resolution mass spectrometry of **3e** (a peak appearing at m/e 174.1149 can be assigned to *tert*-butylphenylcarbodiimide[11]), and (iii) X-ray analyses of **3e** and **3i**.[12]

Attempts to rearrange compounds **3** or to hydrolyze their imino function met with failure: thermolysis of **3e** resulted in loss of pivalaldehyde with concomitant formation of the known benzimidazolone **5**,[13] while acid hydrolysis furnished the *N*-hydroxyurea **6**,[14] neither **7** nor **8** being detected (Scheme II). Solvolytic reactions of **3i**, such as methanolysis and acetolysis, gave rise to the open-chain compounds **9a,b**, which on heating to 250 °C recyclized to the starting ring, not to the isomeric oxadiazolidinone akin to **7**.[15]

Experimental Section

Melting points are uncorrected. IR spectra were measured on a Pye-Unicam SP 1100 spectrometer (in cases not indicated, liquids were recorded neat, solids in KBr). ^{1}H NMR spectra were taken on a Varian EM-390 instrument, ^{13}C NMR spectra were run on Varian XL-100 and Bruker AM-300 or WM-400 spectrometers (in cases not indicated, $CDCl_3$ was used as solvent; chemical shifts are in δ relative to internal Me_4Si). Mass spectra were determined on a Varian MAT CH-7 instrument (70 eV).

Substituted 2-*tert*-Butyl-3-imino-1,4,2-dioxazolidines 3. General Procedure. A mixture of **1**,[16] the isocyanide,[17] and the aldehyde (30 mmol each) in anhydrous benzene (10 mL) was transferred to an autoclave and heated to 100 °C for 24 h; acetone was employed in tenfold excess without additional benzene. Reaction conditions were 70 °C for 7 days for **3k** and 100 °C for 48 h for **3l**. After evaporation of the solvent and other volatiles in vacuo, the product was isolated by crystallization or distillation [in the case of **3k**, a short spinning-band column was used in order to separate di-*tert*-butyldiaziridinone (IR in accord with that in the literature[18])]. Most runs gave trace amounts of the symmetrical *N,N'*-disubstituted urea derived from the isocyanide employed [identified by comparison (mp, IR) with authentic samples]. Data of compounds **3** are summarized in Table I [**3m** omitted (cf. ref 7); preparation analogous to that of **3a–i** except for prolonged heating (48 h)].

(i) Thermolysis and (ii) Hydrolysis of the 1,4,2-Dioxazolidine 3e. (i) Compound **3e** (0.55 g, 2 mmol) was heated neat to 300 °C for 15 min such as to allow volatiles to distill into 50 mL of a solution of 2,4-dinitrophenylhydrazine (2,4-DNPH) (0.50 g, 2.51 mmol) in 99:1 methanol–12 N HCl. After 1 h at 20 °C and 4 h at 5 °C the 2,4-dinitrophenylhydrazone of pivalaldehyde was collected by filtration, 0.43-g (81%) yield, identified by comparison (mp, IR) with an authentic sample. The residue from heating **3e** was dissolved in benzene; on addition of light petroleum 1-*tert*-butyl-2,3-dihydro-2-benzimidazolone (**5**) separated as plates: 0.26-g (68%) yield; mp 144–145 °C (lit.[13] mp 145–146 °C); IR (KBr) 3300–2700 (br, NH), 1690 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 9 H, *t*-Bu), 6.9–7.5 (m, 4 H, Ar), 10.47 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 29.5 (q, Me), 58.0 (s, CMe_3), 109.4, 111.9, 120.3, and 120.8 (d, CH of Ar), 129.0 and 130.5 (s, quaternary C of Ar), 156.2 (s, C-2); MS (70 eV, 90 °C), m/e (relative intensity) 190 (M^+, 74), 134 (100).

(ii) The above 2,4-DNPH reagent (5 mL, 0.25 mmol) was added to a solution of **3e** (0.055 g, 0.2 mmol) in methanol (5 mL). After 1 h at room temperature cooling to 5 °C caused separation of the 2,4-dinitrophenylhydrazone of pivalaldehyde: 0.041-g (77%) yield. In another run a solution of **3e** (0.50 g, 1.81 mmol) in tetrahydrofuran (5 mL) was mixed with water (0.2 mL) and concentrated sulfuric acid (0.1 g). After 2 h at room temperature ether (5 mL) and water (5 mL) were added. The organic layer was separated and dried over anhydrous magnesium sulfate. Solvent removal in vacuo at room temperature gave crystalline *N*-*tert*-butyl-*N*-hydroxy-*N'*-phenylurea (**6**), 0.32-g (85%) yield, identified by comparison (mp, IR) with an authentic sample.[14]

***N*-*tert*-Butyl-*N'*-cyclohexyl-*N*-[(α-methoxybenzyl)oxy]urea (9a).** The 1,4,2-dioxazolidine **3i** (2.0 g, 6.61 mmol) was refluxed in methanol (20 mL) for 30 min. After solvent removal in vacuo, addition of ether, and cooling to −10 °C the product separated as coarse needles: 1.46-g (66%) yield; mp 78 °C; IR (KBr) 3430 (NH), 1680 and 1515 (amide I and II) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.2 (m, 10 H, CH_2 of *c*-C_6H_{11}), 1.40 (s, 9 H, *t*-Bu), 3.4–3.7 (m, 1 H, CH of *c*-C_6H_{11}), 3.56 (s, 3 H, Me), 5.43 (s, 1 H, CHPh), 6.49 (d, J = 7 Hz, 1 H, NH), 7.1–7.5 (m, 5 H, Ph). Anal. Calcd for $C_{19}H_{30}N_2O_3$: C, 68.23; H, 9.04; N, 8.38. Found: C, 68.30; H, 9.14; N, 8.39.

***N*-[(α-Acetoxybenzyl)oxy]-*N*-*tert*-butyl-*N'*-cyclohexylurea (9b).** A solution of **3i** (0.5 g, 1.65 mmol) in anhydrous acetic acid (5 mL) was heated to 100 °C for 30 min. The solvent was evaporated in vacuo and the residue treated with ether–light petroleum. After several days at −10 °C the product crystallized as needles: 0.31-g (52%) yield; mp 74–75 °C; IR (KBr) 3405 (NH), 1745 (ester), 1670 and 1520 (amide I and II) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.1 (m, 10 H, CH_2 of *c*-C_6H_{11}), 1.38 (s, 9 H, *t*-Bu), 2.08 (s, 3 H, Me), 3.5–3.8 (m, 1 H, CH of *c*-C_6H_{11}), 6.08 (d, J = 8 Hz, 1 H, NH), 6.84 (s, 1 H, CHPh), 7.1–7.5 (m, 5 H, Ph). Anal. Calcd for $C_{20}H_{30}N_2O_4$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.31; H, 8.35; N, 7.76.

Thermolysis of 9a,b. General Procedure. The urea **9a** or **9b** (3 mmol) was heated neat to 250 °C for 30 min. Cooling to room temperature gave a dark residue whose IR spectrum (film) was essentially identical with that of **3i**. Traces of **9a** and **9b** respectively were detected by TLC.

Acknowledgment. We thank Dr. L. Grotjahn of Gesellschaft für Biotechnologische Forschung mbH, D-3300 Braunschweig-Stöckheim, West Germany, for performing the high-resolution mass spectral analysis of compound **3e**. Thanks are equally due to Fonds der Chemischen Industrie for financial support.

Registry No. **3a**, 99948-57-9; **3b**, 99948-58-0; **3c**, 99948-59-1; **3d**, 99948-60-4; **3e**, 99948-61-5; **3f**, 99948-62-6; **3g**, 99948-63-7; **3h**, 99948-64-8; **3i**, 99948-65-9; **3k**, 99948-66-0; **3l**, 99948-67-1; **3m**, 99948-68-2; **5**, 31562-06-8; **6**, 29586-31-0; **9a**, 99948-69-3; **9b**, 99948-70-6; CH_3CHO, 75-07-0; 4-$CH_3C_6H_4NC$, 7175-47-5; $(CH_3)_3CCHO$, 630-19-3; PhCHO, 100-52-7; CH_3COCH_3, 67-64-1; $PhCOCH_3$, 98-86-2; *t*-BuNO, 917-95-3; *c*-C_6H_4NC, 931-53-3; PhNC, 931-54-4; *t*-BuNC, 7188-38-7; 4-ClC_6H_4NC, 1885-81-0; 4-$NO_2C_6H_4NC$, 1984-23-2; *t*-BuCHO, 630-19-3; 2,4-$(CH_3)_2C_6H_3NHN{=}CHBu$-t, 13608-36-1.

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Homogeneous, Palladium-Catalyzed, Selective Hydrogenolysis of Organohalides

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The hydrogenolysis of organohalides with molecular hydrogen over an heterogeneous transition-metal catalyst (e.g., Pd/C) is a well-known and widely applied reaction, performed at low hydrogen pressure and ambient temperature.[1] However, this nonselective dehalogenation

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Table I. Reductive Dehalogenation of Halides with PMHS as Hydrogen Donor[a]

entry	halide	reactn conditions: temp, °C	reactn conditions: time, h	product[b] (% yield)
1	C_6H_5I	60	3	C_6H_6 (53)
2	C_6H_5Br	110	18	C_6H_6 (75)
3	C_6H_5Cl	110	18	*c*
4	$4\text{-}BrC_6H_4Cl$	110	18	C_6H_5Cl (65)
5	$C_6H_5CH{=}CHBr$	60	3	$C_6H_5CH{=}CH_2$ (37)
6	$CH_3CH(Br)CO_2H$	110	3	$CH_3CH_2CO_2H$ (35)
7	$C_6H_5COCH_2Br$	110	3	$C_6H_5COCH_3$ (80)
8	$4\text{-}BrC_6H_4COCH_3$	110	3	$C_6H_5COH_3$ (96)
9	$4\text{-}O_2NC_6H_4Br$	110	3	$C_6H_5NO_2$ (93, 84[d])
10	$4\text{-}BrC_6H_4C_6H_4Br\text{-}4'$	110	5	$C_6H_5C_6H_5$ (72)
11	$4\text{-}BrC_6H_4CHO$	110	3	C_6H_5CHO (93)
12	$4\text{-}BrC_6H_4CO_2H$	110	18	$C_6H_5CO_2H$ (77, 70[d])
13	$C_6H_5CH(Br)CO_2H$	110	18	$C_6H_5CH_2CO_2H$ (55)

[a] Halide, 1 mmol; catalyst; $Pd(PPh_3)_4$, 0.05 mmol; base, tribenzylamine, 1.4 mmol; PMHS, 0.4 mL; solvent, $MeCN/Me_2SO$ (1:1). [b] Yields determined by GLC or HPLC unless otherwise indicated. [c] No reaction. [d] Isolated yield.

Table II. Hydrogenolysis of Organohalides with Formate Ion as Hydrogen Donor[a]

entry	halide	reactn conditions: temp, °C	reactn conditions: time, h	product[b] (% yield)
1	$C_6H_5COCH_2Br$	100	18	$C_6H_5COCH_3$ (98)
2	$C_6H_5CH{=}CHBr$	110	3	$C_6H_5CH{=}CH_2$ (35)
3	$4\text{-}BrC_6H_4CH{=}CH_2$	110	3	$C_6H_5CH{=}CH_2$ (40)
4	$4\text{-}IC_6H_4NO_2$	100	18	$C_6H_5NO_2$ (75)

[a] Halide, 1.0 mmol; sodium formate, 5 mmol; catalyst, $Pd(PPh_3)_4$, 0.03 mmol; solvent, CH_3CN/Me_2SO (1:1). [b] Yields determined by GLC or HPLC.

procedure is of limited application in the presence of reducible functional groups such as nitro, aldehydes, or olefins. Hydrodehalogenation with other reagents such as Raney nickel, lithium aluminum hydride, organotin hydrides, and organosilicon hydrides are also incompatible with several functional groups.[2]

The reactivity of a dissolved transition-metal complex as a homogeneous catalyst is generally accepted to be more selective than the corresponding heterogeneous catalyst. Unfortunately, almost no carbon–halogen hydrogenolysis is found to occur when the heterogeneous Pd/C catalyst is replaced by a homogeneous Pd(0) complex.

In order to take advantage of the chemoselectivity of a homogeneous Pd(0) catalyst and nevertheless cause it to be as reactive as a heterogeneous palladium catalyst, a better contact between the soluble catalyst and the hydrogen source should be achieved. This goal may be accomplished by substituting the molecular hydrogen by a soluble hydrogen donor such as polymethylhydrosiloxane (PMHS) or sodium formate.

Results and Discussion

The replacement of molecular hydrogen by an appropriate hydrogen donor, capable of transferring hydrogen in a homogeneous catalyzed hydrogen-transfer reaction, was proved to be an efficient and chemoselective route for hydrogenolysis of carbon–halogen bonds.

Thus, dehalogenation of organobromides and organoiodides was performed using PMHS as the soluble hydrogen source. For example, 4,4′-dibromobiphenyl was converted to biphenyl in 68% yield after 3 h of reaction with PMHS at 110 °C. Polymethylhydrosiloxane, which is known as a mild, air-stable reducing agent,[3] was also used as a hydrogen donor in a palladium(0)-catalyzed reductive formylation.[4] Results of transfer hydrogenolysis of various organohalides in $Me_2SO/MeCN$ (1:1) as solvent are summarized in Table I. PMHS was found to hydrodehalogenate aryl halides (entries 1–4 and 8–10), vinyl halides (entry 5), α-halo ketones, and acids (entries 6 and 7). While aryl iodides and aryl bromides underwent smooth hydrogenolysis, aryl chlorides did not react under these conditions (entry 3). Unsaturated functional groups like nitro, aldehydes, olefins, and ketones were found to tolerate the reaction conditions of reductive dehalogenation (entries 9, 11, 5, and 7, respectively).

Note should be taken of the pronounced reactivity of homogeneous palladium(0) in catalyzing the hydrogenolysis with a soluble hydrogen donor, as compared to its inefficiency as a catalyst under low pressures of hydrogen gas. A plausible explanation for these differences is the kinetic competition between the hydrogen source and the organohalide undergoing oxidative addition to the coordinatively unsaturated catalyst. The low solubility of gaseous hydrogen combined with the existing high organohalide-to-catalyst ratio favors the oxidative addition of the organohalide and minimizes the probability of the hydrogen molecule to react in a similar manner.

This kinetic problem could be solved by applying high hydrogen pressure in the presence of a homogeneous catalyst. Indeed, under 1200 psig of hydrogen gas, 4,4′-dibromobiphenyl was debrominated to give 83% yield of biphenyl, while only 18% yield was obtained when a low pressure of hydrogen was applied.[5]

High-pressure reductive hydrogenolysis seems to be closely related to the high-pressure formylation of aromatic halides catalyzed by homogeneous Pd(0) complexes.[6] In both cases, the kinetic barrier is overcome by applying high hydrogen pressures. Also, in both cases these conditions are not tolerable for aromatic nitro functions which are hydrogenated, resulting in polymeric products.[6] When

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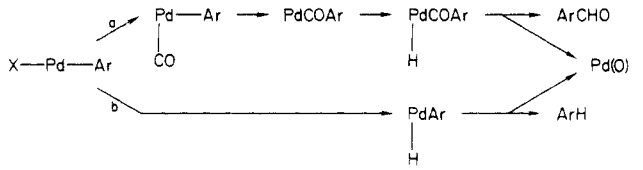
Scheme I



a heterogeneous catalyst is used, nonselective reactions occur, even under low pressures of hydrogen. The adsorption of hydrogen gas into the metal surface and the formation of a reaction zone in which the hydrogen concentration is high enough to compete the aryl halide addition explain the heterogeneous catalyst activity, even under low hydrogen pressure.

In spite of the obvious advantages of the homogeneous catalyzed transfer hydrogenolysis reaction, there are only a few scattered reports of it.[7] A similar reaction applying sodium formate as a hydrogen donor in DMF solution was reported,[8] where debromination of aryl bromides occurred. This reagent was also studied in this work, in MeCN/Me_2SO (1:1) solution and was found to be applicable also to vinyl bromides, α-bromo ketones, and aryl iodides. Results are given in Table II.

Conversion of α-bromostyrene under these conditions was nearly 100%; however, only 35% of styrene was detected (entry 2) by GLC, probably as the result of excessive polymerization of styrene under the experimental conditions. A similar result was observed in the reaction of 4-bromostyrene (entry 3) which gave a quantitative conversion of the starting material but only 40% yield of styrene.

The existence of this homogeneous catalyzed transfer hydrogenolysis of organic halides enables one to gain additional information on the mechanism of the H-transfer formylation of aryl halides performed under similar conditions.[4] While in the formylation reaction a fast carbonyl insertion is followed by a slow H-transfer and reductive elimination (Scheme I, path a), in the transfer hydrogenolysis reaction a direct reductive elimination of the hydrido Pd (II) arene seems to be the final step in the catalytic cycle (Scheme I, path b). The close relation between these two reactions can also be observed when the reaction is carried out under low carbon monoxide pressures. Under such conditions, the product of transfer hydrogenolysis is accompanied by the product of H-transfer formylation, as a result of the competition between the pathways.

Experimental Section

General Procedure of Transfer Hydrogenolysis of Organohalides. In a typical example, a mixture of 8 mL of CH_3CN/Me_2SO (1:1), 50 mg (0.03 mmol) of $Pd(PPh_3)_4$, 400 mg (1.4 mmol) of tribenzylamine, 157 mg (1.0 mmol) of bromobenzene, and 0.4 mL of PMHS were placed under nitrogen atmosphere in a sealed reaction vessel, stirred magnetically, and heated on an oil bath at 110 ± 1 °C. After 18 h the reaction mixture was cooled to room temperature and diluted with acetonitrile to 10 mL, and benzene (59 mg, 0.75 mmol; 75% yield) was determined by GLC in the crude filtered solution.

Isolation of nonvolatile products was achieved by the addition of 1:1 mixture of 1 N HCl and ether, followed by filtration of the precipitated catalyst, tribenzylamine salt, and polymer. The aqueous layer was then extracted with ether. After removal of the ether, the residue contained mostly the desired product, which was finally purified by distillation or chromatography.

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Some Observations on *N*-Chlorosuccinimide Halogenations. A New Bromination Technique

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Although there has been recent controversy concerning the nature of the chain-carrying radicals in *N*-bromosuccinimide (NBS) brominations,[1-3] it now seems clear that most of the data are consistent with competing succinimidyl radical (S·) and Br· chains, with no conclusive evidence for participation of two electronic states of S·.[1h,2c-e]

In unreactive media, CH_2Cl_2, $CHCl_3$, and hydrocarbons containing only primary and secondary C–H bonds, quite clean S· chains can be observed in the presence of olefins which lack allylic C–H bonds and act as halogen atom traps, but in more reactive media Br· chains become increasingly difficult to suppress.[4]

Much less information is available on the chain carriers in *N*-chlorosuccinimide reactions, although, a priori the high rate of Cl· reactions compared to Br· might lead one to expect that they would be much more difficult to suppress.[5] We here report some of our observations on this reagent.

Reaction Rates. Some comparisons of rates of photoinduced decompositon of NCS in methylene chloride and chloroform under varying conditions are listed in Table I. Although they represent single points, they are representative of a larger number of runs, and the differences

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