by passage through molecular sieves. All melting points are corrected. Infrared spectra were recorded with a Perkin-Elmer infrared spectrophotometer, Model 21, with a 927 slit program. The nmr spectra were recorded with a Varian nmr spectrometer, Model A-60.

[20] L. A. Bigelow and H. Eatough, "Organic Syntheses," Coll Vol I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 80.

[21] F. G. Willson and T. S. Wheeler, ref. 20, p. 102.

deuterated products were recorded in deuteriochloroform. Since benzylaniline, *meso*-1,2-dianilino-1,2-diphenylethane, and *dl*-1,2-dianilino-1,2-diphenylethane each have two benzylic hydrogens, the areas of the respective nmr peaks served to measure the composition of the reduction products. Examination of a known authentic mixture suggested that the results given in Table I are accurate to within ±2%. Furthermore, only nmr signals characteristic of the above-mentioned reduction products or of residual benzalaniline or its hydrolysis products were observed. Specifically, no bibenzyl signals were observed in any of the nmr spectra (possible product from reductive rupture of C–N bonds in the dimers).

Reduction of Benzalaniline by Means of the 1:1 Lithium-Biphenyl Adduct.—The blue-green solution of the 1:1 lithium-biphenyl adduct was prepared by stirring 0.52 g (0.075 g-atom) of lithium pieces with 11.58 g (0.075 mole) of biphenyl in 100 ml of THF. After 10 hr at room temperature, there was almost no trace of undissolved lithium. To this solution was added in one portion 0.05 g (0.005 mole) of benzalaniline dissolved in 50 ml of THF. The reaction mixture was stirred at room temperature for 96 hr during which time the mixture gradually became brownish red. After a terminal reflux period of 1 hr, the solution was cooled and hydrolyzed. Ethyl ether was added to enhance the volume of the organic extract. The separated ether layer was dried over anhydrous calcium sulfate and the solvent was thereupon removed by vacuum evaporation. The organic layer was dissolved in 150 ml of benzene and the resulting solution was saturated with gaseous hydrogen chloride. The precipitated amine hydrochlorides were collected on a glass frit and the filtrate was resaturated with gaseous hydrogen chloride. This treatment was repeated until no more solid was obtained. The solid hydrochloride mixture was warmed with a 10% solution of sodium hydroxide in aqueous ethanol (75%). By dilution of the cooled mixture with water the mixture of amines was obtained. An nmr analysis was carried out in the aforementioned manner.

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Reactions of Triphenyltin Hydride with Certain Acid Chlorides and Carboxylic Acids

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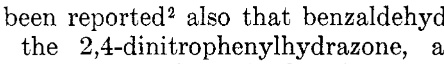
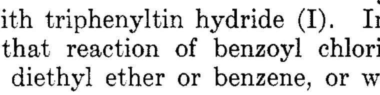
With the exception of triptoyl chloride and ferrocenoyl chloride, the principal reduction product of the reaction of certain aliphatic, bridgehead, and aromatic acid chlorides with triphenyltin hydride is the corresponding ester; a minor reduction product (less than 16%) is the corresponding aldehyde. Triptoyl chloride gives mostly aldehyde, while ferrocenoyl chloride gives ferrocenecarboxylic anhydride. Triphenyltin hydride reacts with bridgehead carboxylic acids and pyrrole-2-carboxylic acid to give the corresponding triphenyltin esters, whereas with ferrocenecarboxylic acid it gives either the triphenyltin ester or *sym*-tetraphenyldiferrocenoyloxyditin; with pyridine-2-carboxylic acid it gives diphenyltin dipicolinate. Thirteen new compounds, including eight new tin esters, are described.

It has been reported[1] that the reduction of benzoyl chloride with tri-*n*-butyltin hydride in ether gives benzaldehyde (54%) as the major reduction product; in the absence of solvent, benzyl benzoate (58%) predominates. Some evidence suggesting the following radical mechanism has been presented.[1]

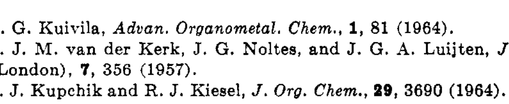
$$R_3Sn\cdot + RCOCl \longrightarrow R_3SnCl + R\underset{\bullet}{C}{=}O \qquad (1)$$



$$R\underset{\bullet}{C}{=}O + R_3SnH \longrightarrow R\underset{\substack{|\\ H}}{C}{=}O + R_3Sn\cdot \qquad (2)$$



$$R\underset{\bullet}{C}{=}O + R\underset{\substack{|\\ H}}{C}{=}O \longrightarrow R\underset{\substack{\|\\ O}}{C}{-}O\overset{\bullet}{\underset{\substack{|\\ H}}{C}}R \qquad (3)$$



$$R\underset{\substack{\|\\ O}}{C}{-}O\overset{\bullet}{\underset{\substack{|\\ H}}{C}}R + R_3SnH \longrightarrow R\underset{\substack{\|\\ O}}{C}{-}O\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}R + R_3Sn\cdot \qquad (4)$$

It has been reported[2] also that benzaldehyde, identified as the 2,4-dinitrophenylhydrazone, and triphenyltin chloride are formed when benzoyl chloride is heated with triphenyltin hydride (I). In contrast, we found[3] that reaction of benzoyl chloride with I in refluxing diethyl ether or benzene, or without solvent at the ambient temperature, gives benzyl benzoate as the major reduction product; in none of our runs could benzaldehyde be detected. The reaction was retarded by radical inhibitors and accelerated by azobisisobutyronitrile, a result which is consistent with the radical mechanism shown above.

Our results with benzoyl chloride led us to investigate the reactions of I with certain other acid chlorides. The results are summarized in Table I. With the exception of triptoyl chloride and ferrocenoyl chloride, the principal reduction product was the ester; a minor reduction product (less than 16%) was the aldehyde. In contrast with the results reported for tri-*n*-butyltin hydride,[1] use of a solvent did not significantly increase the yield of aldehyde. It is interesting to note that 2-thenoyl chloride resembled benzoyl chloride[3] in its behavior since only a very small amount of aldehyde was formed. Triptoyl chloride gave a relatively high yield of aldehyde. In this case steric factors may prevent the occurrence of reaction 3. Ferrocenoyl chloride unexpectedly gave ferrocenecarboxylic anhydride. How the anhydride was formed in this case remains to be ascertained. It had been prepared previously by the reaction of pyridine and traces of water with ferrocenoyl chloride.[4] Its formation was also observed, instead of the expected peroxide, in the reaction of ferrocenoyl chloride and sodium peroxide.[5]

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(1) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 81 (1964).

(2) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 356 (1957).

(3) E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 3690 (1964).

(4) E. M. Acton and R. M. Silverstein, *ibid.*, **24**, 1487 (1959).

(5) H. H. Lau and H. Hart, *ibid.*, **24**, 280 (1959).