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ON THE PREPARATION OF 2-HALO ALKYL SUBSTITUTED 1,3-DIOXOLANES AND 1,3-DIOXANES

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SUMMARY

Several methods for the preparation of 2-perfluoromethyl-substituted 1,3-dioxolanes and 1,3-dioxanes were tried. The method of Nerdel for the preparation of 1,3-dioxolanes, making use of the condensation between carbonyl compounds and oxiranes, was found to be suitable for perhalogenated ketones and aldehydes, and may even be extended to oxetanes, affording 2-perhaloalkylated 1,3-dioxanes.

The yield of the cyclic acetals drops with increasing substitution.

INTRODUCTION

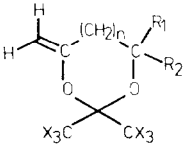
Neither 1,3-dioxolanes nor 1,3-dioxanes may be prepared by direct condensation between a perhalocarbonyl compound and respectively 1,2- and 1,3-diols. Although the reaction is rapid and mostly exothermic up to the hemi-acetal stage, further ring closure normally is impossible.

RESULTS AND DISCUSSION

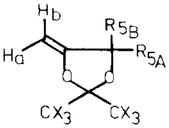
H. Simmons and D. Wiley [1] prepared dichlorotetrafluoroacetonates in good yield by the condensation of dichlorotetrafluoroacetone with ethylene chlorhydrin in alkaline medium

TABLE 1

YIELDS OF 1,3-DIOXOLANES AND 1,3-DIOXANES FROM ALKYNYLCARBINOLS WITH PERHALOKETONES.



with $(ClF_2C)_2CO$	n = 0			n = 1	
R_1,R_2	H,H	H,Me	Me,Me	H,H	Me,Me
Yield	85	70	58	50,0	~ 5
B.p. °C	154	50/18 mm	60/18 mm	77/20 mm	GC
Entry	I	II	III	IV	V

with $(CF_3)_2CO$	n = 0			
R_1,R_2	H,H	H,Me	Me,Me	
Yield	68	40	25	
B.p. °C	110	118	40/18 mm	
Entry	VI	VII	VIII	

(potassium carbonate in pentane), characterized by a nucleophilic substitution of the chlorine atom in the hemi acetal stage.[*] We tried now to apply the condensation of hexafluoroacetone (HFA) on ethylene chlorhydrine but the yield of the desired 2,2-bis-CF_3-1,3-dioxolane was only 26.0 %.

A simpler procedure, starting from ethylene glycol itself, failed.[*] It consisted in treating the rapidly formed hemiacetal (by absorbtion of the theoretical amount of HFA in the diol at room temperature), followed by treatment of the reaction mixture with tosyl chloride in pyridine or potassium carbonate in pentane. Only a very minor amount of the 1,3-dioxolane was formed (NMR).

Another possibility for the preparation of 2-perhaloalkyl-1,3-dioxolanes and corresponding 1,3-dioxanes consists in the mercuric oxide catalysed condensation of the appropriate ketones or aldehydes with ynols, as described by H.E. Simmons and D.W. Wiley [1] for the reaction of dichlorotetrafluoroacetone on propargyl alcohol and 3-butyn-1-ol. We find however that the yield drops rapidly with increasing branching of the carbinols[**] using hexafluoroacetone instead of dichlorotetrafluoroacetone (Table 1). Moreover, a subsequent catalytic reduction of the alkylidene acetals with either Pd or Pt-catalyst, mostly failed [except for I and II (Table 1)]. During the hydrogenation of 2,2-bis-(chlorodifluoro)-4-methylidene-1,3-dioxolane (IV) 2'-oxobutyl-bis-chlorodifluoromethyl-carbinol was formed, the structure being confirmed by ^{1}H-NMR, I.R. and M.S. In an attempt to find a possible mechanism, we examined the possibility of a hydrogenolysis, followed by an aldol condensation as depicted in Chart I.

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[*] We recently have extended their method in using monotosylated diols [2] as the starting material, and the latter procedure is especially suitable if one deals with two different hydroxy functions (e.g. primary and secondary in nature), thus rendering the preparation of the monotosylate attractive.

[**] The ethynylcarbinols used by us were commercially available [FLUKA] whereas the propargylcarbinols were prepared by the Reformatzky reaction of propargyl bromide with aldehydes or ketones [3].

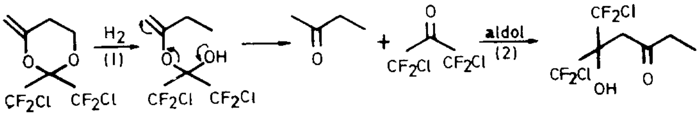

CHART I

However, 2-butanone brought in reaction together with dichlorotetrafluoroacetone under the same reaction oonditions, did not afforded the expected carbinol. As a possible alternative we propose the reaction to be involved in a [1,3]-sigmatropic (antarafacial) reaction on the catalyst surface after hydrogenolysis as shown in Chart II.

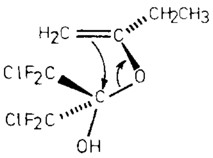

CHART II

One of the best procedures for the preparation of fluorinated dioxolanes was found to be an extension of a procedure described by F. Nerdel [4] et al., where they describe a preparation of 1,3-dioxolanes by condensation of aldehydes and oxiranes, using tetraethylammonium bromide as the catalyst.

Because perhaloketones are much more reactive than nonhalogenated carbonyl compounds, the reaction was also successful for branched oxiranes and even oxetanes, affording 1,3-dioxanes.[*] For the latter, somewhat more drastic reaction conditions are required.

The results are presented in Table 2.

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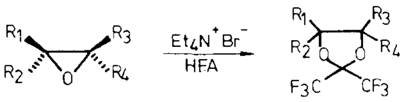
[*] All oxiranes were prepared using classical procedures [7], the oxetanes were synthetized by the methods of R. Meltzer [8] and S. Searles [9] et al.

TABLE 2

CONDENSATION OF HEXAFLUORACETONE ON OXIRANES (AFFORDING DIOXOLANES) AND ON OXETANES (AFFORDING DIOXANES) ACCORDING TO NERDEL'S EXTENDED METHOD



R_1R_2	Me,H	Me,H	Me,H	Ph,H	Ph,Me	CH_2Cl,H
R_3R_4	H,H	Me,H	H,Me	H,Me	H,H	H,H
Yield	70.0	35.0	60.0	63.0 (a)	20.0 (b)	90.0
B.p. °C	112	123	120	59/0.3 mm	105/15 mm	40/12 mm

	R_1=Me $R_2=R_3=R_4=R_5=R_6$=H	$R_3=R_4$=Me $R_1=R_2=R_5=R_6$=H
Yield	40.0	75.0
B.p. °C	130	145 (c)

[a] Mainly trans, accompained by < 10 % cis.

[b] Main product is hydratropaldehyde, see text.

[c] M.p. 18°C.

The yield was found to drop with increasing branching, and trifluoroacetaldehyde gives the best results, (almost 80% with chloromethyloxirane or with methyloxirane). With 2-methyl-2-phenyloxirane the main product however was hydrotropaldehyde (NMR, IR), presumably formed by a rearrangement similar to that proposed by Blackett [5] et al.

Under no circumstances did 1,1,1-trifluoroacetone yield any dioxolane by our method, polymerization of the ketone being the only occuring reaction.

It is interesting to note that the reaction occurs with retention of configuration, thus cis-dimethyloxirane gives exclusively cis-2-bis-CF_3-4,5-diMe-1,3-dioxolane. The reaction is also "kinetically controlled". The ratio of the cis-, and trans-isomers of 2-CF_3-4-CH_2Cl-1,3-dioxolane is 1/4 (prepared from trifluoroacetaldehyde). The cis isomer being the most stable [6], is also the less abundant in this condensation. Attemps to epimerise the reaction mixture to the equilibrium state failed, even under drastic conditions (10% CF_3COOH at elevated temperatures). These statements indeed prove the kinetic nature of the dioxolane formation under the given conditions.

In a further extension, it has been possible to react oxiranes with ethyl trifluoroacetate, which afforded with 2-chloromethyloxirane the two isomers of 2-CF_3-2-OEt-4-CH_2Cl-1,3-dioxolane in a 1/1 ratio.

A draw-back of the generality of the method concerning the preparation of substituted 1,3-dioxanes, is the difficulty to prepare oxetanes [10].

We tried therefore to prepare the dioxanes by the Grignard reaction of trifluoromethylmagnesium iodide on 2-methoxy-4,6-diMe-1,3-dioxane, which was hoped even to react stereospecifically [11]. However the Grignard reagent is very difficult to prepare [12] and the formation of it, failed in our hands. Formation of the reagent by an exchange procedure [13] using isopropylmagnesium bromide was also unsuccessful and although the use of phenylmagnesium bromide did indicate a possible exchange, reaction with the dioxane did not proceed to the expected 2-CF_3-4,6-diMe-1,3-dioxane.

Presumably trifluoromethylmagnesium iodide was too unstable under the employed reaction conditions.

EXPERIMENTAL

Preparation of 4-methylidene-1,3-dioxolanes and dioxanes

2-bis-(chlorodifluoro)-4-metnylidene-1,3-dioxolane

(Table 1, entry 1)

3.0 g propargyl alcohol (FLUKA) are carefully mixed under cooling in a 50 ml round-bottemed flask with the stoechiometric amount of $(CF_2Cl)_2CO$; 0.2 g HgO are added and the reaction mixture is kept at 35°C for three hours. Distillation gives the expected dioxolane in a 85.0 % yield. B.p. : 154 °C. (Literature [1]: b.p. 51-53°/13 mm.). ^1H-NMR-data: see table 3. C: 28,3 % Found: 29,9 ; H: 0,70 % Found: 0,77 ; F: 29,0 % Found: 29,6.

2-bis-(chlorodifluoro)-4-methylidene-5-methyl-1,3-dioxolane (nc)

(Table 1, entry II)

Following exactly the same procedure 1.4 g 1-butyn-3-ol (FLUKA) are mixed with 3.5 g $(CF_2Cl)_2CO$ yielding the expected dioxolane. B.p. 50 °C/ 18 mm. Yield: 70.0 %. ^1H-NMR-data: see table 3. C: 31,3 % Found: 30,9 ; H: 2,23 % Found: 2,07 ; F: 28,3% Found: 28.8.

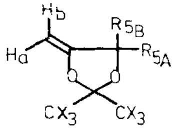
All other 4-methylidene dioxolanes and dioxanes are prepared following the same method. The NMR-data are listed in Table 3. Experimental data are to be found in Table 1.

Reduction of 2-bis-(chlorodifluoro)-4-methylidene-1,3-dioxolane

1 g dioxolane is dissolved in 25 ml methanol. Some 5 % Pt/C catalyst is added and the reduction is carried out at 60 psi, at room temperature. After the uptake of one equivalent of H_2, the reduction was interupted and methanol was distilled off. GC on

TABLE 3

SHIFT- AND J-VALUES OF SOME 2-BIS-(TRIHALOMETHYL)-4-METHYLIDENE-1,3-DIOXOLANES IN CCl_4 (TMS INTERNAL) [(a)]



CX_3	, R_{5A}	, R_{5B}	(CH_3)	H_{5A}	H_{5B}	H_a	H_b	$^2J_{H_aH_b}$	$^4J_{H_aH5_A}$	$^4J_{H_aH5_B}$	$^4J_{H_bH5_A}$	$^4J_{H_bH5_B}$	$^4J_{H5CH_3}$
CF_2Cl	H	H	-	4.82	4.82	4.76	4.19	-3.75	-2.60	-2.04	-1.75	-1.75	-
CF_2Cl	Me	H	1.53	5.09	-	4.67	4.09	-3.32	-2.20	-	-1.90	-	6.2
CF_2Cl	Me	Me	1.57	-	-	4.56	4.02	-3.00	-	-	-	-	-
CF_3	H	H	-	4.75	4.75	4.75	4.21	-	-	-	-	-	-
CF_3	Me	H	1.52	4.96	-	4.68	4.12	-3.20	-2.20	-	-1.80	-	5.2

[a] The extracted spectral parameters were checked by simulation (SIMEQ 16/II).

carbowax: 1 peak,: identified as 2'-oxobutyl-bis-(chlorodifluoromethyl)-carbinol.

^{1}H-NMR: $\delta_{H_{4'}}$ = 1.10 (t) ; $\delta_{H_{3'}}$ = 2.55(q) ; $\delta_{H_{1'}}$ = 2.94(s)
δOH = 7.15 (s).

IR: ν_{OH} = 3.280 cm^{-1} ; $\nu_{C=O}$ = 1725 cm^{-1}.

M.S: $M^{\cdot +}$: absent ; $^m/e$ = 241(M^+-Et) (30) ;
$^m/e$ = 235(M^+-Cl) (10) $^m/e$ = 221(241 - HF) (5) ;
$^m/e$ = 85(CF_2Cl^+) ($\underline{100}$).

Preparation of oxiranes

2-Me-oxirane was commercially available (FLUKA).
The other oxiranes were prepared by stirring together the appropriate alkene with NBS in an aqueous suspension and by heating the formed bromohydrin in aqueous alkaline solution [7].

Preparation of oxetanes

3,3-diMe-oxetane was prepared by pyrolysis of 2-oxo-5,5-diMe-1,3-dioxane formed by reaction of 2,2-diMe-1,3-propanediol with diethyl carbonate as has been described by S. Searles [9] et al. Yield: 60.0 % B.p.: 80°C.
2-Me-oxetane resulted from heating the chloroacetate of 2,4-butanediol in aqueous alkaline solution. The chloroacetate was formed by reaction of the diol with acetylchloride following procedures of Meltzer [8] and Searles [9]; yield: 31.0 % ; b.p.: 60°C.

Preparation of 1,3-dioxolanes

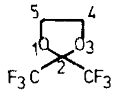
2-bis-CF$_3$-4-Me-1,3-dioxolane (nc)

(Table 4, Entry I)

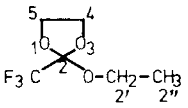
2.6 g 3-Me-oxirane and 0.15 g $Et_4N^+Br^-$ are weighted in a pressure tube in which 7.4 g HFA are concensed with cooling at -70°. The tube is heated at 100°C for 2 hours. Distillation gives a

TABLE 4

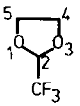
SHIFT-VALUES (IN P.P.M. FROM TMS INTERNAL) OF SOME FLUORINATED DIOXOLANES, 10 % vol IN CCl_4.



Compounds I to VII



Compounds VIII & IX



Compounds X to XIII

Entry		H_2	$H_{2'A}$	$H_{2'B}$	$H_{2''}$	H_4	$H_{4'A}$	$H_{4'B}$	H_{5c}	H_{5t}	Me_4	Me_5	
I	2-bis-CF_3-4-Me-1,3-dioxolane	-	-	-	-	4.57	-	-	4.36	3.67	1.42	-	-
II	2-bis-CF_3-cis-4,5-diMe- "	-	-	-	-	4.65	-	-	4.65	-	1.27	1.27	-
III	" trans " " "	-	-	-	-	3.96	-	-	-	3.96	1.27	1.27	-
IV	2-bis-CF_3-cis-4-Me-5ϕ- "	-	-	-	-	4.90	-	-	5.60	-	0.92	-	7.28
V	" trans " "	-	-	-	-	4.18	-	-	-	4.71	1.37	-	7.26
VI	2-bis-CF_3-4,5-Me,ϕ- "	-	-	-	-	-	-	-	4.36	4.36	1.72	-	7.23
VII	2-bis-CF_3-4-CH_2Cl-1,3-dioxolane	-	-	-	-	4.71	3.78	3.58	4.52	4.14	-	-	-
VIII	2-CF_3-OEt-4-CH_2Cl-1,3-dioxol. Isomer A	-	3.70	3.67	1.26	4.55	3.73	3.41	4.44	3.94	-	-	-
IX	" " " B		3.76	3.73	1.27	4.58	3.71	3.64	4.30	4.06	-	-	-
X	2-CF_3-4 CH_3-1,3-dioxolane cis	5.09	-	-	-	4.25	-	-	4.11	3.51	1.36	-	-
XI	" " trans	5.17	-	-	-	4.41	-	-	4.17	3.48	1.32	-	-
XII	2-CF_3-4-CH_2Cl- " cis	5.18	-	-	-	4.56	3.45	3.70	4.00	4.24	-	-	-
XIII	" " trans	5.25	-	-	-	5.07	3.47	3.62	4.26	4.01	-	-	-

J-VALUES (IN Hz) OF SOME FLUORINATED 1,3-DIOXOLANES

	$^2J_{H5cH5t}$	$^2J_{H2'AH2'B}$	$^3J_{H4H5c}$	$^3J_{H4H5t}$	$^3J_{H4Me4}$	$^3J_{H4H4'A}$	$^3J_{H4H4'B}$	$^3J_{H2'H2''}$	$^4J_{H5'Me4}$	$^2J_{H4'AH4'B}$
I	7.5	—	5.75	8.9	—	—	—	—	—	—
II	—	—	6.7	—	6.5	—	—	—	0.3	—
III	—	—	—	9.25	6.2	—	—	—	0.2	—
IV	—	—	7.7	—	6.2	—	—	—	—	—
V	—	—	—	8.6	5.8	—	—	—	—	—
VI	—	—	—	—	—	—	—	—	—	—
VII	8.0	—	6.2	6.7	—	8.8	4.3	—	—	11.1
VIII	8.4	8.8	8.0	6.2	—	9.0	4.7	7.0	—	10.8
IX	8.0	9.1	6.7	7.3	—	7.1	3.9	7.0	—	11.4
X	7.60	—	5.8	8.6	6.2	—	—	—	—	—
XI	7.40	—	6.2	6.9	6.2	—	—	—	—	—
XII	8.40	—	6.4	6.4	—	9.5	4.4	—	—	10.8
XIII	8.20	—	6.4	4.5	—	8.5	4.5	—	—	10.9

colourless liquid. B.p. 112°C ; Yield: 70.0 %. ^{1}H-NMR: Table 4. C: 32,1 % Found: 32.1 ; H: 2.67 % Found: 2.71 ; F: 50.8 % Found: 51.6.

2-bis-CF$_3$-4,5-diMe-1,3-dioxolane (nc)

(Table 4, Entry II & III)

In the same way cis-resp. trans-2,3-diMe-oxirane are condensed with 7.4 g HFA. cis-dioxolane; Yield: 35.0 % ; B.p.: 123°C. C: 35.2 % Found: 34.7 ; H: 3.36 % Found: 3.21 ; F: 47.8 % Found: 48.2.

This consist in a 40:60 mixture of the cis:trans isomers, separated by GC. (Table 4 for ^{1}H-NMR data).

2-bis-CF$_3$-4-Me-5-Ø-1,3-dioxolane

(Table 4, Entry IV, V)

3.0 g β-Me-styreneoxyde are condensed, in the same way as previously described, with 3.7 g HFA. Distillation gives a colourless liquid: B.p.: 58-60°/0.3 mm. Yield: 63.0 %. GC: carbowax 120°C: 2 peaks 9:1 trans:cis. ^{1}H-NMR data in table 4. C: 48.0 % Found: 47.4 ; H: 3.3 % Found: 2.9 ; F: 38.0 % Found: 38.4.

2-bis-CF$_3$-4-Me-4-Ø-1,3-dioxolane

(Table 4, Entry VI)

6.0 g α-Me-styreneoxyde are condensed with 7.2 g HFA. Distillation gives a colourless liquid: B.p.: 95-105°C/15 mm. GC: carbowax 160°C : 2 peaks 1:3.

peak 1: 2-bis-CF$_3$-4Ø-4Me-1,3-dioxolane; ^{1}H-NMR: Table 4A & 4B. C: 48.0 % Found: 48.3 ; H: 3.3% Found: 2.8 ; F: 38.0 % Found: 38.0.

peak 2: hydratropaldehyde; ^{1}H-NMR : $\delta_{Me} = 1.37$(d) ; $\delta_{C\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix}} = 9.77$ (d) ; $\delta_{H2} = 3.48$(o) ; $\delta_{Ø} = 7.12$; $^3J_{Me,H_2} = 7.0$ Hz ; $^3J_{H_2,C\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix}} = 1.3$ Hz.

2-bis-CF_3-4-CH_2Cl-1,3-dioxolane (nc)

(Table 4, Entry VII)

9.2 g epichlorohydrine are condensed with 16 g HFA. Distillation gives a colourless liquid. B.p. 40°C/12 mm ; Yield: 90.0%. ^1H-NMR: Table 4A, 4B.

C: 27.9 % Found: 27.0 ; H: 1.93 % Found: 1.87 ;
F: 44.1 % Found: 45.0.

2-CF_3-4Me-1,3-dioxolane (nc)

(Table 4, Entry X, XI)

3 g Me-oxirane are condensed with 2 g CF_3CHO (TFA), prepared by the pyrolysis of the ethyl hemiacetal [ALDRICH] in polyphosphoric acid at 100°C. Care must be taken for the spontaneous exothermic polymerization of TFA that occurs readily above -20°C. Distillation gives a colourless liquid. B.p.: 105°C ; Yield: 75.0 %. GC carbowax 100°C: 2 peaks 1:4 cis:trans. C: 38.4 % Found: 38.2 ; H: 4.48 % Found: 4.37 ; F: 36.5 % Found: 36.2.

2-CF_3-4-CH_2Cl-1,3-dioxolane (nc)

(Table 4, Entry XII, XIII)

5.5 g epichlorohydrine are condensed with 2.5 g CF_3CHO. Distillation gives a colourless liquid. B.p.: 145-147°C ; Yield: 79.0 %. GC carbowax 130°C: 2 peaks 1:3 cis:trans. C: 31.6 % Found: 31.2 ; H: 3.16 % Found 3.24 ; F: 30.0 % Found: 29.3.

2-CF_3-2-OEt-4-CH_2Cl-1,3-dioxolane (nc)

(Table 4, Entry VIII & IX)

9.2 g epichlorohydrine are condensed in a sealed tube with 14,2 g ethyl trifluoroacetate and 0.5 g $Et_4N^+Br^-$, at 170°C during 12 hours. Distillation gives a colourless liquid: B.p.: 158-160°C. GC on QF1 at 150°C; 2 peaks 1:1 (2 isomers). Exact assignments of cis-trans isomers could not be made.
C: 38.5 % Found: 37.8 ; H: 4.58 % Found: 4.65 ; F: 26.1 % Found: 26.7.

Preparation of 2-bis-CF_3-1,3-dioxanes

2-bis-CF_3-5,5-diMe-1,3-dioxane. (nc)

(Table 2)

4.3 g 3,3-diMe-oxetane are weighed into a pressure tube together with 7.4 g HFA and 0.15 g $Et_4N^+Br^-$. The sealed tube is left at 150° for 10 hours. Distillation gives a colourless liquid: B.p. 145°C ; Yield: 75.0 %. ^{1}H-NMR: $\delta_{Me} = 1.02$; $\delta_{H_{4,6}} = 3.70$; $^5J_{H_{4,6}',F} = 0.8$ Hz.
C: 38.0 % Gound: 37.6 ; H: 3.96 % Found: 3.84 ; F: 45.2 % Found: 45.3.

2-bis-CF_3-4-Me-1,3-dioxane (nc)

(Table 2)

In the same way 3.6 g 2-Me-oxetane are brought into reaction with 8.2 g HFA. Distillation gives a colourless liquid. B.p. 130°C ; Yield: 40.0 %. NMR : $\delta_{Me} = 1.3$; $\delta_{H_{4,6}} = 4.15$; $\delta_{H5e} \simeq 1.7$; $\delta_{H_{5a}} \simeq 1.8$; $^3J_{Me,H_2} = 6.0$ Hz.
C: 35.3 % Found: 35.6 ; H: 3.36 % Found: 3.29 ; F: 47.9 % Found: 48.3.

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