Xanthate Pyrolysis—Enhanced Olefin Production in Nematic Liquid-crystalline Solvents

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Summary Experimental evidence is presented showing for the first time that liquid-crystalline solvents can direct the course of a chemical reaction.

ALTHOUGH studies concerning the role of solvents in organic reactions abound,[1] these studies have concentrated upon differences among isotropic media. Few reactions[2] have been studied in ordered liquid phases despite the fact that liquid-crystalline phases have been known for some time.[3] We have been studying the pyrolysis of xanthates[4] in liquid-crystalline solvents and have discovered an interesting effect of such ordered solvents upon product formation.
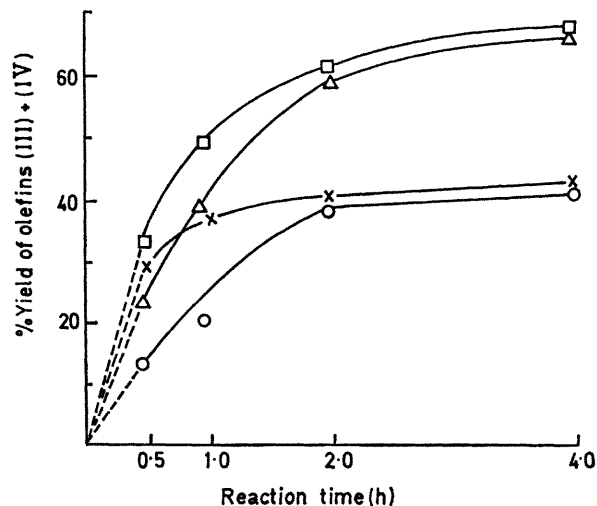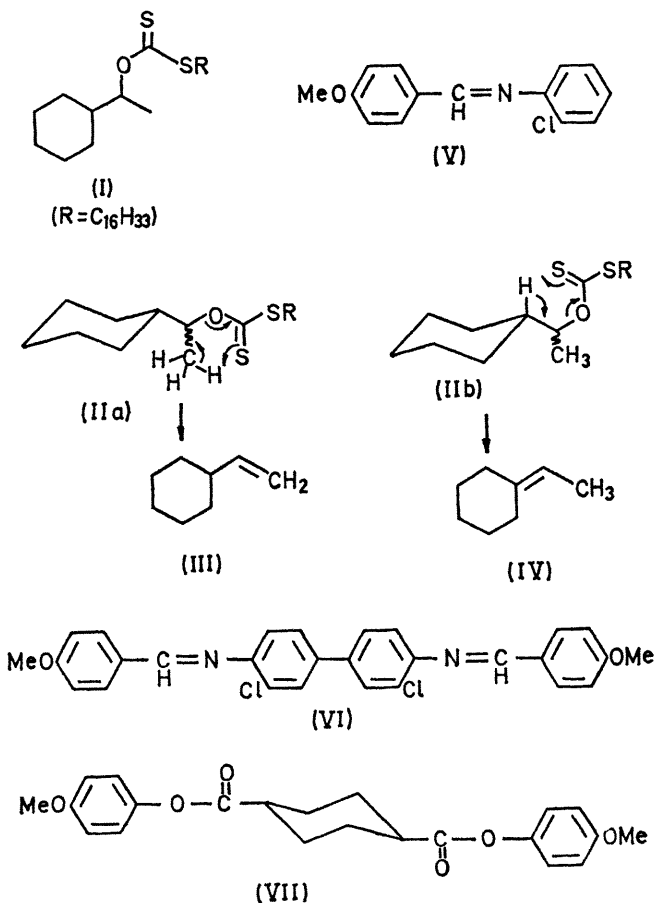

FIGURE. Pyrolysis of xanthate (I) in various solvents. Reactions run at $160 \pm 0.2°$. Concentration of (I) = 4%. Points shown are the average of 2 runs. ×: solvent (V), non-liquid-crystalline; △: solvent (VI), liquid-crystalline; □: solvent (VII), liquid-crystalline; ○: decalin, non-liquid-crystalline. Yields are calculated from g.c. traces using a cyclohexene standard. Sensitivity factor = sample/standard = 0·85.

Xanthate pyrolysis is a unimolecular reaction in which olefins are produced via a cyclic six-membered transition state.[4] The pyrolysis of xanthate (I), for which there are two such transition states, (IIa) and (IIb), leads to mixtures containing vinylcyclohexane and ethylidenecyclohexane, (III) and (IV). We have attempted to determine whether an ordered nematic liquid-crystalline phase might have some effect upon the distribution of olefins in the product

mixture.[5] Interpretation of our data has been complicated by the fact that in sealed systems with an ordinary non-liquid-crystalline solvent, the production of total olefin decreases sharply when the extent of olefin production reaches 30—40% (see Figure). On the other hand, olefin production in the liquid-crystalline phase continues at a good rate until 60—70% of the theoretical amount is obtained.

It is likely that this effect is due to the ordered nematic phase and not to any particular effects of functional groups within the solvents used. The non-liquid-crystalline solvent (V) and the nematic solvent (VI), which have essentially the same functionality, give different results. Furthermore, the non-liquid-crystalline, non-polar solvent, decalin gives results similar to the more polar, but similarly isotropic solvent (V), while the nematic solvent (VII), an ester, behaves like the nematic solvent (VI), a basic amine.

Even though the details of this effect are yet to be clarified, the implication for synthetic chemistry is clear. When it is necessary to run the xanthate pyrolysis in a closed system,† a nematic solvent will enhance the yield of olefin. It has long been thought that liquid-crystalline solvents might have specific advantages over ordinary isotopic solvents used in preparative organic syntheses.[3] This is the first actual demonstration of such utility.

† Typically the olefinic product is distilled as it is formed during a xanthate pyrolysis. This is obviously inefficient when working with mg quantities or ineffective with high molecular weight olefins. See ref. 4a.

[1] E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, 1968, Part 2, Medium Effects.
[2] T. Svedberg, Kolloid-Z., 1916, 18, 54; T. Svedberg, ibid., p. 101; W. E. Bacon and G. H. Brown, Mol. Cryst. Liquid Cryst., 1969, 6, 155.
[3] G. W. Gray, "Molecular Structures and the Properties of Liquid Crystals," Academic Press, New York, 1962.
[4] (a) C. H. DePuy and R. W. King, Chem. Rev., 1960, 60, 431; (b) W. S. Briggs and C. Djerassi, J. Org. Chem., 1968, 33, 1625.
[5] W. E. Barnett and W. H. Sohn, results to be published.