is quite possible that a structure such as **5** is not even an energy minimum on the reaction surface, making it virtually impossible to trap. In this extreme, the conversion of **9** to **10** might be written as follows.[16] A theoretical investigation of the rearrangement surface would be instructive.

Experimental Section

NMR spectra were recorded on Varian T-60 or A-60 spectrometers. Polystyrene calibrated IR spectra were taken on a Beckman Acculab 6 instrument. High-resolution mass measurements were made at the University of Florida. Analytical and preparative thin-layer chromatography employed Merck Silica Gel 60 PF-254 + 366 in 0.25- and 1.0-mm layers.

9,9-Dibromobicyclo[6.1.0]nona-2,4,6-triene (6).[17] To a well-stirred mixture of 48.5 g of bromoform (0.192 mol), 10.0 g of 1,3,5,7-cyclooctatetraene (0.096 mol), 0.10 g of triethylbenzylammonium chloride, and 0.20 mL of ethanol, 24 mL of 50% aqueous sodium hydroxide was added over a 10-min period while cooling the mixture in a water bath. The mixture was stirred overnight with cooling. After the addition of 200 mL of water, the mixture was extracted thrice with 50-mL portions of dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered through glass wool. The dichloromethane was removed under vacuum, followed by the removal of the excess cyclooctatetraene and bromoform by distillation at 0.4 mmHg (room temperature). The residue was chromatographed (silica gel/petroleum ether), resulting in 8.5 g of **6** (32%).

Reaction of 6 with Methyllithium. To an ice cold solution of 2.01 g of **6** (7.61 mmol) in 15 mL of anhydrous ether was added 9.12 mmol of methyllithium (2 M in ether) over a 20-min period. After an additional 30 min at 0 °C, 30 mL of water was added. The organic layer was separated and the aqueous layer was washed with additional ether. After drying the combined extracts, the ether was removed under vacuum on the rotary evaporator. Distillation of the residue resulted in 0.32 g of indene [42 °C (0.8 mmHg), 36%].

Reaction of 6 with *n*-Butyllithium. A flask containing 1.12 g of **6** (4.1 mmol) and 10 mL of dry THF was cooled to −78 °C in a dry ice–acetone bath. A dry nitrogen atmosphere was maintained on the system. To this was added 6.9 mL of 1.58 M *n*-butyllithium (4.4 mmol) over a 15-min period. The temperature was maintained between −75 and −70 °C. The solution was stirred for an additional period of 45 min. After allowing the solution to warm to room temperatures 60 mL of water was added. The mixture was extracted with two 30-mL portions of petroleum ether. The organic extracts were dried over $MgSO_4$ and the solvent was removed under slight vacuum. The residue, 0.569 g, was diluted to 3 mL with $CDCl_3$. A 0.6-mL aliquot of this solution was added to 0.016 g of toluene in an NMR tube. Integration of the indene CH_2 and the toluene CH_3 gave an *area* ratio of 3:9.5. From this it was calculated that indene was produced in this reaction in a yield of 10%.

2,3:6,7-Dibenzo-9,9-dibromobicyclo[6.1.0]nona-2,4,6-triene (7).[17] A 1-L three-neck flask was equipped with a mechanical stirrer, reflux condenser, and a dropping funnel and flushed with nitrogen. To this was added 5.3 g of *sym*-dibenzocyclooctatetraene (26 mmol), 528 g of bromoform (2.09 mol), 2 mL of ethanol, and 1.0 g of triethylbenzylammonium chloride. The solution was warmed to 40 °C and 300 mL of 50% aqueous NaOH was added very slowly over a 10-h period with stirring. The temperature was maintained at 40–45 °C. The mixture was then stirred at room temperature for an additional 15 h. Water (200 mL) was then added and the lower organic layer was removed. The aqueous layer was washed twice with 100 mL of dichloromethane. The combined organic extracts were dried over $MgSO_4$ and filtered through glass wool. The dichloromethane was removed under vacuum using a rotary evaporator. Most of the bromoform was removed by vacuum distillation. The residue was chromatographed through a large alumina column (petroleum ether) to remove polymer. The remaining bromoform (and tetrabromoethylene) was removed by additional vacuum distillation. This residue was chromatographed through silica gel (1 × 40 cm, petroleum ether). After ca. 550 mL of solvent eluted, three 50-mL fractions were collected. The first contained mostly starting material, but the second and third contained starting material and **7** in 1:1 and 1:3 ratios, respectively. The last two fractions were subjected to preparative thin-layer chromatography (1.0 mm silica gel, 5% CH_2Cl_2/petroleum ether). A total of 0.238 g of **7** was isolated (2.4% conversion). In addition, 1.56 g of *sym*-dibenzocyclooctatetraene was recovered. For **7**: mp 198–201 °C; IR (KBr pellet) ν_{max} 3100 (w), 3065 (w), 3055 (w), 3025 (w), 3000 (w), 1491 (m), 1440 (m), 1396 (m), 765 (s), 574 (m), and 498 cm^{-1} (m); NMR ($CDCl_3$) δ 3.20 (s, 2 H, cyclopropyl), 6.66 (s, 2 H, olefinic), 7.13 (m, 6 H, aromatic), and 7.67 (m, 2 H, aromatic); high-resolution mass spectrum *m/e* 373.9321 (M), 375.9280 (M + 2), 377.9279 (M + 4) [calcd for $C_{16}H_{12}Br_2$: 373.9305, 375.9285, and 377.9264, respectively].

Reaction of 7 with Methyllithium. To a solution of 0.179 g of **7** (0.477 mmol) in 5 mL of dry THF was added 0.85 mL of 1.77 M methyllithium (0.477 mmol) at −5 °C over a 2-min period. The solution was stirred for 60 min at −5 °C. The solution was allowed to warm to room temperature and 20 mL of water was added. The solution was extracted with three 30-mL portions of dichloromethane. After drying over $MgSO_4$ the solvent was removed under vacuum. The residue was subjected to thin-layer chromatography. An NMR spectrum of the leading band was shown to be that of 2,3-benzofluorene[9] (0.036 g, 35%). The sample was recrystallized from chloroform with cooling in a freezer: mp 192–198 °C.

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Registry No. 6, 70813-87-5; **7**, 70813-88-6; 1,3,5,7-cyclooctatetraene, 629-20-9; indene, 95-13-6; *sym*-dibenzocyclooctatetraene, 262-89-5; 2,3-benzofluorene, 243-17-4.

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[16] The conversion of 9 to indene represents an "electron pusher's delight." Considering the high degree of unsaturation in 9 and the necessity of at least one ring opening, one ring closure and one hydrogen shift, a number of other less attractive mechanisms can be proposed.

[17] The general procedure of M. Makosza and M. Fedorynski, *Synth. Commun.*, 3, 305 (1973), was followed.

Catalytic Reduction of Trifluoroacetic Acid under Mild Conditions

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It has been previously recognized that activated carbonyl compounds, such as α-keto esters[1] or trifluoromethyl ketones,[2] can be hydrogenated more readily than their nonactivated derivatives. Similar behavior has, however, not yet been observed for activated carboxylic acids. Previous studies[3] have indicated that trifluoroacetic acid can only be reduced to 2,2,2-trifluoroethanol in the presence of rhenium blacks under rather vigorous conditions [207 °C (300 atm)]. Higher perfluoroalkanoic acids can be reduced under somewhat milder conditions

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[1] F. Fleck, A. Rossi, M. Hinder, and H. Schinz, *Helv. Chim. Acta*, **33**, 130 (1950).

[2] R. G. Jones, *J. Am. Chem. Soc.*, **70**, 695 (1948).

[3] H. Smith Broadbent, G. C. Cambell, W. J. Bartley, and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959).

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Table I. Reduction of Trifluoroacetic Acid with Various Catalysts

catalyst[a]	$k_0 \times 10^5$, mol/s·g catalyst
0.1 g of 5% Rh/C	7.6
0.1 g of 5% Rh/Al_2O_3[b]	0.7
0.05 g of Rh black	3.1
0.05 g of Ir black[c]	7.6
0.05 g of $Rh_2O_3 \cdot 5H_2O$	9.5

[a] 1.9 g of CF_3COOH, 11.2 atm of H_2, 113 °C. [b] About 10-min induction period. [c] About 22-min induction period.

[110–200 °C (40–400 atm)] over a supported ruthenium catalyst.[4]

We have now demonstrated that neat trifluoroacetic acid can be reduced in the liquid phase under very mild conditions [50–150 °C (4–12 atm)] to 2,2,2-trifluoroethanol in the presence of a rhodium or iridium catalyst. In about 2–3 h 90% yields can be obtained.

Initial rates of reduction were determined from the slopes of the concentration–time plots. These were derived from the observed pressure drops. No deviation from linearity appeared until about 30% conversion. This indicates that the initial rates are independent of the bulk concentration of trifluoroacetic acid (zero order).

The reaction rate increases with catalyst concentration and reaches a maximum at about 5 wt %. This suggests that at catalyst concentrations higher than ~5% the reaction rate is controlled by the diffusion of hydrogen to the catalyst surface.

The hydrogen pressure dependence was investigated at 73 °C for 2.5 wt % catalyst concentration. For these conditions the initial rate between 6 and 12 atm can approximately be expressed as: $r_0 = 3.8 \times 10^{-7} P^{0.81}$ mol s^{-1}.

An Arrhenius plot between 59 and 82 °C (2.5 wt % catalyst concentration, 11.5 atm of H_2) gives an apparent activation energy of about 8.2 kcal/mol. At higher temperatures there is no further increase of the initial rate constant, perhaps due to decreasing hydrogen solubility in the reaction solution. Various other rhodium and iridium catalysts were also found to be effective for the reduction of trifluoroacetic acid (Table I). The rate of hydrogenation of perfluoropropionic and perfluorobutyric acids at comparable reaction conditions is about 20 times lower.

These results represent the first example of an easy preparation of 2,2,2-trifluoroethanol from trifluoroacetic acid. Furthermore, our data strongly suggest that perfluorocarboxylic acids should be used only with caution as solvents for liquid-phase hydrogenations over platinum metal catalysts since they are directly reducible.

Experimental Section

Chemicals. Highest purity trifluoroacetic acid (PCR Research Chemicals, Inc. redistilled and iron free) and commercially available catalysts (Strem Chemicals, Inc., Alfa) were used in all hydrogenation reactions. All organic chemicals were analyzed for purity by gas chromatography (Porapak QS column) prior to use.

Hydrogenation Procedure. The hydrogenation reactions were carried out in thick-wall glass reactors attached to the metal line and to the pressure gauge (0–20 atm). The volume of the whole system, including the reactor, was 0.206 L. The acid and an appropriate amount of catalyst were charged into the reactor. After degassing, the reaction mixture was pressurized with hydrogen in a constant temperature oil bath. The contents of the reactor were stirred with a magnetic stirrer. The course of the reaction was followed by the pressure decrease. The products were analyzed by GC (Porapak QS column), using pentafluorobenzene as an internal standard.

Registry No. Trifluoroacetic acid, 76-05-1; 2,2,2-trifluoroethanol, 75-89-8.

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(4) German Patent 1 944 381, September 2, 1969.

Reactions of Trinitrotoluenes with Sodium Borohydride in a Phase Transfer Catalytic System

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Aromatic mononitro compounds are not attacked by sodium borohydride under mild conditions, and under rigorous conditions the reactions afford azo and azoxy compounds.[1,2] With *m*-dinitrobenzene and 1,3,5-trinitrobenzene, the aromatic ring is reduced.[3,4] However, the reaction of *o*-dinitrobenzene with sodium borohydride yields nitrobenzene and benzofurazan in low yield.[5]

It is known that the nitro group on the meta position of 2,3,4- and 2,4,5-trinitrotoluene is readily replaced by nucleophiles.[6] During the production of 2,4,6-trinitrotoluene about 5% of the crude product comprises unsymmetrical isomers, principally the 2,3,4- and 2,4,5-trinitrotoluenes, which are commonly removed by treating the crude trinitro product with aqueous sodium sulfite. The unsymmetrical trinitro isomers are converted into the water-soluble sodium 2,4-dinitrotoluene-3- and -5-sulfonates.[7]

Investigations for the conversion of both 2,3,4- and 2,4,5-trinitrotoluenes to 2,4-dinitrotoluene are of obvious interest because the dinitrotoluene can be nitrated further to yield symmetrical 2,4,6-trinitrotoluene. Thus, the reactions of these trinitrotoluenes with sodium borohydride were investigated.

Results and Discussion

The reaction of 2,4,5-trinitrotoluene with sodium borohydride was carried out in diglyme under a nitrogen atmosphere at room temperature (23–24 °C). Samples were taken at 15-min time intervals and treated with dilute aqueous HCl solution. Products were extracted with CH_2Cl_2 and analyzed using a high-pressure liquid chromatograph (LC). The results show that the reaction gives 2,4-dinitrobenzene at a slow rate.

Recently phase-transfer catalysis has been recognized as a general and versatile technique applicable to many organic syntheses. The technique appeared as a method for overcoming problems of mutual solubility as well as offering the potential for activation of anions.[8] Thus an investigation on the reaction of trinitrotoluene with sodium borohydride in the presence of a phase-transfer catalyst was initiated. The two-phase systems consisted of trinitrotoluene in methylene chloride[9] and an aqueous solution of sodium borohydride with a small amount of ethylhexadecyldimethylammonium bromide (EHDMABr). The two-phase system was vigorously stirred or shaken in a separatory funnel at room temperature. The products

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[†] Abstracted in part from M.S. Thesis of S. T. Attarwala, Polytechnic Institute of New York, 1979.