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THE THERMAL DIMERIZATION OF CYCLOPROPENE

Paul Dowd and Avram Gold

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138

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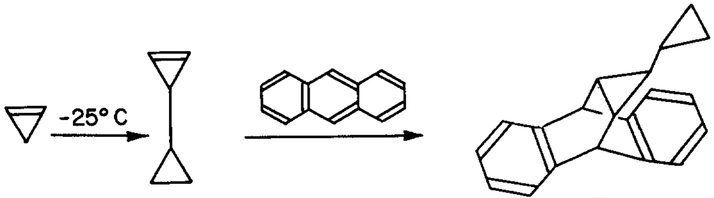
Cyclopropene(I) is one of the most reactive known olefins (1). A manifestation of this reactivity is seen in the tendency of the molecule to polymerize with explosive violence at room temperature. We have discovered that if cyclopropene (I) is allowed to react under carefully controlled conditions at low temperature (-25°) in dilute methylene chloride or n-pentane solution, the dimer (II) may be isolated following preparative vapor phase chromatography on a 10' x 3/8", 20% SE-30 on Chromosorb W column at room temperature. This highly reactive hydrocarbon (II) shows in its nmr spectrum ($CDCl_3$): a two-proton narrowly split olefinic doublet at τ 2.9, a one-proton doublet of triplets at τ 8.4, a one-proton multiplet at τ 9.2, and a four-proton multiplet at τ 9.8. The mass spectrum shows exact mass 80.0601; calcd. for C_6H_8, 80.0626. The strongest peaks in the mass spectrum are found at m/e 79 (relative abundance 97%) and 39 (100%) corresponding to the two possible cyclopropenium ions.

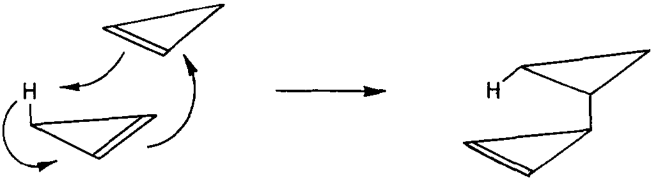


I   II   III

The hydrocarbon (II) is extremely labile. It must be stored at -78°. If the nmr and mass spectra are not taken at -60°, the spectra of higher, as yet unidentified, oligomers of cyclopropene are obtained. An indication of the reactivity of this compound may be gained from the observation that at 10° in chloroform it forms an anthracene adduct (III) m.p. 117-117.5°

(10% yield). This compound (III) shows in its nmr spectrum ($CDCl_3$): an eight-proton aromatic multiplet at τ 2.90, a two-proton triplet at τ 5.70, a two-proton quartet at τ 8.75 and a six-proton multiplet at τ 9.6-10.2. The mass spectrum shows exact mass 258.1410; calcd. for $C_{20}H_{18}$, 258.1408 with major peaks at m/e 258 (relative abundance 90%), 191 (100%) and 178 (100%) corresponding to the molecular ion, dibenzotropylium [?], and anthracene respectively. The ultraviolet spectrum shows $\lambda_{max}^{cyclohexane}$ 266 mμ (ε 1,370) and 273 mμ (ε 1,710) in good agreement with other known ethonanthracenes. Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.94; H, 7.00.

The mechanism of the dimerization reaction has not been established. A possibility for this reaction is the "ene" mechanism shown below (2). Such a mechanism may also be important in the polymerization of the dimer (II) and in the polymerization of cyclopropene (I). The observation of a similar dimerization in the case of triphenylcyclopropene (2) and the extremely mild conditions necessary for the reactions observed here lend support to this suggestion. A free radical initiated process is an alternative possibility which has been suggested in the past for the polymerization of cyclopropene (1c). We have found that the rate of dimerization is not reduced or inhibited by the presence of nitrobenzene or p-benzoquinone.



References

1. (a) N. J. Demjanow and M. Dojarenki, *Ber.*, **56**, 2200 (1923); (b) M. J. Schlatter, *J. Am. Chem. Soc.*, **63**, 1733 (1941); (c) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960); (d) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966). We have used procedure described in reference 1d for the preparation of cyclopropene.

2. R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).