

LANTHANIDE-INDUCED CONTACT SHIFTS IN POLYGLYCOLDIMETHYLETERS  
 VI. CALCULATION OF FERMI CONTACT AND DIPOLAR CONTRIBUTIONS  
 FROM THE TEMPERATURE DEPENDENCE OF THE SHIFTS<sup>\*</sup>

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In studies of lanthanide (Ln) induced shifts it is usually assumed that the shifts are of dipolar origin, possible contributions from a Fermi contact (Fc) interaction are difficult to establish. If the former mechanism predominates one expects (1) that the shifts induced by one Ln complex can be converted into those of another by multiplying them with a constant factor. Deviations from this proportionality factor are taken as evidence for the presence of Fc contributions to the observed shift. For Pr and Eu compounds Sanders and Williams (2) found a ratio of approximately 3 for the proton shifts of a few phosphates and phosphonates. However, for the <sup>31</sup>P shifts a ratio as low as 0.5 was observed, taken as evidence by them for the occurrence of Fc interactions.

DME:	CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub>
	3.3 1.6 1.6 3.3
GLYME-3:	CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub>
	3.4 2.1 2.3 2.3 2.1 3.4
GLYME-4:	CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub>
	2.9 1.8 1.9 3.0 3.0 1.9 1.8 2.9
GLYME-5:	CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub>
	2.8 1.7 1.8 2.6 2.8 2.8 2.6 1.8 1.7 2.8
GLYME-6:	CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub>
	2.9 1.7 1.6 2.6 2.7 2.6 2.6 2.7 2.6 1.8 1.7 2.9

In the figure the Pr/Eu shift ratios for a number of 1 : 1 Ln(DPM)<sub>3</sub> glyme complexes are listed. Though most ratios are approximately 3, the external and penultimate CH<sub>2</sub> groups in each glyme show lower values of about 2. In part V we have shown that the oxygen atoms that surround these groups are just the sites to which the lanthanide complex coordinates preferentially, bringing the external and penultimate CH<sub>2</sub> groups in close proximity to the lanthanide ion. Apparently there are small Fc contributions to the proton shifts for these groups, that may explain the lower shift ratios. A necessary condition for this is that the Eu<sup>3+</sup>-induced Fc shifts are of opposite sign

to and of greater magnitude than those induced by Pr<sup>3+</sup>, actually observed (3), and that for both ions the Fc shift reinforces the dipolar shift.

<sup>\*</sup> Parts I to V appeared earlier in Tetrahedron Letters, 4863 (1971), 2067 (1972), 1465 (1973), 1467 (1973), and 1471 (1973), respectively.

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Both the Fc and the dipolar shift are in first order proportional to  $1/T$ . Recently Bleaney (4) has shown that for the Pr complexes the first order contribution of the dipolar shift is equal to zero, and the second order contribution proportional to  $1/T^2$ . Hence the  $\text{Pr}^{3+}$ -induced shift,  $\delta_{\text{Pr}}$ , can generally be expressed as  $\delta_{\text{Pr}} = a/T + b/T^2$  (I), the first term representing the Fermi contact ( $\delta_{\text{Fc}}$ ) and the second term the dipolar contribution ( $\delta_{\text{Dp}}$ ). An ideal system for studying this relation is the  $\text{Pr}(\text{FOD})_3$ , DME complex, because the binding constant is high ( $10^5 \text{ l mol}^{-1}$ ) and no conformational changes are observed. In figure 1 of part III we plotted  $\delta_{\text{Pr}}$  as a function of  $1/T^2$ , neglecting the  $1/T$  Fermi contact term. Good straight lines were obtained with almost zero intercept for the  $\text{CH}_3$  protons, but with a significantly non-zero intercept for the  $\text{CH}_2$  protons ( $-2.7 \pm 0.4 \text{ ppm}$ ). Since for Pr the temperature independent paramagnetism is small the non-zero intercept for the  $\text{CH}_2$  protons points to Fc contributions to the shift. If the data are fitted to the relation I, by a quadratic least squares analysis,  $\delta_{\text{Fc}}$  and  $\delta_{\text{Dp}}$  can be determined. At  $31.5^\circ\text{C}$  it was found for the  $\text{CH}_3$  protons  $\delta_{\text{Fc}} = 0.8 \pm 0.4 \text{ ppm}$ ,  $\delta_{\text{Dp}} = -26.0 \pm 0.5 \text{ ppm}$ , and for the  $\text{CH}_2$  protons  $\delta_{\text{Fc}} = -5.0 \pm 0.5 \text{ ppm}$ ,  $\delta_{\text{Dp}} = -25.2 \pm 0.6 \text{ ppm}$ . Clearly, for the  $\text{CH}_3$  proton shifts the Fc contribution can be neglected, while about 17% of the  $\text{CH}_2$  proton shift originates from this interaction. Finally it should be noticed that the Fc contribution indeed reinforces the dipolar contribution for the  $\text{CH}_2$  proton shift, as we were forced to assume to explain the low Pr/Eu shift ratios found for these protons.

#### References

1. D.R. Crump, J.K.M. Sanders, and D.H. Williams, *Tetrahedron Letters*, 4419 (1970)
2. J.K.M. Sanders and D.H. Williams, *Tetrahedron Letters*, 2813 (1971)
3. W.B. Lewis, J.A. Jackson, J.F. Lemons, and H. Taube, *J. Chem. Phys.*, 36, 692 (1962)
4. B. Bleaney, *J. Magn. Resonance*, 8, 91 (1972)

## SYNTHESIS OF TETRA-ALKOXY- AND TETRA-ARYLOXYETHENES

BY

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Several tetra-alkoxyethenes have been synthesized from dialkoxy-monoaryl-oxymethanes by treatment with sodium hydride. The occurrence of dialkoxy carbenes as possible reaction intermediates is discussed. Best results (45–60%) were obtained with dialkoxy-mono-*p*-chlorophenoxymethanes.

Tetra-aryloxyethenes have been prepared by a similar procedure in which diaryloxymethyl chlorides were used as starting compounds.

Although tetramethoxyethene has been synthesized in several ways<sup>1,2</sup>, and its interesting properties have been thoroughly investigated<sup>3</sup>, other tetra-alkoxyethenes are scarcely known. In the literature we found only one preparation of tetraethoxyethene<sup>4</sup>, and the method used gave a very low overall yield.

Among the tetra-aryloxyethenes, less reactive but also interesting electron-rich olefines<sup>3</sup>, the only known representative is the unsubstituted tetraphenoxyethene<sup>5,6</sup>. It was first prepared by *Scheibler*<sup>5</sup> from diphenoxymethyl chloride and the strong base triphenylmethyl sodium. We found a useful method for the preparation of other diaryloxymethyl chlorides and succeeded in converting all of them into tetra-aryloxyethenes using the more readily available sodium hydride.

*Scheibler's* method cannot be used for the synthesis of tetra-alkoxyethenes because most dialkoxy-methyl chlorides decompose<sup>7</sup> even at room temperature thus:



<sup>1</sup> R. W. Hoffmann and H. Häuser, *Tetrahedron* **21**, 891 (1965); R. W. Hoffmann, *Angew. Chemie* **83**, 595 (1971).

<sup>2</sup> R. A. Olofson, S. W. Walinsky, J. P. Marino and J. L. Jernow, *J. Am. Chem. Soc.* **90**, 6554 (1968).

<sup>3</sup> R. W. Hoffmann, *Angew. Chemie* **80**, 823 (1968).

<sup>4</sup> S. M. McElvain and R. L. Clarke, *J. Am. Chem. Soc.* **69**, 2661 (1947).

<sup>5</sup> H. Scheibler and M. Debner, *J. Prakt. Chem.* [4] **7**, 60 (1958).

<sup>6</sup> R. N. McDonald and R. A. Krueger, *J. Org. Chem.* **30**, 4372 (1965).

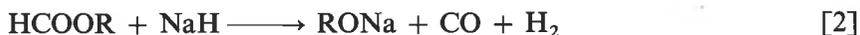
<sup>7</sup> J. W. Scheeren, *Tetrahedron Letters* **1968**, 5613.

It seemed, however, worthwhile to investigate whether tetra-alkoxyethenes could be obtained from more stable dialkoxymethyl derivatives.

Several dialkoxymethyl fluorides were treated with sodium hydride in dimethoxyethane. Generally no reaction occurred at room temperature, and on heating only decomposition products were obtained.

With naphthylsodium instead of sodium hydride the fluorides reacted even at  $-20^{\circ}$ , but due to several side reactions the reaction mixtures were rather complex; yields of tetra-alkoxyethenes were low (10% with methoxy-, 3% with ethoxy-, no yield with other alkoxy derivatives).

Better results were obtained starting with aryloxy derivatives,  $\text{HC(OR)}_2\text{OAr}$ . Those with  $\text{Ar} = p\text{-chlorophenyl}$  appeared to be especially useful in the synthesis of tetra-alkoxyethenes. After stirring several dialkoxy-mono- $p$ -chlorophenoxymethanes with sodium hydride for 10–20 hours in refluxing dimethoxyethane we isolated the corresponding tetra-alkoxyethenes in yields between 45 and 60%. Small amounts of trialkyl orthoformates were found as side products. We suppose that they originate from reactions between alkyl formates, formed by decomposition in accordance with [1], and sodium hydride<sup>8</sup> [2], followed by substitution of the aryloxy residue [3].



Tetra-alkoxyethenes are only very slowly formed from dialkoxy-monophenoxymethanes. Starting with dialkoxy-mono(2,4-dichlorophenoxy)methanes the reactions are much faster than with  $p$ -chlorophenoxy derivatives, but the amounts of side products are much larger.

As was mentioned previously, the easily available diaryloxymethyl chlorides are useful starting compounds in the synthesis of tetra-aryloxyethenes. Although triaryl orthoformates are formed as side products on treatment with sodium hydride, the chlorides are sufficiently stable to permit the isolation of the desired ethenes in yields between 40 and 70%. It appeared that in these cases fluorides,  $\text{HC(OAr)}_2\text{F}$ , or  $p$ -chlorophenoxy derivatives,  $\text{HC(OAr)}_2\text{OC}_6\text{H}_4\text{Cl-}p$ , could not be used because their reactivity towards bases is much lower than that of the corresponding aliphatic compounds.

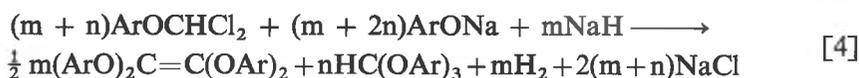
Because diaryloxymethyl chlorides have to be prepared in two steps (*via* triaryloxymethanes<sup>9</sup>) from aryl dichloromethyl ethers, it seemed

<sup>8</sup> J. C. Powers, R. Seidner and T. G. Parsons, *Tetrahedron Letters* **1965**, 1713.

<sup>9</sup> J. W. Scheeren, J. H. M. van Roy and A. P. M. van der Veek, *Rec. Trav. Chim.* **90**, 745 (1971).

that it should be possible to simplify the synthesis of tetra-aryloxyethenes by *Scheibler's* method. To this end aryl dichloromethyl ethers were treated with sodium hydride in the presence of the corresponding phenolate. It appeared that in most cases investigated tetra-aryloxyethenes were formed by this one-step procedure.

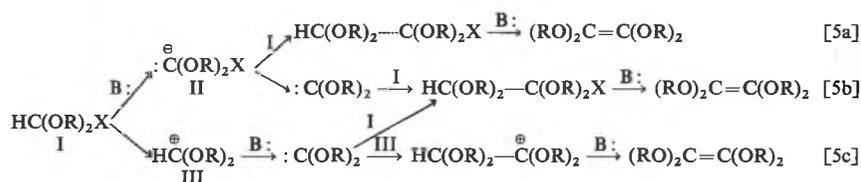
One could expect that under these circumstances aryl dichloromethyl ethers will be converted into diaryloxymethyl chlorides because they react only slowly with sodium hydride. These initially formed intermediates will be converted partly into tetra-aryloxyethenes under the influence of the base, and partly substituted further by the phenolate present giving rise to orthoformates. An overall equation may be formulated as in [4].



The yields of tetra-aryloxyethenes in this procedure are generally rather low (see experimental section). In some instances, however, they exceed the overall yields in the more laborious procedure, in which the synthesis of diaryloxymethyl chlorides and treatment with sodium hydride are performed separately. In general the  $m/n$  ratio is highest if the relevant phenolate is added drop by drop to a mixture of an aryl dichloromethyl ether and sodium hydride.

Although no special attention has been paid to mechanistic aspects of the synthetic procedures described, some remarks may be made about the possible role of carboxonium ions and carbenes as intermediates in these reactions.

*A priori* three different pathways<sup>2</sup> may be proposed for the formation of tetra-alkoxy- or tetra-aryloxyethenes from starting compounds  $\text{HC}(\text{OR})_2\text{X}$  ( $\text{R}$ =alkyl or aryl) in which  $\text{X}=\text{Cl}$ ,  $\text{F}$  or  $\text{OAr}$ , on treatment with a strong base ( $\text{B}^-$ ):



They differ mainly in the order in which the abstraction of a proton by the base and the elimination of the nucleophilic group  $\text{X}$  from the parent compound proceed. Immediate proton abstraction leads to a

carbanion from which the end products may arise either *via* a nucleophilic substitution and elimination [5a] or *via* a carbene [5b]. A carbene may also arise *via* a carboxonium ion formed by dissociation of I followed by proton abstraction [5c]. Alternatively, the carbene intermediate may be formed by concerted proton abstraction and elimination.

It seems probable that the formation of tetra-alkylthio-ethenes<sup>10,11</sup> from alkyl trithio-orthoformates,  $\text{HC}(\text{SR})_3$ , by reaction with a strong base proceeds *via* carbanions as intermediates [5a]. Triethyl trithio-orthoformate is, however, at least seven powers of ten more acidic than triethyl orthoformate<sup>12</sup>, which demonstrates that carbanion stabilization by alkoxy groups is of minor importance. Consequently, when triethyl orthoformate is refluxed for ten hours with sodium hydride at 150° it is recovered unchanged. Because proton abstraction by sodium hydride is not reversible, formation of carbanions in this experiment should have been demonstrated by the appearance of decomposition products.

It is true that the acidity of the starting compounds in our synthetic procedures,  $\text{HC}(\text{OR})_2\text{OAr}$  and  $\text{HC}(\text{OAr})_2\text{Cl}$ , will be higher than that of triethyl orthoformates, because of the presence of better carbanion-stabilizing substituents, especially in  $\text{HC}(\text{OAr})_2\text{Cl}$ . However in these cases also proton abstraction should be slow as compared with trithio-orthoformate.

On the other hand the carboxonium ion character of the compounds I is, in the case of  $\text{X}=\text{F}$ , apparent from the fact that fluorine exchange in several dialkoxymethyl fluorides is very fast at room temperature. Whereas the methine proton in the NMR spectrum of diphenoxymethyl fluoride appears as a doublet ( $\delta = 6.35$  and  $7.08$  in  $\text{CCl}_4$ ) owing to coupling with the neighbouring fluorine, the methine signal of most dialkoxymethyl fluorides is a slightly broadened single peak; only with dimethoxymethyl fluoride is the expected doublet visible ( $\delta = 5.16$  and  $5.97$  in  $\text{CCl}_4$ ) but the peaks are broad and become sharp only at a considerably lower temperature.

Our results cannot be used for making a conclusive choice between the various pathways 5a, b and c. However, the much lower reactivity towards bases of diaryloxymethyl fluorides and diarylmethyl *p*-chlorophenoxides in comparison with that of the corresponding dialkoxy derivatives is much more in agreement with a mechanism *via* an inter-

<sup>10</sup> A. Frohling and J. F. Arens, *Rec. Trav. Chim.* **81**, 1009 (1962).

<sup>11</sup> J. Hine, R. P. Bayer and G. G. Hammer, *J. Am. Chem. Soc.* **84**, 1751 (1962).

<sup>12</sup> L. H. Slaugh and E. Bergman, *J. Org. Chem.* **26**, 3158 (1962).

mediate with carboxonium character than with a pathway *via* a carbocation; whereas the aliphatic carboxonium ions  $\text{HC}(\text{OR})_2^{\oplus}$  and also the corresponding carbenes  $\text{RO}\ddot{\text{C}}\text{OR}$  are much more stabilized by resonance than their aromatic analogues,  $\text{HC}(\text{OAr})_2^{\oplus}$  and  $\text{ArO}\ddot{\text{C}}\text{OAr}$ , the reverse is true for the anions  $\text{HC}(\text{OR})_2^{\ominus}$  and  $\text{HC}(\text{OAr})_2^{\ominus}$ .

## Experimental part

(with the technical assistance of Mrs. F. G. J. Janssen)

For the isolation or purification of distillable compounds a Vigreux column (30 × 12 mm or 25 × 10 mm) was used. All boiling and melting points are uncorrected.

Products were identified by their NMR spectra recorded with a Varian T60 or HA-100 spectrometer from 10% solutions in  $\text{CCl}_4$ . (Tetra-aryloxyethenes were dissolved in  $\text{CDCl}_3$ .) Hexamethyldisiloxane was used as an external standard. In comparison with data obtained with TMS as an internal reference all peaks are shifted 20 Hz to lower field.

### 1. Dialkoxy-*p*-chlorophenoxyethanes, $\text{HC}(\text{OR})_2\text{OC}_6\text{H}_4\text{Cl-}p$

The compounds with R = propyl, isobutyl, *sec*-butyl or neopentyl were obtained by treatment of an excess (about 20%) of the appropriate orthoformates with *p*-chlorophenol and about 0.1 mole % of *p*-toluenesulfonic acid as a catalyst. The alcohol liberated was evaporated from the reaction mixture under reduced pressure (20 mm) and the product isolated by distillation at lower pressure (Table I).

Table I

Aryl dialkyl orthoformates  $\text{HC}(\text{OR})_2\text{OC}_6\text{H}_4\text{Cl-}p$

R	B.p. (°C/mm)	$n_D^{20}$	$\delta_{\text{H-C}}$	Yield
Methyl	122°/13	1.5078	6.20	95%
ethyl <sup>13</sup>	98°/0.2	1.4936	5.80	95%
<i>n</i> -propyl	111°/0.5	1.4896	5.80	80%
isobutyl	112°/0.5	1.4830	5.75	70%
<i>sec</i> -butyl	97°/0.1	1.4844	6.00	70%
neopentyl	127°/0.6	1.4776	5.80	80%
cyclohexyl			6.00	95%

<sup>13</sup> J. W. Scheeren and W. Stevens, Rec. Trav. Chim. **88**, 897 (1969).

<sup>14</sup> *Idem*, *ibid.* **85**, 793 (1966); J. W. Scheeren, A. P. M. van der Veek and W. Stevens, *ibid.* **88**, 195 (1969).

If under these circumstances the exchange-reaction is very slow (R = methyl and ethyl), separation of the desired product from *p*-chlorophenol is difficult (R = methyl), or decomposition occurs (R = cyclohexyl) the aryldialkyl orthoformates were prepared from dialkoxyethyl acetates<sup>14</sup>. For R = cyclohexyl the orthoformate could not be distilled. After removing the acetic acid from the reaction mixture at low pressure (0.5 mm) at a temperature below 80°, the remaining aryldicyclohexyl orthoformate was practically pure.

### 2. Dialkoxyethyl fluorides HC(OR)<sub>2</sub>F

0.2 Mole of a dialkoxyethyl butyrate (for the synthesis of compounds with R = methyl or ethyl) or valerate<sup>14</sup> (for R = *n*-propyl or isobutyl) was added to 0.3 mole of dry KHF<sub>2</sub>. The conversion is very slow, and in the syntheses of the propyl and isobutyl derivatives 30 ml of hexamethyl phosphoric acid triamide were added to speed up the exchange. By continued distillation of the fluorides formed from the reaction mixture under diminished pressure (12 mm) the procedure could be completed in about 8 hours, but the products contained alkyl formates (5–10%) and alkyl carboxylates (5–10%) as impurities. Further purification of the methyl derivative is possible by redistillation even at normal pressure (Table II).

Because of their low boiling points dimethoxyethyl and diethoxyethyl fluoride had to be trapped in a vessel cooled in solid CO<sub>2</sub>.

Table II

Dialkoxyethyl fluorides HC(OR)<sub>2</sub>F

R	B.p. (°C/mm)	$\delta_{\text{HC}} \leq$	Yield
Methyl	65–67°	5.65	84%
ethyl	28°/45	5.85	85%
<i>n</i> -propyl	45°/12	5.90	50%
isobutyl	65°/12	5.80	65%

### 3. Tetra-alkoxyethenes (RO)<sub>2</sub>C=C(OR)<sub>2</sub>

#### a. From dialkoxy-*p*-chlorophenoxyethanes.

To a stirred boiling suspension of 2.9 g (0.12 mole) of sodium hydride in 25 ml of dimethoxyethane 0.1 mole of a dialkoxy-*p*-chlorophenoxyethane was added dropwise within 20 minutes.

Boiling and stirring were continued for at least 10 hours (20 hours for the methoxy compound). The mixture was cooled to room temperature and *p*-chlorophenolate and unreacted sodium hydride were filtered off. The residue was fractionated under reduced pressure. Besides the desired olefine (Table III), some orthoformate was obtained.

The products hydrolyse very easily into (RO)<sub>2</sub>CH—COOR. Therefore, they have to be stored in alkali-washed and carefully dried vessels.

Even at very low pressure tetracyclohexyloxyethene could not be isolated by distillation. After removal of the phenolate and hydride from the reaction mixture it was obtained by evaporation of the solvent followed by fractionated sublimation at 100°

(0.4 mm) to separate it from orthoformate. Because of its high sensitivity to moisture and oxygen its melting point was not very sharp. The same was found for the other solid product, tetraneopentoxyethene.

Table III

Tetra-alkoxyethenes  $(RO)_2C=C(OR)_2$ 

R	B.p. (°C/mm)	$n_D^{20}$	Yield
Methyl*	48°/15	1.4244	45 %
ethyl**	77°/15	1.4212	55 %
propyl	123°/15	1.4301	60 %
isobutyl	143°/13	1.4312	60 %
sec-butyl	93°/1.1	1.4312	55 %
neopentyl	114°/0.6		50 %
cyclohexyl			55 %

\* lit<sup>15</sup> B.p. = 140°.

\*\* lit<sup>4</sup> B.p. = 195–196°  $n_D^{25}$  = 1.4213.

b. *Reaction of dialkoxymethyl fluorides with sodium hydride.*

Dimethoxymethyl fluoride was added to a stirred suspension of sodium hydride in dimethoxyethane. After stirring for three hours at room temperature the NMR spectra showed no evidence of any conversion. The mixture was then refluxed again for four hours. After distillation methyl formate, dimethoxymethyl fluoride and methyl orthoformate were the only isolable compounds. In a similar experiment diethoxymethyl fluoride failed to yield tetra-ethoxyethene but decomposed above 30° into ethyl formate and ethyl fluoride.

c. *Reaction of dialkoxymethyl fluorides with naphthylsodium.*

A solution of 0.1 mole of a dialkoxymethyl fluoride in 20 ml of tetrahydrofuran was added dropwise into a stirred solution of 0.1 mole of naphthylsodium in 75 ml of tetrahydrofuran<sup>16</sup>. After completion of the addition the reaction mixture turned yellow. 15 ml of hexamethyl phosphoric acid triamide were added and the mixture was carefully distilled, first at atmospheric pressure to remove the solvent, then at reduced pressure. Main fractions appeared to be alkyl formate and orthoformate. Also highboiling products containing naphthyl and alkoxy groups had been formed. Tetra-alkoxyethenes could be isolated only in very low yields (10% for tetramethyl, 3% for tetraethyl, <1% for other ethenes).

4. *Diaryloxymethyl chlorides HC(OAr)<sub>2</sub>Cl*

An appropriate triaryloxymethane<sup>9</sup> was dissolved in 4 equivalents of acetyl chloride\*. If necessary methanolfree chloroform or acetonitrile was added to complete dissolution.

\* We found no faster conversion with trichloroacetyl chloride in contrast to the report of H. Böhme and V. Neidlein, Chem. Ber. **95**, 1859 (1962).

<sup>15</sup> R. W. Hoffmann and H. Häuser, Tetrahedron Letters **1964**, 197.

<sup>16</sup> H. Normant and B. Angelo, Bull. Soc. Chim. **1960**, 354.

After addition of 1 ml of a 5*N* HCl solution in dry ether the reaction mixture was kept at room temperature for at least 24 hours. The products could be isolated by distillation (Table IV).

The procedure is restricted to the preparation of diaryloxymethyl chlorides in which the aryl residues do not contain more or stronger electron-withdrawing groups than one chloro substituent.

For use in the synthesis of tetra-aryloxyethenes the crude diaryloxymethyl chlorides can be used without distillation. It is sufficient to remove the solvent and aryl acetate from the reaction mixture. This procedure must be used in the synthesis of the *p*-methoxy compound because di-*p*-methoxyphenoxyethyl chloride decomposes at its distillation temperature.

Table IV

Diaryloxymethyl chlorides HC(OAr)<sub>2</sub>Cl

Ar	B.p. (°C/mm)	$\delta_{\text{HC}} \leq$	Yield
Phenyl <sup>5</sup>	122°/0.6	**	70%
<i>p</i> -tolyl	138°/0.1	7.25	65%
2,6-dimethylphenyl	145°/0.6	7.15	40%
<i>p</i> -chlorophenyl	170°/0.6	7.70 (in dime-	75%
<i>p</i> -methoxyphenyl	183–185°/0.3*	toxy- ethane)	40%
		**	

\* Under decomposition.

\*\* Proton absorption in the aromatic area.

#### 5. Diphenoxymethyl fluoride HC(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>F

0.1 Mole of diphenoxymethyl chloride was added to 0.2 mole of KHF<sub>2</sub>. Distillation of the reaction mixture gave diphenoxymethyl fluoride at 105–110°/1 mm in 60% yield.

The methine proton of the product appears in the NMR spectrum as a doublet (6.35 and 7.08) due to coupling with the neighbouring fluorine.

#### 6. Tetra-aryloxyethenes (ArO)<sub>2</sub>C=C(OAr)<sub>2</sub>

##### a. From diaryloxymethyl chlorides.

A solution of 0.1 mole of a diaryloxymethyl chloride in 25 ml of dimethoxyethane was added dropwise and under stirring to a refluxing suspension of 0.13 mole of sodium hydride in 25 ml of the same solvent. Boiling and stirring were continued for at least 3 hours (6 hours for the *p*-chlorophenyl derivative). After cooling, the reaction mixture was filtered. Sometimes a first fraction of the desired olefine could be obtained from the residue on the filter (mostly sodium chloride and unreacted sodium hydride) by destruction of hydride with ethanol and washing with abundant water. The olefine was left on the filter during this treatment.

A second fraction of the product was obtained from the filtrate by partial evaporation of the solvent and addition of equal volumes of ether and petroleum ether, and a small amount of water. The precipitate was filtered, dried and recrystallized from petroleum ether (60–80°) (Table V).

Tetraphenoxyethene is sparingly soluble in the solvents used so that it stays mainly on the filter when the reaction mixture is filtered. The *p*-chlorophenoxy compound remains completely dissolved in dimethoxyethane and can be obtained only by evaporation of the solvent. The lower yields of the 2,6-dimethylphenyl and *p*-chlorophenyl compounds are mainly due to their greater solubility in organic solvents.

b. *From aryl dichloromethyl ethers.*

0.1 Mole of an aryl dichloromethyl ether was added to a suspension of 0.15 mole of sodium hydride in 25 ml of dimethoxyethane. A solution of 0.15 mole of an appropriate sodium phenolate in diethylene glycol dimethyl ether was then added dropwise during one hour to the stirred suspension and the mixture was refluxed for three hours. After cooling and filtration the product was isolated as described above (Table V).

The aryl dichloromethyl ethers used in this synthesis have to be free from phosphorus pentachloride and aryl formate, because both react vigorously with sodium hydride.

Table V

Tetra-aryloxyethenes (ArO)<sub>2</sub>C=C(OAr)<sub>2</sub>

Ar	M.p.	Yield Method 6a	Yield Method 6b
Phenyl	170°*	75 %	45 %
<i>p</i> -tolyl	190°	70 %	25 %
2,6-dimethylphenyl	190°	45 %	1 %
<i>p</i> -chlorophenyl**	139°	40 %	20 %
<i>p</i> -methoxyphenyl	117°	50 %	
α-naphthoxy**	256°		10 %

\* lit<sup>6</sup> M.p. = 168–169°.

\*\* Also identified by C, H analyses.

c. *Reaction with diphenoxymethyl fluoride.*

After refluxing diphenoxymethyl fluoride in dimethoxyethane with sodium hydride for 3 hours and working-up of the reaction mixture as described under 6a only starting material was isolated.

Mass spectra of the tetra-alkoxy- and tetra-aryloxyethenes.

All mass spectra (Varian-Mat S.M. 1-B) showed the molecular ion peak in agreement with the proposed structure. The peaks [M—R]<sup>+</sup> and [M—COR]<sup>+</sup> were also characteristic for all the compounds. From the occurrence of the relevant metastable peaks (in the first field free region) it was determined for R=CH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub> that [M—COR]<sup>+</sup> was formed from <sup>o</sup>M<sup>+</sup> as well as from [M—R]<sup>+</sup>.

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