still too low for proton abstraction from the diazonium ion.[6]

On the other hand, there is a qualitative parallel between the products of nitrous acid and nitroprusside deaminations. Thus, with nitrous acid, cyclohexylamine gave 68% cyclohexanol and 20% cyclohexene,[7] and 2-octylamine gave 20% 1- and 2-octene and 27% 2-octanol.[8] There are differences in product *ratios*, however, which indicate that hydroxide ion is involved in the nitroprusside deamination. The higher ratio of 1- to 2-butanol with nitroprusside (5:1 *vs.* 2:1[9]) is evidence for an S_N2 attack of hydroxide ion on the 1-butyldiazonium ion. Alternatively, the possibility exists that all the products are formed directly from an amine–nitroprusside complex.

The first step in these nitrosations almost certainly involves addition of the amine to the coordinated nitric oxide.[10]

$$RNH_2 + Fe(CN)_5NO^{2-} \rightleftharpoons RNH_2NOFe(CN)_5^{2-}$$

The lower basicity of aromatic amines is consistent with their inertness to nitroprusside.

The resulting complex might react directly with a molecule of amine, with displacement of the *N*-nitrosamine.

$$\underset{1}{RNH_2NOFe(CN)_5^{2-}} + RNH_2 \longrightarrow RNHNO + H^+ + RNH_2Fe(CN)_5^{3-}$$

$$RNHNO \longrightarrow RN{\equiv}N^+{:}OH^- \longrightarrow R^+ \longrightarrow \text{products}$$

Another possibility involves loss of water from 1, leading to a diazonium ion complex which would then react with a molecule of amine.

$$\underset{1}{RNH_2NOFe(CN)_5^{2-}} \xrightarrow{-H_2O} RN{\equiv}N{-}Fe(CN)_5^{2-} \xrightarrow{RNH_2} RNH_2Fe(CN)_5^{3-} + RN{\equiv}N^+ \longrightarrow R^+ \longrightarrow \text{products}$$

The intermediates apparently are too short-lived to be detected by conventional spectrophotometry.

When nitroprusside is allowed to react with amines in presence of air, small amounts of oxidized products are formed, together with the compounds listed above. These materials (Table I) are produced only in the presence of *both* nitroprusside and air, and their yields increase when the reactions are carried out under pure oxygen. Control experiments show that they are *not* produced by reaction of the corresponding alcohols with nitroprusside. Autoxidation of an intermediate nitroprusside–amine complex seems to be a reasonable pathway for these oxidative deaminations.

Experimental Section[11]

Materials.—Allylamine, benzylamine, 1-butylamine, cyclohexylamine, diethylamine, and 2-octylamine were obtained from the usual commercial sources and were distilled prior to use. Sodium nitroprusside dihydrate (Fisher) was used without further purification.

Reaction of Nitroprusside with Amines.—The reaction of cyclohexylamine (under nitrogen) and benzylamine (under oxygen) with nitroprusside will be described in detail. Procedure and product identification were similar in all other cases.

A solution of sodium nitroprusside dihydrate (24.0 g, 0.084 mol) in 90 ml of water was flushed with nitrogen and was added dropwise, under nitrogen, to a deaerated solution of cyclohexylamine (1.4 g, 0.014 mol) and sodium carbonate (0.75 g, 0.007 mol) in 30 ml of water. An immediate, but slow, evolution of gas occurred. The reaction mixture was stirred for *ca.* 10 hr, during which a small amount of brown solid gradually precipitated. Potassium carbonate (*ca.* 20 g) was then added (to salt out organic materials) and the mixture extracted with five 40-ml portions of ether. The ethereal extract was dried (magnesium sulfate) and the ether taken off. There remained 0.9 g of a pale yellow oil, the infrared spectrum of which was identical with that of cyclohexanol. When the oil was submitted to vpc (135°, 6 ft × 0.25 in., 20% Carbowax 20M on 80–100 Chromosorb P column, He pressure 18 psi), two peaks were observed. Retention times corresponded to cyclohexene (9%) and cyclohexanol (120%), respectively.

A solution of sodium nitroprusside dihydrate (25.5 g, 0.086 mol) in 100 ml of water was added dropwise to a solution of benzylamine (1.5 g, 0.014 mol) and sodium carbonate (1.5 g, 0.014 mol) in 45 ml of water. The solution was stirred under oxygen for *ca.* 24 hr. Potassium carbonate (*ca.* 20 g) was then added and the mixture extracted with five 20-ml portions of ether. The ethereal extract was dried (magnesium sulfate) and the ether stripped off. There remained 1.1 g of an orange oil. When the oil was submitted to preparative vpc (125°, 20 ft × 0.375 in., 30% SE-30 on 60–80 Chromosorb W column, He pressure 20 psi), two peaks were observed, the retention times and infrared spectra of which corresponded to benzonitrile (40%) and benzyl alcohol (116%), respectively.

Registry No.—Nitroprusside, 1784-20-9; benzylamine, 100-46-9; allylamine, 107-11-9; cyclohexylamine, 108-91-8; 2-octylamine, 693-16-3; 1-butylamine, 109-73-9; diethylamine, 109-89-7.

Acknowledgment.—This work was partially supported by the Petroleum Research Fund (Grant 1316-Gl), administered by the American Chemical Society.

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[6] No carbon-deuterated benzyl alcohol was obtained from reaction of benzylamine with nitroprusside in D_2O, indicating that phenyldiazomethane is not an intermediate in the deamination.

[7] H. Söll in Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, XI/2, G. Thieme Verlag, Stuttgart, 1958, p 133 ff.

[8] R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

[9] F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932).

[10] C-Nitrosations of ketones with nitroprusside have been observed; *cf.* J. H. Swinehart, *Coord. Chem. Rev.*, **2**, 387 (1967).

[11] Infrared spectra were determined with a Beckman IR-10 instrument. Vpc determinations were performed on a Varian Aerograph 1700 instrument; vpc peak areas were calibrated with standards.

Reaction of Perfluoroalkyl Halides with Grignard Reagents

Elizabeth S. Lo*[1]

Research Department, Thiokol Chemical Corporation,
Trenton, New Jersey 08607

Received July 1, 1970

The reactions of perfluorocarbon halides (Cl, Br or I) with Grignard reagents reported in the literature[2-6] were mainly for the syntheses of fluorocarbon Grignard reagents. These alkyl or aryl exchange reactions were carried out at low temperatures (0 to −70°), because of the thermal instability of the fluorocarbon Grignard reagents. The present investigation was a study of this reaction at higher temperatures (>25°).

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[1] Address correspondence to author at 102 Maclean Circle, Princeton, N. J. 08540.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 3423 (1952).

[3] O. R. Pierce, A. F. Meiners, and E. T. McBee, *J. Amer. Chem. Soc.*, **75**, 2516 (1953).

[4] R. J. DePasquale and C. Tamborski, *J. Organometal. Chem.*, **13**, 273 (1968).

[5] W. L. Respress and C. Tamborski, *ibid.*, **11**, 619 (1968).

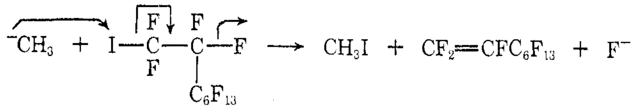
[6] R. J. DePasquale, *ibid.*, **15**, 233 (1968).

Haszeldine[2] reported that the reflux of heptafluoropropylmagnesium chloride in butyl ether gave mainly C_3F_7H (76%) and C_3F_6 (6%). The present study indicated that the addition of methylmagnesium chloride to hot linear perfluoroalkyl iodides, $CF_3(CF_2)_nI$ ($n = 7, 9$) gave essentially terminal olefins and some internal olefins. Small amounts of condensation products were also present as indicated by gas chromatography. The amount of 1-hydroperfluoroalkanes $CF_3(CF_2)_nH$, if present, was small.

The reaction of CH_3MgCl with $I(CF_2)_4I$ at 60° gave perfluorobutadiene as the major product. A small amount of perfluorobutene-1 was also present indicating that some fluorination of the iodo compound took place. When $CF_3CFClCFClCF_3$ was allowed to react with Grignard reagent, 2-butenes were the major products, not the butadiene. In this case the dechlorination reaction was preferred. There was, however, some terminal olefin present as shown by the infrared analysis. A similar reaction was run with ICF_2CF_2I.[7] The major product was tetrafluoroethylene. The reaction of perfluoroheptyl bromide with methylmagnesium chloride at 70° gave heptene-1 and heptenes-2.[8]

The formation of terminal olefins by the present method has not been reported previously. Up to now terminal perfluoroalkenes (>C_3) were prepared by the pyrolysis[9] of the sodium salts of the corresponding carboxylic acids. The lack of 1-hydroperfluoroalkanes among the major products in the present study may indicate the absence of a regular Grignard intermediate $CF_3(CF_2)_nCF_2MgX$.[10] Thus the formation of terminal olefins may be best explained by an E2 elimination mechanism.[11] The internal olefins were the result of isomerization[12] of the terminal olefins by the fluoride ions present in the reaction media.

$$CH_3MgCl \longrightarrow {}^-CH_3 + {}^+MgCl$$



$${}^-CH_3 + I-\underset{F}{\overset{F}{C}}-\underset{C_6F_{13}}{\overset{F}{C}}-F \longrightarrow CH_3I + CF_2{=}CFC_6F_{13} + F^-$$

A similar dehalofluorination reaction of perfluoroalkyl halides reported in the literature[13] was the exothermic reaction of C_3F_7I with lithium at −74°, which gave essentially C_3F_6 and only a trace of C_3F_7H. No information concerning such reactions with a longer alkyl chain was described.

Experimental Section

Spectra.—The ^{19}F nmr spectra were obtained with a 60-MHz Varian DP-60 spectrometer. The gas chromatographic data were obtained with a Nester–Faust "Prepkro" unit using a column (0.25 in. × 24 ft) packed with 30% SF-96 on Chromosorb P. Infrared spectra were run on a Beckman IR-2 spectrophotometer and also on a Perkin–Elmer Model 137 double-beam spectrophotometer. A Bendix time-of-flight mass spectrometer (Model 12-101) was employed to record the mass spectra at 70 eV.

Materials.—Methylmagnesium chloride in tetrahydrofuran (THF) (2.9 mol/l.) was purchased from Fisher Scientific Co. Perfluoroalkyl iodides and diiodides were purchased from Thiokol Chemical Corp. These iodides were linear as shown by ^{19}F nmr analysis. Perfluoroheptyl bromide and perfluoro-2,3-dichlorobutane were purchased from Peninsular ChemResearch Co.

Reaction of Perfluoroalkyl Iodides with Methylmagnesium Chloride.—In a typical experiment a round-bottom flask was equipped with a stirrer, a thermometer, a dropping funnel, a dry nitrogen inlet, and a vapor trap connected to a condenser. The dropping funnel and the condenser were capped with Drierite tubes. Perfluoroalkyl iodides (109 g), containing $C_8F_{17}I$ (85%) and $C_{10}F_{21}I$ (15%), were placed in the flask and heated to 60°. The heat was turned off before the addition of CH_3MgCl (0.445 mol) in THF (150 ml). The dropping rate of the Grignard reagent was such that the exotherm of the reaction maintained the solution temperature at 70–75°. The distillate (95 ml), collected in the vapor trap in 1 hr, was drained into an ice-cooled separatory funnel. Upon standing a colorless lower layer was separated, washed with water, dried ($MgSO_4$), and fractionated. The fraction (52 g) boiling at 100–115° was further fractionated by gas chromatography at 105°. The major peaks were collected and identified by mass, infrared, and ^{19}F nmr spectroscopy. The following perfluoro compounds were found: octene-1 (63%), *trans*-octene-2 (20%), decene-1 (8%), three other decenes (5%), and two unknown peaks (4%).

The residue in the flask was a light brown, thick solution. Water (100 ml) was added to dissolve some of the inorganic salts and the mixture was then filtered. The filtrate separated into two layers. The upper aqueous layer gave a positive iodine test. The lower layer (23.5 g) was dried ($MgSO_4$). Infrared analysis indicated the presence of –CH, –CF=CF– [5.6 (w) and 5.8 μ (m)], and –CF groups. Gas chromatography showed that the major peak was that of the solvent. Numerous small peaks were those found in the distillate and the unreacted alkyl iodides. A few minor new peaks, at longer retention times, were also present indicating some higher molecular weight fractions.

Reaction of Perfluoroheptyl Bromide with Methylmagnesium Chloride.—Perfluoroheptyl bromide (44.9 g, 0.1 mol) was heated to 65° in a flask equipped as described above. The heat was turned off before the addition of CH_3MgCl (0.29 mol in 100 ml of THF). During the 0.5-hr addition, the solution temperature was maintained at 68–70° by the exotherm of the reaction. Colorless distillate was collected in the vapor trap. It was drained into a separatory funnel and cooled by Dry Ice. The lower fluorocarbon layer (14.5 g) was analyzed by gas chromatography and infrared. The following perfluoro components were identified: *n*-heptene-1 (50.2%), *trans*-heptene-2[8] (20.6%), *cis*-heptene-2[8] (6.7%), CH_3Br (4.3%), and THF (6.9%); other small peaks composed 12.3%. The residue in the flask was a dark liquid containing a substantial amount of inorganic salts. Infrared analysis indicated the presence of –COH, –CH, and –CF=CF– (5.75 and 5.85 μ). Gas chromatographic analysis indicated the presence of THF, unreacted $C_7F_{15}Br$, and some higher condensation products.

Reaction of Perfluoroalkylene Diiodides with Methylmagnesium Chloride.—In this experiment, the equipment was slightly modified. A Dry Ice trap was connected to the top of the condenser. A sample of perfluoro telomer diiodide (100 g) containing the following diiodides, $I(CF_2)_4I$ (47%), $I(CF_2)_6I$ (21%), and higher diiodides (32%), was heated to 50°. The heat was turned off before the addition of the Grignard reagent. Methylmagnesium chloride (1.16 *M* in 400 ml of THF) was added rapidly (1.5 hr) to the diiodides. The colorless liquid (21.5 g) collected in the Dry Ice trap was fractionated by gas chromatography at 0°. Five peaks were collected and identified by infrared as $CF_3CF_2CF{=}CF_2$[14] (5.5%), $CF_2{=}CFCF{=}CF_2$[14] (45.5%), perfluorocyclohexene (12.5%), CH_3Cl (8.9%), CH_3I (11.9%), and four other small peaks (total 16.7%).

Reaction of Perfluoro-2,3-dichlorobutane with Methylmagnesium Chloride.—Methylmagnesium chloride (0.87 mol) in 300 ml of THF was placed in a 1-l. flask. $CF_3CFClCFClCF_3$ (81 g) was added to the Grignard reagent with stirring. The exotherm of the reaction raised the solution temperature from 25 to 60° during the 50-min addition period. The temperature dropped

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[7] E. S. Lo, unpublished data.

[8] E. S. Lo, J. D. Readio, and H. Iserson, *J. Org. Chem.*, **35**, 2051 (1970).

[9] J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Amer. Chem. Soc.*, **75**, 4525 (1953).

[10] H. Gilman and R. G. Jones, *ibid.*, **65**, 2037 (1943).

[11] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1962, p 478.

[12] D. J. Burton and F. E. Herkes, *J. Org. Chem.*, **33**, 1854 (1968), and the references cited therein.

[13] J. A. Beel, H. C. Clark, and D. Whyman, *J. Chem. Soc.*, 4423 (1962).

[14] Identified by infrared spectrum according to R. N. Haszedine, *ibid.*, 4423 (1952).

almost immediately upon completion of the addition. Heat was applied to maintain the temperature at 60° for 0.5 hr. The lower fluorocarbon layer (50 g) collected in the Dry Ice trap showed a major peak and a few minor peaks in the gas chromatographic analysis. Infrared analysis indicated the presence of terminal olefin (5.6 μ, weak) and internal olefins (5.75 and 5.85 μ). The major component (80%) was identified as a mixture of *cis*- and *trans*-butene-2 (5.75 μ).[14]

Registry No.—Perfluoroheptyl bromide, 375-88-2; perfluoro-2,3-dichlorobutane, 355-20-4; methylmagnesium chloride, 676-58-4.

Acknowledgments.—The author is indebted to Dr. J. D. Readio for the instrumental analyses and Mr. J. Krushnowski for laboratory assistance.

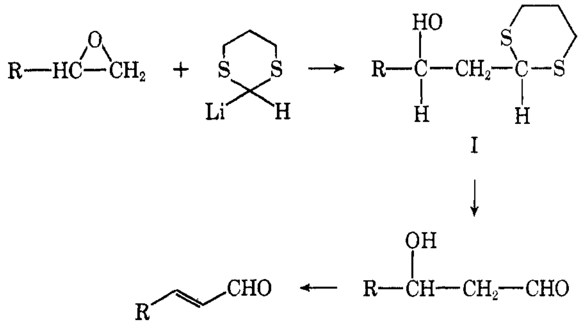
An Improved Aldehyde Synthesis from 1,3-Dithianes

E. Vedejs* and P. L. Fuchs

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received July 16, 1970

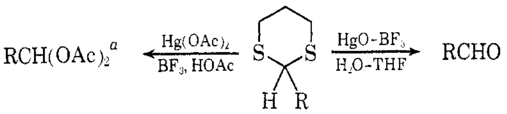
As part of a synthetic project, we required a general route to substituted acroleins. The dithiane method seemed to hold considerable promise in this direction since 2-(hydroxyalkyl)dithianes are readily available from epoxides,[1] and hydrolysis followed by dehydration should result in the desired products.



However, it became apparent that hydrolysis of I would pose difficulties. A thorough search of the literature for experimental details revealed only one example of hydrolysis of a 2-substituted 1,3-dithiane to an aldehyde, 2-phenyl-1,3-dithiane to benzaldehyde.[2,3] Accordingly, we examined the hydrolysis of some simple 2-alkyl-1,3-dithianes under conditions which hydrolyze 2,2-dialkyl-1,3-dithianes to ketones. Disappointingly low yields (20–40%) of heptanal were obtained from 2-*n*-hexyl-1,3-dithiane using $HgCl_2$ with HgO or $CdCO_3$ in refluxing aqueous methanol. Other published conditions[1a] such as the *N*-bromosuccinimide method or the silver nitrate method were even less successful and initial experiments failed to produce any aldehyde (nmr analysis) from 2-isopropyl-1,3-dithiane. Poor material balance was the rule in the various experiments, and in the mercuric chloride reactions, 30–40% of the starting material was lost, presumably due to the formation of insoluble mercury derivatives.

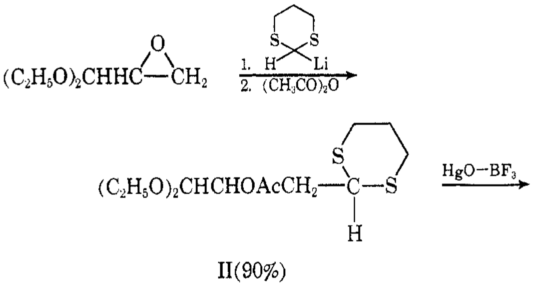
After screening a number of potential reagents,[4] we examined the combination of mercuric acetate and boron trifluoride etherate. Remarkably, a solution of this reagent in acetic acid effected the transacetalization of several 2-substituted 1,3-dithianes into the known acetaldiacetates (Table I) within a few minutes at room temperature. Under similar conditions, red mercuric oxide and boron trifluoride etherate in aqueous tetrahydrofuran hydrolyzed 1,3-dithianes to the corresponding aldehydes[5] in high yield. This method proved to be especially advantageous in the case of II, which was prepared from the epoxide of acrolein diethyl acetal.[6] The $HgO-BF_3$ reagent afforded the aldehyde in 80% yield, while $HgCl_2$ served only to destroy starting material. In addition to demonstrating the mildness of our condi-

Table I



Entry no.	Yield of acetaldiacetate, %	R	Registry no.	Yield of aldehyde, %
1	76[b]	C_6H_5-	5425-44-5	90[c]
2	73[b]	$C_6H_5CH{=}CH-$	26958-41-8	86[c]
3	78[c]	*i*-C_3H_7-	6007-25-6	78[e]
4		*n*-$C_6H_{13}-$	26958-42-9	60[d]
5		$(C_2H_5O)_2CHCHOAcCH_2-$		80[c]
6		$C_6H_5OCOC_6H_{10}-$	26958-43-0	84[c, f]

[a] E. Späth, *Monatsh. Chem.*, **36**, 29 (1915). [b] Yield of recrystallized product. [c] Yield of crude product, homogeneous by nmr. [d] Yield of pure aldehyde isolated by distillation. [e] Yield of aldehyde determined by glpc. [f] 1-Benzoyloxycyclohexanecarboxaldehyde.



II(90%)

$$\underset{\text{III}(80\%)}{(C_2H_5O)_2CHCHOAcCH_2CHO} \xrightarrow{\text{DBU}} \underset{(77\%)}{(C_2H_5O)_2CHCH{=}CHCHO}$$

DBU = 1,5-diazabicyclo[5.4.0]undec-5-ene

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(1) (a) D. Seebach, *Synthesis*, 17 (1969); (b) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969); E. J. Corey and D. Seebach, *ibid.*, **4**, 1075, 1077 (1965).

(2) D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).

(3) Hydrolysis of a 2-alkyl-1,3-dithiane ($HgCl_2$, yield unspecified) is mentioned briefly by J. A. Marshall and H. Roebke, *Tetrahedron Lett.*, 1555 (1970). Transacetalization of a 2-alkyl-1,3,5-trithiane to the methoxyacetal is also reported in ref 1 without experimental details.

(4) Salts of Pb(III), Zn(II), and Tl(I) were tried without success. Copper(II) acetate with BF_3 produced some aldehyde (25% in the case of 2-*n*-hexyl-1,3-dithiane), but 50% of the starting material could not be accounted for.

(5) Aldehydes were also isolated from the reaction of dithianes with $Hg(OAc)_2-BF_3$ in dry *tert*-butyl alcohol, presumably *via* fragmentation of the corresponding *tert*-butyloxonium ion to aldehyde and isobutylene. Thus, cinnamaldehyde (78%) and cinnamaldehyde acetaldiacetate (13%) were produced from the corresponding dithiane, 2 mol of mercuric acetate, and 2 mol of boron trifluoride etherate in 200 mol of dry *tert*-butyl alcohol.

(6) D. I. Weisblat, B. J. Magerlein, D. R. Myers, A. R. Hanze, E. I. Fairburn, and S. T. Rolfson, *J. Amer. Chem. Soc.*, **75**, 5893 (1953).