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Communications to the Editor

Thermolysis Rates and Products of the Putative Ketochloroallyl Groups in Poly(vinyl chloride), As Inferred from the Behavior of Analogous Model Compounds

In the continuing debate concerning the nature of the labile structures in poly(vinyl chloride) (PVC), a controversial proposal has been that of Minsker et al., who have argued that the ketochloroallyl moiety **2** is the only structural defect that contributes significantly to the thermal instability of the polymer.[1] This grouping has been postulated to result from air oxidation of the adventitious structure, **1** (eq 1),[1] and its suggested instability has been ascribed entirely to the occurrence of reaction 2.[1,2] The supposed rapidity of that reaction has now, in fact, been reaffirmed by molecular orbital calculations.[2] Other conceivable thermolysis reactions of **2** evidently have not been considered, and the possibility that *cis*- and *trans*-**2** have widely divergent thermal stabilities apparently has been dismissed.[2]

$$\underset{\mathbf{1}}{-CH_2CH{=}CHCHCl-} \xrightarrow{O_2} \underset{\mathbf{2}}{-COCH{=}CHCHCl-} \quad (1)$$

$$\mathbf{2} \xrightarrow{\Delta} -CO(CH{=}CH)_{n+1}\text{-}CHCl- \;+\; n\mathrm{HCl} \quad (2)$$

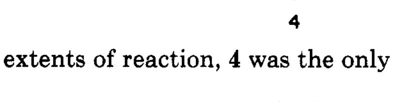
In earlier work with low-molecular-weight model compounds, we found that the intrinsic thermal stability of *trans*-**2** is relatively high—so high, in fact, that this group is unlikely to be a significant starting structure for the stepwise thermolysis of the polymer that produces polyene sequences.[3] We now report related studies that pertain to the thermal stability of *cis*-**2** and to the anticipated fates of both that arrangement and its trans analogue in thermally degrading PVC.

Ketone **3a**, a *trans*-**2** model, had been obtained previously in a yield of 64% from a Horner–Emmons reaction of 2-chloropentanal with a carbanion intermediate derived from diethyl (2-oxohexyl)phosphonate.[3,4] That reaction was carried out at ambient temperature in tetrahydrofuran (THF), and the carbanion was generated in the same solvent from the phosphonate and sodium hydride.[4] In the present investigation, 2-chloropentanal was allowed to react in THF at −75 °C with a dimethyl (2-oxohexyl)phosphonate carbanion that had been formed in THF at −78 °C, using $KN(SiMe_3)_2$/18-crown-6 as the basic reagent.[5] This condensation gave, in 70% yield, a 3:2 mixture of **3b** and **3a**, respectively, from which pure **3b** was isolated by preparative liquid chromatography.[6]

$$BuC({=}O)CH{=}CHCHClPr$$

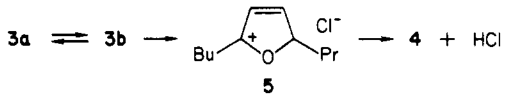
3a, trans
b, cis

When **3a** and **3b** were exposed to temperatures that caused their dehydrochlorination, neither compound displayed a tendency to undergo a transformation resembling reaction 2. Instead, both isomers were converted into a known substance,[7] furan **4** (eq 3). At moderate temperatures and extents of reaction, **4** was the only detectable organic product resulting from the loss of HCl, but under more vigorous conditions, the furan was slowly destroyed, presumably owing, in part at least, to its attack by the acid evolved. The production of **4** from **3b** is not entirely without precedent, since the literature reports at least one example of a similar cyclization involving a *cis*-γ-bromo-α,β-unsaturated ketone.[8]



4 (3)

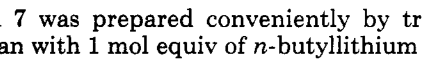
A very attractive route to the furan is shown in eq 4. Here the immediate precursor of ion pair **5** is required to be **3b**, because the cyclization of **3a** is precluded by molecular geometry. Although the conversion of **3b** into **3a** is not a major process, it does occur to some extent under thermolysis conditions. For example, when a dilute solution of **3b** in *o*-dichlorobenzene was heated at 170 °C, **3a** and **4** were formed in a 1:9 ratio, respectively. Thus the thermolysis of the ketones is a rather complex process, and we now have an explanation for the peculiar Arrhenius parameters determined previously[3] for the thermal dehydrochlorination of **3a** and an analogous dichloro ketone.



5 (4)

The observations just described imply that the thermal dehydrochlorination of **3b** is faster than that of **3a**. Quantitative kinetic measurements have confirmed this conclusion and have shown that the difference between the rates is very large indeed. At 170 °C in *o*-dichlorobenzene under argon, the following results were obtained for the chloro ketones and for two compounds comprising crude models for internal allylic and tertiary chloride arrangements in PVC (model compound, dehydrochlorination rate constant in units of s^{-1}): **3a**, 5.8×10^{-7}; **3b**, 2.7×10^{-3}; *trans*-4-chloro-5-decene, 4.8×10^{-5}; 5-chloro-5-methylnonane, 1.6×10^{-4}.[9] These data reveal that the cis ketone is more reactive than its trans isomer *by a factor of about 5000* and that it also is less stable than the other models examined. In the case of compound **3b**, neighboring-group participation by carbonyl oxygen evidently acts as a powerful stimulus for the C–Cl heterolysis leading to **5**.[10] On the other hand, for both ketones, the "normal" mode of dehydrochlorination (as in eq 2) apparently is greatly disfavored by the electron-withdrawing effect of the conjugated carbonyl group.[11]

If *cis*-**2** is to be an effective point of departure for the growth of a PVC polyene sequence, then its thermolysis product, **6**, also needs to experience a rapid loss of HCl. In order to assess the probability that this requirement would be met, we have measured the thermal stability of two additional model compounds.



6

Alcohol **7** was prepared conveniently by treating 2-propylfuran with 1 mol equiv of *n*-butyllithium and then introducing an equimolar amount of butanal. Both steps were carried out in THF at ca. −20 to −30 °C, and the isolated yield of the purified product was 55%. Use of a variety of reagents and reaction conditions did not allow us to achieve the direct conversion of **7** into the corresponding α-chlorodialkylfuran. Most of these trials gave,

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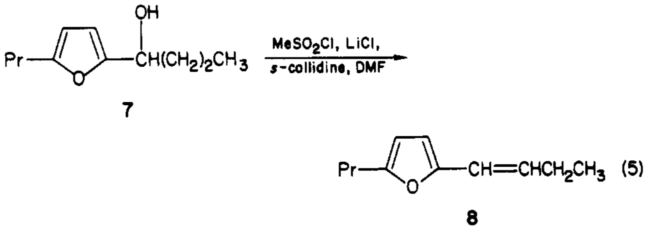
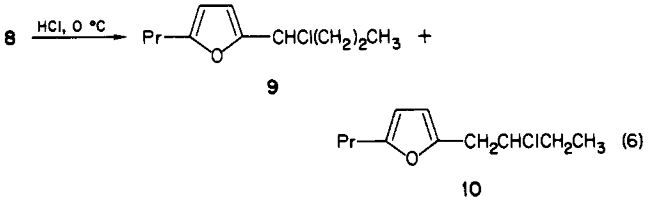
instead, a mixture of *cis*- and *trans*-**8** (largely *trans*-**8**), which was obtained, for example, in 40% yield with the Collington-Meyers reagent[12] (eq 5; DMF = *N,N*-dimethylformamide). However, when **8** was allowed to react with HCl in $CDCl_3$ at 0 °C, both **9** and its isomer, **10**, were formed (eq 6), although ^1H NMR measurements showed that **9** was changing irreversibly into **10** under these conditions. Owing to the resonance stabilization of its carbocationoid precursor, **9** presumably was the main product produced initially, and its kinetic instability can, of course, be rationalized on this basis as well.





These findings strongly suggested that the thermal dehydrochlorination rate of **9** would be much faster than that of **10** and that it should be possible to determine the rate for **9** (which could not be isolated in pure form) from mixtures of the two chlorides. Both expectations were fulfilled. At 170 °C in *o*-dichlorobenzene under argon, pure **10** (obtained as the final product from HCl and **8**) had a dehydrochlorination rate constant of only $2.7 \times 10^{-7}\ s^{-1}$. Under identical conditions, the rate of **9** was difficult to measure accurately owing to its great rapidity and to complications stemming, apparently, from the competing rearrangement of **9** into **10**. Nevertheless, replicate runs with chloride mixtures gave constants for **9** within the range of $(6 \pm 3) \times 10^{-3}\ s^{-1}$. Thus, in our experiments, **10** was very stable, while **9** was at least as reactive as the cis chloro ketone, **3b**.

Summarizing the implications of our findings, we conclude that *cis*-**2** structures in PVC would rapidly initiate the growth of polyenes upon heating, owing to the quick conversion of *cis*-**2** into **6**, whose α-chloroalkyl group would dehydrochlorinate with great facility. What obviously remains to be decided is whether the *cis*-**2** concentrations in PVC specimens are high enough to cause major effects on the overall rate of thermolysis. These concentrations should be even less than those of *trans*-**2**, on thermodynamic grounds, and our extensive studies of PVC using ^{13}C NMR spectroscopy[13] have provided no evidence for the occurrence of either structure or structures derived therefrom.[14] However, additional NMR studies might prove to be worthwhile, since our lower detection limits have usually been above the amounts of **2** which, according to Minsker et al.,[1] are present in the polymer.

Acknowledgment. We thank Dr. S. L. Haynie for a gift of *trans*-4-chloro-5-decene.

References and Notes

(1) For recent reviews, see: Minsker, K. S.; Abdullin, M. I.; Kolesov, S. V.; Zaikov, G. E. *Dev. Polym. Stab.* **1983**, *6*, 173. Minsker, K. S.; Lisitsky, V. V.; Kolesov, S. V.; Zaikov, G. E. *J. Macromol. Sci., Rev. Macromol. Chem.* **1981**, *20*, 243.
(2) Minsker, K. S.; Kolesov, S. V.; Yanborisov, V. M.; Berlin, A. A.; Zaikov, G. E. *Polym. Degrad. Stab.* **1984**, *9*, 103.
(3) Haynie, S. L.; Villacorta, G. M.; Plitz, I. M.; Starnes, W. H., Jr. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1983**, *24* (2), 3.
(4) Villacorta, G. M.; Starnes, W. H., Jr., to be published.
(5) Cf.: Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.
(6) Details of all experiments described herein will be published subsequently. Structures of all new compounds were established by instrumental analytical methods, including IR, ^1H and ^{13}C NMR, and gas chromatography/mass spectrometry.
(7) Lissi, E. A.; Encinas, M. V.; Castañeda, F.; Olea, F. A. *J. Phys. Chem.* **1980**, *84*, 251.
(8) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129.
(9) All of the rate constants in this paper were determined by acid-base titrimetry, using the general procedure that was adopted in earlier work.[3] Differences between some of these constants and those reported previously[3] probably can be attributed, at least in part, to different extents of HCl autocatalysis resulting, in turn, from differences in the rate of argon flow. In the earlier investigation,[3] no effects of flow rate upon the kinetics were found, but studies with widely varying flow rates now have shown that, in certain cases, these effects are quite significant (Seshadri, S. R.; Panek, M. G.; Starnes, W. H., Jr., to be published). The same flow rate was used for all of the kinetics experiments performed in the present study.
(10) Cf.: Pasto, D. J.; Serve, M. P. *J. Am. Chem. Soc.* **1965**, *87*, 1515.
(11) Starnes, W. H., Jr. *Dev. Polym. Degrad.* **1981**, *3*, 135.
(12) Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044.
(13) Starnes, W. H., Jr.; Schilling, F. C.; Plitz, I. M.; Cais, R. E.; Freed, D. J.; Hartless, R. L.; Bovey, F. A. *Macromolecules* **1983**, *16*, 790 and references cited therein.
(14) For other arguments against contributions by **2** to PVC thermolysis, see: Hjertberg, T.; Sörvik, E. M. *Polymer* **1983**, *24*, 685.
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Fracture-Induced Free Radicals in Amine-Cured Epoxy Resins

We are using electron paramagnetic resonance (EPR) to investigate the role of macromolecular chain scission in the deformation and failure modes of amine-cured epoxy resins. These are the thermosetting polymers which are widely used as matrix materials in composite structures. In this communication we report on the nature of the free radicals created in epoxy resins as a result of fracture-induced macromolecular chain scissions. Previous EPR studies have shown that free radicals can be generated in polymers as a result of some form of grinding,[1-4] e.g., ball milling or sawing. We have adopted the grinding technique to ensure the chemical stability of the fracture-induced radicals since it is not too difficult to design an apparatus that allows the samples to be ground while maintained at 77 K and kept free of oxygen.

The epoxy system studied was the diglycidyl ether of bisphenol A (DGEBA) cured with stoichiometric amounts of ethylenediamine, ethylenediamine-d_4, and diethylenetriamine. Homopolymerized samples of DGEBA containing ≈4 wt % *N,N*-dimethylbenzylamine as an initiator were also investigated.