Photochemistry of Benzaldehyde in Hydrochloric Acid. Limitation of the Scope of Photoreduction–Chlorination

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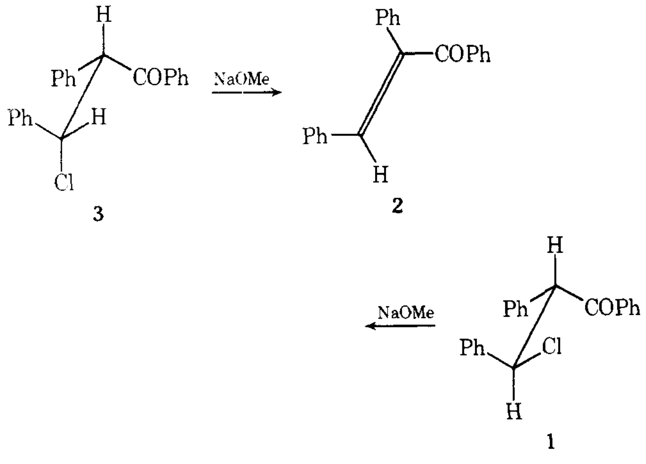
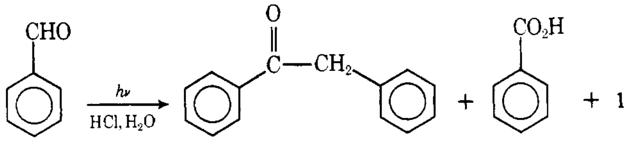
Organic reactions involving substitution of an aromatic ring proton by a nucleophile concomitant with reduction of a conjugated side chain are numerous and broad in scope. Examples include the rearrangements of *N*-chloroanilines,[2] aromatic azasulfonium salts,[3] and *N*-phenylhydroxylamines,[4] the Sommelet–Hauser rearrangement,[5] and the Wallach rearrangement.[6] We have reported a photochemical reaction of this general type involving the conversion of nitrobenzenes in hydrochloric acid to 2,4,6-trichloroanilines,[7] which involves an *o*- or *p*-chloronitrosobenzene intermediate. We now wish to report that benzaldehyde, which, like nitrobenzene, is easily reduced and has a low-lying n,π^* excited state, does not undergo photoreduction–chlorination in hydrochloric acid, but participates instead in a complex disproportionation reaction.

Irradiation of benzaldehyde (850 mg, 4.0×10^{-2} M) in 12 M aqueous HCl (200 mL) for 60 h with a 450-W Hg lamp (Vycor filter) caused much insoluble material to form. Workup by extraction followed by chromatography on silica gel gave 3-chloro-1,2,3-triphenyl-1-propanone (**1**, 112 mg, mp 153–155 °C). The analytical sample of **1** yielded a combustion analysis appropriate for $C_{21}H_{17}OCl$ and showed IR and NMR spectra consistent with the structure. Compound **1** was converted essentially quantitatively to the known[8] (*E*)-1,2,3-triphenyl-2-propen-1-one (**2**) when treated with potassium *tert*-butoxide in 50% benzene-*tert*-butyl alcohol.

By the criteria of mixture melting point and IR and NMR spectra, compound **1** was not identical with the reported[8] 3-chloro-1,2,3-triphenyl-1-propanone (mp 175–176 °C), **3** (configuration not reported). Compound **3**, formed by saturating a mixture of one part deoxybenzoin and five parts benzaldehyde with dry HCl,[8] also underwent dehydrohalogenation when treated with potassium *tert*-butoxide in 50% benzene-*tert*-butyl alcohol to give (*E*)-1,2,3-triphenyl-2-propen-1-one (**2**). On this basis, it appeared that **1** was a diastereomer of **3**. In order to assign the configurations of the two diastereomers, the rate constants for the dehydrohalogenation of each at 25 °C by sodium methoxide in methanol were determined. The rate constants for **1** and **3** [giving the (*E*)-enone] were 6.8×10^{-2} and 5.7×10^{-1} M^{-1} s^{-1}, respectively. The *Z* isomer of **2** is not isomerized to the *E* isomer by sodium methoxide in methanol.[8] Accordingly, with the assumption that anti elimination would be favored over a syn or nonconcerted elimination in this system,[9] it appears that the photoproduct **1** has the threo configuration and **3** has the erythro configuration.



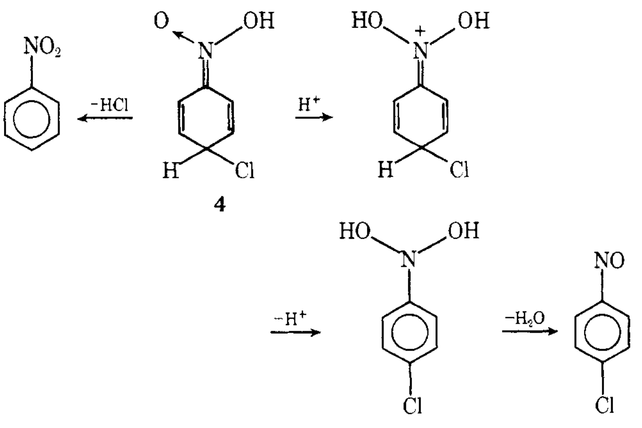
The conversion of benzaldehyde to **1** is complex. Though we have not elucidated the entire pathway, we have obtained evidence that deoxybenzoin is formed photochemically and reacts with benzaldehyde in the dark to give **1**. Thus, when a suspension of deoxybenzoin and benzaldehyde in 12 M aqueous HCl was stirred in the dark for 1 week, **1** was formed in 90% yield. Moreover, when the photochemical reaction in 12 M aqueous HCl was conducted for a shorter time (13.5 h) with a more dilute solution of benzaldehyde (2.5×10^{-3} M), deoxybenzoin was found to be a major product. Gas chromatograms of the materials extracted into benzene showed two major peaks corresponding to unreacted benzaldehyde (63%) and deoxybenzoin (24% based on consumed benzaldehyde). Separation by column chromatography yielded **1** (4%) and benzoic acid (~25%), in addition to deoxybenzoin, benzaldehyde, and an unidentified product.



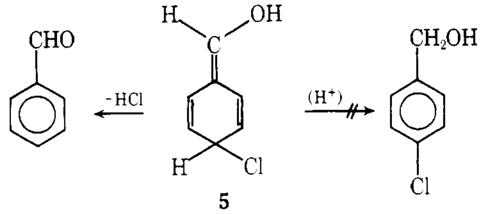
It should be noted that the reaction corresponds to an overall disproportionation process. Thus, the two-electron oxidation of one benzaldehyde to benzoic acid is balanced by the conversion of two benzaldehydes to deoxybenzoin, a two-electron reduction. The origin of the deoxybenzoin remains especially obscure since it does not appear to be derivable from hydrobenzoin by a dark reaction in hydrochloric acid. When *meso*-hydrobenzoin (1.0×10^{-3} M) in concentrated HCl was stirred for 18 h and extracted with benzene, gas chromatograms revealed no trace of deoxybenzoin. The photoreaction of benzaldehyde (1.0×10^{-4} M) in 12 M aqueous HCl is inefficient ($\Phi < 0.005$). The reaction is half as efficient in 6 M HCl, and a dilute solution of benzaldehyde in water showed practically no photochemical reactivity. These results show that HCl is involved in a kinetically important step of the photoreaction. Additional mechanistic details were not investigated.

Whereas we find these results interesting as a demonstration of a novel photochemical reaction, we find even more interesting the showing that the photoreduction–chlorination reaction, which is a general photoreaction of nitrobenzenes,[7] does not extend to the most conspicuous carbonyl analogue. Photoreduction–chlorination of benzaldehyde would give *o*- or *p*-chlorobenzyl alcohol, which forms the corresponding chloride in concentrated HCl. No evidence for this or any other ring-chlorinated product was found.

This result may be rationalized by the mechanism proposed



for photoreduction–chlorination of nitrobenzene.[7] The reaction involves a Meisenheimer-type adduct, **4**, which is formed by a sequence of steps involving electron transfer from chloride ion to $^3n,\pi^*$ nitrobenzene, protonation, and coupling of the radicals at a ring carbon atom.[7] The adduct is converted to the reduction–chlorination product (in competition with reversion to starting material) by an acid-catalyzed tautomerization. Reasons are not apparent why any of the corresponding steps leading to the adduct, **5**, from benzaldehyde would fail. Even if the adduct **5** were to be formed, however, the reduction–chlorination product would not be likely to result, since no good possibility exists for the crucial protonation leading to tautomerization.



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Experimental Section

Melting points were determined using capillary tubes with a Mel-Temp apparatus. Infrared spectra were recorded with a Baird AB-2 spectrophotometer. Electronic spectra were recorded with a Cary Model 11 or a Beckman DB-G instrument. NMR spectra were recorded with a Varian A-60 spectrometer. GC was carried out with an F and M Model 720 or a Hewlett-Packard 5750 chromatograph using 0.25 in. by 10 ft columns of 5% silicone gum rubber (SE-52 or SE-30) on Chromosorb G or 10% Carbowax 20M on Chromosorb W. TLC was carried out using Eastman Kodak K 301R silica gel sheets. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Preparative irradiations were conducted using a Hanovia Model 679A-36 Hg lamp (450-W) with a Vycor filter sleeve in a quartz immersion well cooled by circulating tap water. Reaction solutions were flushed with prepurified N_2 before and during irradiations and were maintained at about 15 °C. A few irradiations were conducted in cuvettes at 25 °C using a GE UA-11 Hg lamp (Vycor filter). Quantum yields were estimated by comparing the loss of benzaldehyde absorption at 249 nm with that for nitrobenzene in 12 M aqueous HCl ($\Phi = 0.11$),[7] making corrections for the differences in absorptivities.

Kinetic measurements on the dehydrohalogenations of **1** and **3** in methanol were carried out in cuvettes at 25 °C using a starting chloro ketone concentration of 4.0×10^{-5} M and monitoring the appearance of the product, **2**, at 290 nm. Pseudo-first-order rate constants were obtained by plotting the data obtained for each at several NaOMe concentrations in the range $4–8 \times 10^{-3}$ M. The second-order rate constants obtained from the pseudo-first-order constants follow: for **1**, $k = 6.8 \pm 1.1 \times 10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$; and for **3**, $k = 5.7 \pm 0.5 \times 10^{-1}\ \mathrm{M^{-1}\,s^{-1}}$.

Preparation of *threo*-3-Chloro-1,2,3-triphenyl-1-propanone (1). Deoxybenzoin (1.0 g) and benzaldehyde (1.0 g) were stirred magnetically for 1 week in 12 M aqueous HCl (500 mL). The reaction solution was evaporated on a rotary evaporator to 300 mL and the copious precipitate was collected with a sintered glass funnel. The yield of dried, crude product was 1.46 g (90%), mp 147.5–151 °C. Three recrystallizations from 95% ethanol gave 1.11 g (68%) of small, white needles, mp 155–156 °C. This was identified as 3-chloro-1,2,3-triphenyl-1-propanone (**1**) (*dl*-threo diastereomer) by the following data: IR (KBr) 3050 (m), 1675 (s), 1600 (m), 1580 (m), 1490 (m), 1450 (s), 1360 (m), 1335 (m), 1310 cm^{-1} (m); UV (95% EtOH) 247 nm (ϵ 18 000); NMR ($CDCl_3$) δ 8.13–8.01 (2 H, m), 7.5–7.0 (13 H, m), 5.72 (1 H, d, $J = 11$ Hz), 5.25 (1 H, d, $J = 11$ Hz). Anal. Calcd for $C_{21}H_{17}OCl$: C, 78.62; H, 5.34; Cl, 11.05. Found: C, 78.65; H, 5.42; Cl, 11.03. **1** was not identical by mixture melting point and spectral data with the reported[8] 3-chloro-1,2,3-triphenyl-1-propanone (**3**), mp 175–176 °C: IR (KBr) 3050 (m), 1675 (s), 1600 (m), 1580 (m), 1500 (m), 1450 (m), 1330 (m), 1300 cm^{-1} (m); NMR ($CDCl_3$) δ 7.9–7.7 (2 H, m), 7.6–7.2 (13 H, m), 5.64 (1 H, d, $J = 11$ Hz), 5.25 (1 H, d, $J = 11$ Hz).

Preparative Dehydrohalogenation of 1 and 3. A solution (5 mL) of potassium *tert*-butoxide (0.1 M) in *tert*-butyl alcohol was added at once to the chloro ketone (100 mg) in 1:1 *tert*-butyl alcohol-benzene (100 mL). The solution was stirred for 30 min and then shaken with 100 mL of 0.01 M aqueous acetic acid. The benzene layer was separated and dried with $MgSO_4$, and the solvent was removed in vacuo. **1** gave 87 mg (98%) of crude product and **3** gave 85 mg (96%). Melting points after one recrystallization from hexane were 100–101 °C. The IR spectrum of each was identical with that of an authentic sample of (*E*)-1,2,3-triphenyl-2-propen-1-one,[8] and mixture melting points with the authentic material were undepressed.

Photoreaction of Benzaldehyde in Hydrochloric Acid. A solution of benzaldehyde (0.85 g, 4×10^{-2} M) in 12 M aqueous HCl (200 mL) was flushed with N_2 for 30 min and irradiated for 18 h. At this point the wall of the immersion well was coated with resinous material and the benzaldehyde λ_{max} at 250 nm of diluted aliquots had decreased from 1.13 to 0.83 OD units. Irradiation for an additional 42 h caused little change in the optical density. The reaction solution was neutralized (to pH 4) with concentrated NaOH and extracted with four 100-mL portions of ether. The extracts and ether washings from the photolysis vessel were combined, dried over $MgSO_4$, and concentrated in vacuo. The concentrated extract was subjected to column chromatography on silica gel (70 g) packed in 1:1 benzene–hexane taking 125-mL fractions. The first few fractions contained small amounts of oil, and fractions 6–12 contained 112 mg of a white solid, mp 153–155 °C, R_f 0.38 in 1:1 benzene–hexane. Later fractions contained oils which were not investigated. The material in fractions 6–12 was identical with 3-chloro-1,2,3-triphenyl-1-propanone (**1**) (*dl*-threo diastereomer) by mixture melting point, IR, and NMR spectra (see above).

In a subsequent run, a solution of benzaldehyde (318 mg, 2.5×10^{-3} M) in 12 M aqueous HCl (1200 mL) was flushed with N_2 for 30 min and irradiated for 13.5 h. The benzaldehyde present was assayed by extracting the reaction mixture with two 50-mL portions of benzene, and analyzing the extract for benzaldehyde by gas chromatography. A control experiment revealed that the efficiency of benzaldehyde detection by this method was 60%. Applying this correction, the amount of consumed benzaldehyde was 118 mg. The reaction solution was extracted again with benzene (two 100-mL portions), and all the extracts were combined, dried over $MgSO_4$, concentrated in vacuo, and made up to 2.0 mL in benzene. GC analysis at 230 °C (SE-52 column) showed a peak for benzaldehyde, a large peak corresponding to deoxybenzoin (24% based on consumed benzaldehyde), and several small peaks which were not identified. Peaks were assigned by peak enhancements with authentic samples on two different columns. Column chromatography on 10 g of silica gel packed in 1:1 benzene–hexane gave the following (50-mL fractions): fraction 1, 35 mg of yellowish oil, R_f 0.35 in hexane, not identified; fraction 2, 5 mg of white solid, R_f 0.38 in 1:1 benzene–hexane, identified as **1** (4%); fractions 3–5, mixture of benzaldehyde and deoxybenzoin; fractions 7–8 (5% EtOAc–benzene eluent), 39 mg of solid, mp 103–112 °C, identified as impure benzoic acid (~25%). Identifications are based on the comparisons of R_f values on TLC with those of authentic samples, and, for benzoic acid, the coincidence of its IR spectrum with that of an authentic sample.

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Registry No.—**1**, 61665-39-2; **2**, 7474-65-9; **3**, 61634-65-9; deoxybenzoin, 451-40-1; benzaldehyde, 100-52-7; hydrochloric acid, 7647-01-0; benzoic acid, 65-85-0.

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