Table I. Attempted Catalytic Hydrogenation of Cyclohexene Using Tulupov's Catalysts

Rxn	"Catalyst"	Solvent	Temp, °C	H_2 pressure, psia	Rxn time, h	Pressure drop, psi
1	Ni(II) stearate	Hexanes	~23	37	48	0
2	Ni(II) stearate	Hexanes	60	38	60	0
3	$NiCl_2$	Ethanol	~23	45	37	0
4	$NiCl_2 \cdot 6H_2O$	Ethanol	~23	47	43	0
5	$NiCl_2$/stearic acid[2]	Ethanol	~23	45	36	0
6	$NiCl_2 \cdot 6H_2O$/stearic acid	Ethanol	~23	35	24	0
7	Cu(II) stearate	Isobutyl alcohol	50	38	28	0
8	$CoCl_2$	Ethanol	~23	46	67	0
9	$CoCl_2$/stearic acid	Ethanol	~23	47	36	0
10	Ni(II) stearate[a]	Hexanes	~23	49	42	0

[a] The olefin used was norbornene.

cyclohexene, had an area less than 0.1% of the cyclohexene peak area.

Discussion

We have been unable to reproduce Tulupov's reported reactions or catalyst solubilities. Since both $NiCl_2$ and stearic acid are quite soluble in ethanol, the reported solubility may be due to impure Ni(II) stearate contaminated with the compounds from which it is made. It does take extensive washing to remove these.

It is more difficult to explain our failure to hydrogenate cyclohexene. Obviously, neither the salts nor their precursors showed any catalytic activity. Since Tulupov observed reactivity with a variety of salts, and we with none, the place to look for the explanation is in those compounds common to all systems: the sodium stearate and cyclohexene. The use of two different batches of sodium stearate from two different manufacturers greatly reduces the probability that there was an inhibitor present. Likewise, use of a second olefin (norbornene, rxn 10) with the same results reduces the possibility of an inhibitor being present in the reactant. It is possible that something is present in Tulupov's stearic acid which is causing the reaction. Having been unable to obtain samples of catalyst from Tulupov, we are not able to investigate this aspect of the problem further. In any event, it is quite clear that all is not well with the reported use of transition metal stearate salts as homogeneous catalysts for olefin hydrogenation.

Experimental Section

Melting points were taken on a Mel-Temp apparatus and were uncorrected. Analytical gas chromatography utilized a Varian Aerograph Model 1400 instrument equipped with a flame ionization detector and using a 0.125 in. × 7 ft 5% SE-30 on 60–80 mesh Chromosorb W column. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ethanol was dried by refluxing over magnesium and distillation under dry nitrogen onto molecular sieves (3A). Hexanes and isobutyl alcohol were dried over molecular sieves (3A).

Metal Stearates. Sodium stearate (13.5 g, Fischer) was dissolved in 900 ml of water and the mixture was heated and stirred until the solution was clear. The hot soap solution then was poured with vigorous stirring onto a solution containing 6 g of $NiSO_4 \cdot 6H_2O$ or 4 g of $CuSO_4$ in 600 ml of warm water. The precipitates were washed by decantation with water and dried in the air at 115 °C for 15 h. Nickel stearate was also made from the sodium stearate prepared from stearic acid (Emery) and sodium hydroxide.

Nickel(II) stearate: green solid; mp 100 °C; yield 84%. Anal. Calcd for $NiC_{36}H_{70}O_4$: C, 69.09; H, 11.34. Found: C, 69.77; H, 10.70.

Copper(II) stearate: light blue solid; mp 106–108 °C; yield 80%. Anal. Calcd for $CuC_{36}H_{70}O_4$: C, 68.56; H, 11.21. Found: C, 68.51; H, 11.66.

Attempted Catalytic Hydrogenation of Cyclohexene. To a stearate salt (~1 g) in ~110 ml of warm solvent was added 12 g of cyclohexene (Eastman Kodak). The solution was poured into a 500-ml hydrogenation bottle and the bottle was then mounted on a low-pressure Parr hydrogenator. Air was removed from the system by alternatively filling the system with hydrogen to 35 psi and venting it at least three times. The solution was shaken at ca. 3 atm hydrogen pressure. Similar procedure was also carried out for the hydrogenation of bicyclo[2.2.1]-2-heptene (Aldrich). The pressure of the system was monitored.

Acknowledgment. We are grateful to the Energy Research and Development Administration for support of this work.

Registry No.—Sodium stearate, 822-16-2; nickel(II) stearate, 2223-95-2; copper(II) stearate, 660-60-6; cyclohexene, 110-83-8; bicyclo[2.2.1]-2-heptene, 498-66-8.

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An Aberrant Rearrangement in the Reaction of 1,2-Dibromo-3,3-difluorocyclopropene with Anthracene[1]

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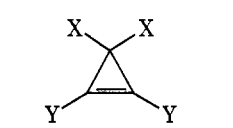
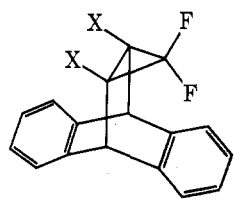
In an attempt to develop a rational synthesis of the as yet unknown, but potentially useful synthon 3,3-difluorocyclopropene (**1a**), we have examined the reaction of anthracene with 1,2-dibromo-3,3-difluorocyclopropene (**1b**).[2] It was anticipated that the [4 + 2] cycloadduct **2** would permit a classical approach to the elusive[3] cyclopropene (**1a**) via reductive

debromination and subsequent thermal cycloreversion of the dibenzohomobarrelene derivative **3**. We now report that contrary to expectations the reaction of anthracene with **1b** affords a rearranged adduct of a type previously unobserved in cycloadditions with tetrahalocyclopropenes.

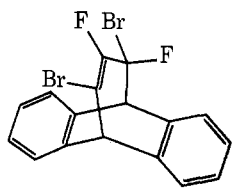
The reaction of anthracene with excess **1b** was carried out in carbon tetrachloride solution in a sealed tube at 120–130 °C until complete consumption (NMR) of anthracene (7 days). Chromatography and recrystallization of the reaction residue afforded a crystalline 1:1 adduct (40%) whose ^{19}F NMR spectrum immediately suggested a rearranged structure. Cycloadducts of **1b** typically show well-separated (15–40 ppm) AB quartets in their ^{19}F spectra centered at around 110–120 ppm (upfield from external $CFCl_3$).[4] By contrast the anthracence–**1b** adduct showed only a fluorine singlet at δ 47.0! The proton spectrum of this adduct consisted of two one-proton singlets at δ 5.27 and 5.11 for the bridgehead hydrogens, in addition to complex aromatic absorptions, suggesting an unsymmetrical structure for the adduct.



1a, Y = H; X = F
b, Y = Br; X = F



2, X = Br
3, X = H



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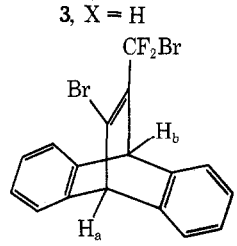

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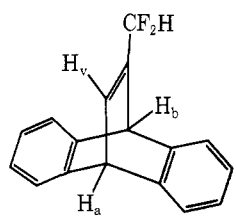

6

While the above spectral results clearly eliminate adduct **2** from further consideration, the ^{19}F data are equally inconsistent with the most obvious rearranged structure **4** which would be derived by electrocyclic ring opening with 1,2-fluorine migration. This mode of ring opening has been frequently observed for tetrahalocyclopropene adducts where at least one of the geminal halogens is chlorine[4,5] or bromine.[4a] However, owing to the low ionization propensity of the C–F bond all of the previous cycloadducts of 3,3-difluoro-substituted cyclopropenes have been observed to be thermally stable to electrocyclic ring-opening reactions.[4,6]

An alternative mode of ring opening involving rupture of one of the peripheral cyclopropane bonds of **2** could presumably lead to the dibenzobarralene derivative **5**, a structure consistent with the observation of a singlet in the fluorine spectrum. That **5** is indeed the structure of this unusual adduct is supported by spectral data for the tri-*n*-butyltin hydride debrominated adduct **6**. The 100-MHz ^1H NMR spectrum of **6** revealed a triplet centered at δ 6.1 with a coupling constant (J_{HF}) of 56 Hz while the fluorine spectrum showed a doublet of doublets at δ 117.1, J_{HF} = 56 and 4 Hz. These results are in complete keeping with the presence of a $-CF_2H$ grouping. The smaller doublet splitting (J_{HF} = 4 Hz) is assigned to allylic fluorine coupling to the vinyl proton (H_v) which is unfortunately obscured in the aromatic region of the proton spectrum. The bridgehead protons H_a and H_b are observed as a pair of doublets, $J_{H_aH_v}$ = 6 Hz and $J_{H_bH_v}$ = 2 Hz, at 5.16 and 5.30, respectively.[7] Final corroboration of structure is provided by the mass spectrum of **6**, which shows a base peak at *m/e* 203 corresponding to loss of the CF_2H radical.

Although diradical rupture of a peripheral cyclopropane bond of **2** followed by 1,2-bromine shift provides an adequate rationale for formation of **5**, we cannot at present rule out the possible rearrangement of **1b** to 1,3-dibromo-3,3-difluoropropyne under the forcing conditions of the reaction.[8] To our knowledge, however, such a rearrangement of a tetrahalocyclopropene, while not unreasonable, is unprecedented.

Experimental Section

Proton magnetic resonance spectra were recorded on Varian A-60A and Varian XL-100 spectrometers; chemical shifts are reported in parts per million downfield from internal Me_4Si. All ^{19}F NMR spectra were recorded on the XL-100 instrument at 94.1 MHz with chemical shifts reported in parts per million upfield from external $CFCl_3$. Infrared spectra were determined on a Perkin-Elmer Model 137 instrument as KBr wafers. Mass spectra were recorded on an AEI-MS 30 spectrometer at 70 eV. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga.

1,2-Dibromo-3,3-difluorocyclopropene (**1b**) was prepared by a slight modification of the published procedure[2] using freshly sublimed antimony trifluoride.

Reaction of Anthracene with 1b. Anthracene (0.890 g, 5.00 mmol), 1,2-dibromo-3,3-difluorocyclopropene (**1b**, 1.75 g, 7.47 mmol), and 25 ml of carbon tetrachloride were placed in a Fischer-Porter tube which was capped and heated at 120 °C for 4 days. NMR analysis of the reaction mixture at this point indicated ca. 50% conversion of the anthracene. Additional **1b** (1.0 g) was added, the tube recapped, and heating resumed at 130 °C. After 3 days at this temperature the anthracene was completely consumed. The dark reaction mixture was concentrated and chromatographed on silica gel with benzene as elutant. Concentration of the first fraction gave 1.94 g (94%) of a oily brown solid which on crystallization from hexane afforded 0.823 g (39.9%) of hard brown crystals. Recrystallization from hexane afforded analytically pure **5**: mp 94–97 °C ν 1616, 1456, 1308, 1276, 1120, 990, 959, 864, 820, 742, 622 cm^{-1}; mass spectrum *m/e* (rel intensity) 414 (3.1), 412 (6.7), 410 (3.5), 334 (49.5), 332 (50.5), 252 (82.6), 202 (100), 200 (74.5), 179 (65.5), 150 (78.9), 127 (30.3), 111 (44.8); δ ($CDCl_3$) 7.5–6.8 (m, 8, aromatic), 5.27 (s, 1, H_b), 5.11 (s, 1, H_a); δ_{CFCl_3}($CDCl_3$) 47.01 (s, $-CF_2Br$).

Anal. Calcd for $C_{17}H_{10}Br_2F_2$: C, 49.55; H, 2.45; Br, 38.79. Found: C, 49.65; H, 2.51; Br, 38.96.

7-Difluoromethyldibenzotricyclo[2.2.2]octa-2,5,7-triene (6). A magnetically stirred mixture of tri-*n*-butyltin hydride (2.24 g, 7.68 mmol) and **5** (1.06 g, 2.56 mmol) containing a catalytic amount of di-*tert*-butyl peroxide was heated at 90 °C for 15 h. Chromatography of the reaction mixture on neutral alumina using benzene–hexane (1:1 v/v) as eluent followed by recrystallization from hexane afforded 0.245 g (37.3%) of a yellow solid. A second recrystallization from hexane–methanol gave 0.137 g of **6**, mp 137.5–138 °C as white flakes homogeneous to thin layer chromatography: ν 1640, 1452, 1368, 1320, 1288, 1059, 994, 738 cm^{-1}; mass spectrum *m/e* (rel intensity) 254 (54.6) 233 (6.6), 203 (100), 202 (63.5), 178 (12.7), 152 (3.2), 151 (3.3), 102 (5.0), 101 (8.5), 87 (3.2), 76 (3.2); δ (CCl_4, 100 MHz), 7.44–6.84 (m, 9, aromatic, H_v), 6.22 (t, J_{HF} = 56 Hz, $-CF_2H$), 5.30 (d, $J_{H_bH_v}$ = 2 Hz, 1, H_b), 5.16 (d, $J_{H_aH_v}$ = 6 Hz, 1, H_a), δ_{CFCl_3}($CDCl_3$) 117.1 (dd, J_{HF} = 56, J_{FH_v} = 4 Hz, 1, $-CF_2-$).

Anal. Calcd for $C_{17}H_{12}F_2$: C, 80.30; H, 4.76. Found: C, 80.40; H, 4.75.

Acknowledgment. The authors express their appreciation to the National Science Foundation for financial support, and to Professor W. S. Brey and Dr. L. W. Jaques for their assistance in recording the 100-MHz and ^{19}F NMR spectra.

Registry No.—**1b**, 6262-46-0; **5**, 59790-60-2; **6**, 59790-61-3; anthracene, 120-12-7.

References and Notes

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(7) (a) With exception of the broad triplet for the $-CF_2H$ proton the pattern of the proton spectrum and the coupling constants for the bridgehead protons H_a, H_b were almost identical with that observed for the model system 7-chlorodibenzobicyclo[2.2.2]octa-2,5,7-triene[7b] in deuteriobenzene [δ (C_6D_6, 60 MHz) 7.17–6.56 (m, 8, aromatic), 6.40 (dd, J = 2.3, 6.5 Hz, 1, vinyl), 4.82 (d, J = 2.3 Hz, 1, bridgehead), 4.50 (d, J = 6.5 Hz, 1, bridgehead); δ ($CDCl_3$) 7.38–6.75 (m, 8, aromatic), 6.68 (dd, J = 2.2, 6.4 Hz, 1, vinyl), 4.94 (overlapping doublets, 2, bridgeheads)]. (b) Prepared by the method of S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 5679 (1965).
(8) As pointed out by a referee, an alternative ionic pathway for rearrangement of **2** involving carbon–bromine ionization with simulaneous electrocyclic cleavage of a peripheral cyclopropane ring bond cannot be excluded on the basis of the limited data. While this mechanistic possibility should not be ignored, the lack of literature precedent for cyclopropyl to allyl conversions of bridgehead halides and the energetically unfavorable accumulation of positive charge at the $-CF_2$ carbon render it suspect in comparison with the postulated diradical mode of ring opening.

Carbonyl Insertion Reactions of Ethyl α-Trimethylsilyldiazoacetate. An Improved Route to Diazoacetate Aldol Products

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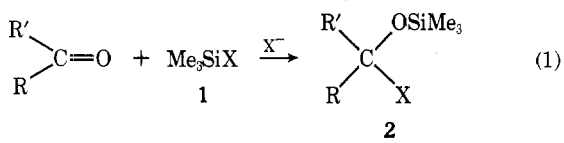
Interest in the carbonyl insertion[1] chemistry of organosilicon compounds has only recently developed in spite of the central role the carbonyl function plays in organic synthesis.[2–4] Of particular interest to us has been the generality of the anion-initiated carbonyl insertion process illustrated below (eq 1). To date we have demonstrated that the reaction of

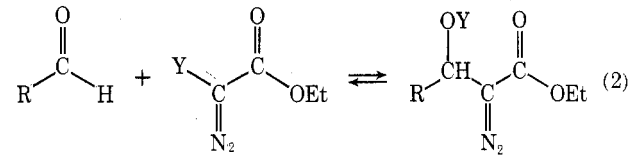


(1)

1 2

trimethylsilyl cyanide (1, X = CN) with an extensive variety of aldehydes and ketones is readily initiated by both cyanide and fluoride ion.[2a,b] The only other silicon pseudohalide which has been found to react in an analogous fashion has been trimethylsilyl azide (1, X = N_3) which forms aldehyde adducts 2 (X = N_3; R′ = H) in excellent yields.[2b] Recently, we have found that thiosilanes 1 (X = SR), in the presence of anionic initiators, will also form aldehyde adducts 2 (X = SR) in excellent yields.[4a] As has recently been demonstrated, these organosilane–carbonyl adducts are valuable intermediates in chemical synthesis.[5,6]

We now wish to report that the carbonyl insertion reactions of ethyl α-trimethylsilyldiazoacetate (**3a**) can be effected (eq 2), and that the reaction is subject to specific anion initiation. Wenkert and McPherson have shown[7] that ethyl diazoacetate adds to aldehydes in the presence of a catalytic amount of sodium hydroxide. Unfortunately, the reaction affords an equilibrium mixture of the aldol product **4b** and starting



(2)

3 4

a, Y = $SiMe_3$; b, Y = H; c, Y = $SnMe_3$

materials where adduct formation is quite unfavorable for some aldehydes and most ketones. Based upon crude thermodynamic approximations, it was predicted that the silyldiazoacetate addition reactions (**3a** → **4a**) should be *more* exothermic than the analogous diazoacetate addition processes (**3b** → **4b**). These predictions have now been verified. The addition of **3a**[8] to both aromatic and aliphatic aldehydes occurs exothermically at room temperature in nearly quantitative yield when catalyzed by the potassium cyanide–18-crown-6 complex.[2b] For sensitive substrates (i.e., the isobutyraldehyde adduct), which were unstable to the heat generated by the reaction, solvents such as chloroform were used to moderate the temperature. Removal of the solvent at room temperature afforded essentially pure aldol adduct **4a**. Analytical samples were obtained by column chromatography on Florisil, *but partial hydrolysis of* **4a** *to the corresponding alcohol* **4b** *was usually observed.* Table I compares the chromatographed yields of the silyldiazo ester insertions with Wenkert's protiodiazo ester reactions where possible. Not only are the yields consistently higher, but the reaction conditions are nonaqueous and essentially neutral. Preliminary results indicate that even tigaldehyde survives the reaction to afford a moderate yield of the 1,2 adduct; no 1,4 adduct could be detected.

Less reactive carbonyl systems such as acetophenone, cyclohexanone, 3-pentanone, and 3-methyl-3-penten-2-one all failed to produce detectable adducts (by NMR). In hope of achieving a still more favorable equilibrium, the analogous reactions of ethyl α-trimethylstannyldiazoacetate[9] (**3c**) were examined, but 3-pentanone was inert to the reagent and hexanal was slowly polymerized.[10] Since the completion of our work, Schollkopf has shown that **3** (Y = Li, MgX) will add to both aldehydes and ketones under very carefully controlled conditions to afford the corresponding aldol-type products in high and moderate yields, respectively.[11] Both thermal and Lewis acid catalyzed reaction conditions failed to generate the aldol adducts **4** from either the silyl or stannyldiazo esters **3a** or **3c**. This is in marked contrast to related carbonyl insertions by other organosilanes.[2–4]

The presumed mode of catalysis by anionic initiators such as cyanide ion (Scheme I) involves the generation of catalytic amount of diazo ester enolate **5** via either of the processes illustrated in eq 3 and 4 followed by carbonyl addition and subsequent silicon transfer steps to regenerate **5**. It is pre-

Table I. Carbonyl Addition Reactions of 3a (Eq 1)

RCH=O	Registry no.	% yield of 4a[a,b]	% yield of 4b[c]
$CH_3(CH_2)_4CHO$	66-25-1	86 (63:37)	68 (R = C_6H_{13})
$(CH_3)_2CHCHO$	78-84-2	93 (76:24)	80
C_6H_5CHO	100-52-7	86 (84:16)	60
p-ClC_6H_4CHO	104-88-1	93 (78:22)	25
p-$CH_3OC_6H_4CHO$	123-11-5	83 (100:0)	
$CH_3CH{=}\overset{CH_3}{\overset{\vert}{C}}CHO$	497-05-0	44 (100:0)	

[a] Calculated on isolated yields of adduct. [b] Values in parentheses refer to the ration of 4a:4b isolated from chromatography. Prior to chromatography only 4a was present. [c] Yields for the base-catalyzed addition of **3b** to illustrated aldehydes (ref 7).