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DIMERIZATIONS OF METHYLENECYCLOPROPANES

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Abstract—The thermal [2 + 2] dimerization of methylenecyclopropanes, including methylenecyclopropane itself, is discussed. The effects of structural features on the ability of this reaction to occur are discussed in terms of the probable mechanism.

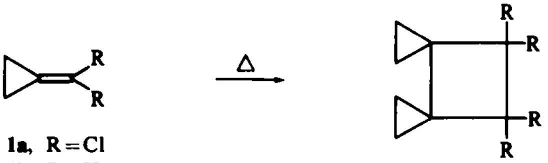
INTRODUCTION

SIMPLE ALKENES do not usually undergo [2 + 2] thermal dimerizations. It has generally been found that in order for such reactions to proceed to any significant extent, there must be either a relatively stable diradical or dipolar intermediate in the two-step cycloaddition process, e.g. the dimerizations of acrylonitrile[1] or allene,[2] or a powerful thermodynamic driving force for destruction of the alkene in favor of the cyclobutane, e.g. polyfluorinated systems.[1, 3]

Recently, we discovered that certain methylenecyclopropanes underwent relatively facile [2 + 2] dimerizations.[4] We now report further details of this reaction and others of this type which seem to intimate that the reaction should be rather general in systems where significant non-bonded interactions are not present in the cyclobutane product.

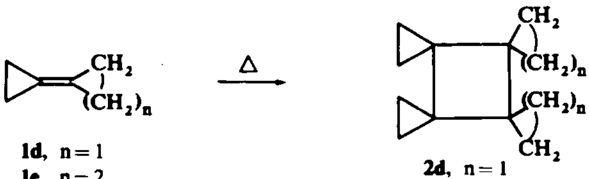
RESULTS

Initially we found that the very reactive dichloromethylenecyclopropane (**1a**) formed the head-to-head dimer quantitatively, at temperatures as low as 100°. With this facile



1a, R = Cl
1b, R = H
1c, R = Me

2a, R = Cl
2b, R = H
2c, R = Me



1d, n = 1
1e, n = 2

2d, n = 1
2e, n = 2

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synthesis of the dispiro[2.0.2.2] octane system, we converted tetrachloride **2a**, to the interesting hydrocarbon, dispiro[2.0.2.2] oct-7-ene (**4**), which proved to be remarkably stable to unimolecular thermal decomposition, but very prone to polymerization at room temperature, even in dilute solution.

3 **4**

The observation of this facile dimerization led to the question of how general this type of reaction was. Soon after, Conia reported the dimerization of biscyclopropylidine (**1d**) which occurred at 210°,[5] and we found that cyclopropylidenecyclobutane (**1e**) also underwent thermal dimerization with relative ease (210°, six hours). At this point we turned to the parent species (**1b**) and found it not nearly so reactive. Nevertheless, it also dimerized to about 20% upon heating at 240–45° for 48 hours.

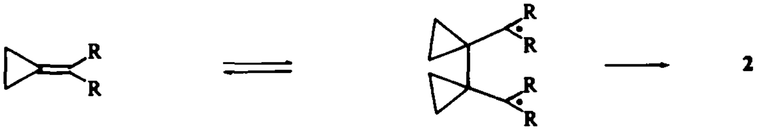
A limit to the generality of the dimerization process was reached, however, with the attempt to dimerize isopropylidenecyclopropane (**1c**). Upon heating 2,2-dimethylmethylenecyclopropane (**5**) at temperatures ranging from 210 to 245° for times ranging from four to eighty hours, *no* dimeric species could be isolated. **5** has been reported to convert quantitatively to **1c** upon heating to 225°.[6] The product mixtures were shown to contain no isolable products boiling above 80°. Moreover NMR spectra and GLPC traces indicated that less than 5% of dimeric, cyclopropane-containing species were present. At higher temperatures, or for longer time runs, no **1c** or **5** could be detected as remaining in the product mixture.

5 **1c**

DISCUSSION

There is no doubt that the major driving force for the conversion of **1** → **2** is the rate-determining destruction of the sp^2 cyclopropane-ring carbon. Having an sp^2 carbon in a cyclopropane ring apparently gives rise to a very substantial increment of strain energy of the order of 12 kcal/mole,[7] the destruction of which would provide for a significant thermodynamic advantage for [2 + 2] cycloadditions of methylenecyclopropanes both in the initial step and also in the overall process.

The reactivity trend of the various methylenecyclopropanes which we have inves-



1 **6**

tigated, seems to be most consistent with a two-step mechanism involving a diradical intermediate (**6**). If such is the case, the initial bond is most-certainly formed at the ring carbons so as to take full advantage of the relief of strain, and to avoid formation of the relatively unstable cyclopropyl radical. For the reaction to be facile, it is apparently necessary that **6** be reasonably stable, as it is for **1a** where R=Cl. When R=H, and primary radicals must prevail, the reaction is sluggish, but not entirely excluded. With R=Me, non-bonded interactions probably impede the cyclization step severely enough so that other reactions compete favorably with dimerization. When the alkyl groups are 'tied back' as with **1d** and **1e**, the problem of non-bonded interactions is apparently somewhat abated, thus allowing a reasonably facile dimerization.

It should be mentioned that if diradical **6** is involved as an intermediate; it must be short-lived, since cyclopropyl carbinyl radicals themselves have been demonstrated to convert irreversibly, and with relative ease, to allyl carbinyl radicals.[8,9] While the activation energy for this process has not been determined, there can be little doubt that it is significant since both gas and liquid phase chlorinations of methylcyclopropane lead to significant amount of *unrearranged* chloromethylcyclopropane.[10,11] On the other hand, the activation energy for cyclization of the tetramethylene diradical should be relatively small (estimated by O'Neal and Benson to be ~6 kcal/mole[12]).

Certainly, no dimers without cyclopropane rings were detected in our experiments. Mechanistically, then, our conclusion must be that the intermediacy of a short-lived diradical is most consistent with the data, although a concerted process cannot rigorously be excluded.

While there does seem to be a steric limitation to the dimerization reaction, the process nevertheless shows promise of wide scope. Moreover, it seems probable that methylenecyclopropanes may participate generally in [2+2] cycloadditions as do the polyfluorinated olefins. It should be mentioned that methylenecyclopropane itself was earlier found to undergo a [2+2] cycloaddition with tetrafluoroethylene.[13] This reaction could however have been attributed to the reactivity of the tetrafluoroethylene, especially since these workers could not observe any similar cycloadditions with maleic anhydride and acrylonitrile both of which are generally reactive in [2+2] processes. It now seems probable that **1a**, (R=Cl), should be very reactive in general [2+2] processes and that such reactions could provide reasonably simple synthetic routes to various spiro-, dispiro-, trispiro- and tetraspiro systems.

EXPERIMENTAL

Analyses were determined by Atlantic Microlab, Inc., Atlanta, Ga. 30308. The GLPC analyses were carried out on a Varian Aerograph Model A-90-P3 gas chromatograph combined with a Leeds and Northrup Model H recorder. IR spectra were recorded with a Perkin-Elmer Model 137 spectrophotometer, KBr prism; NMR spectra on a Varian Model A-60-A spectrometer, utilizing TMS as an internal standard; mass spectra on a Hitachi Perkin–Elmer RMU-6E mass spectrometer; and UV spectra on a Cary 15 spectrometer.

2,2-*Dichloromethylenecyclopropane.*[14] 80g of allene was condensed in to a 1 liter flask equipped with mechanical stirrer, dry ice condenser and dropping-funnel with N_2 inlet, containing 0·4 l pentane and 40 g NaOMe (cooled to −40°). Then 96 g ethyl trichloroacetate was added all at once and the mixture allowed to warm slowly while stirring. At −10°, refluxing began and at −8° the solution turned a tar color. The mixture was allowed to warm overnight, collecting excess allene in a dry ice trap, and ~200 ml water added. The aq. layer was washed with 200 ml pentane layers combined, dried and distilled at atm pressure through a 1 ft vigreaux column. The fraction distilling between 90–100° was collected (60% pure), the only contaminant being ethyl methyl carbonate (yield~30%). The NMR of 2,2-dichloromethylenecyclopropane showed three triplets at δ 2·10 (*j* 2·8 Hz) [2H], 5·65 (*J* 2½ Hz) [1H] and 6·03 ppm (*J* 3 Hz) [1H]. The dichloride was utilized without further purification.

Dichloromethylenecyclopropane (**1a**). Essentially quantitative conversion of 2,2-dichloromethylenecyclopropane to **1a** was achieved by slowly dropping the impure dichloride through a 1 ft vigreaux column heated to 250–300° and collecting emerging vapors at the bottom in a dry ice trap. The product was essentially free of dimer **2a**. The NMR of **1a** showed only a singlet at δ 1·48 ppm and the mass spectrum a parent peak at *m/e* 122. **1a** was still contaminated with ethyl methyl carbonate and was utilized as such in the next step.

7,7,8,8-*Tetrachlorodispiro*[2.0.2.2]octane (**2a**). The impure **1a** obtained above was refluxed neat at ~110° for eight hr, cooled and filtered. The filtrate was examined by NMR for unrearranged 2,2-dichloromethylenecyclopropane. If present, the filtrate was recycled through the pyrolysis procedure. The resultant yellow crystals were recrystallized (MeOH) to yield **2a**: essentially quantitatively white plates, m.p. 167–169; NMR, two symmetrical multiplets centred at δ 0·64 and 1·13 ppm and mass spectrum with a parent peak at *m/e* 244.

7,8-*Dichlorodispiro*[2.0.2.2] *oct-7-ene* (**3**). 16 g Zn dust, 6 g **2a** and 150 ml absolute EtOH were refluxed for 5 hr, after which the mixture was filtered. Petrol was added to the filtrate and the mixture washed with water and dilute HCl. The petrol was dried and evaporated to give pale yellow crystals. Recrystallization (EtOH) gave 3·7 g (87%) of dichloride **3**: white crystals, m.p. 50–51°; NMR, two symmetrical multiplets at δ 0·50 and 0·85 ppm; λ_{max} (hexane) 203 mμ (ε 1·0 × 10^3). (Calc. for $C_8H_8Cl_2$: C, 54·8; H, 4·58. Found: C, 54·60; H, 4·44%).

Dispiro[2.0.2.2]*oct-7-ene* (**4**). Using 18 g powdered Na metal, 30 g t-BuOH and 300 ml dry THF, 10·8 g of **3** was reduced by the procedure of Gassman.[15] After eight hr reflux, the solution was decanted from the Na residue. The residue was washed with pentane, the pentane added to the product mixture and the mixture washed numerous times to remove *all* THF. The remaining pentane solution was dried and the pentane removed by distillation through a 1½ ft column packed with glass helixes. The residue (~40 ml) was then fractionally distilled through a vigreaux column with the fraction coming over between 110°–120° being virtually pure **4** (4·5 g, 69%). A significant amount of polymerization may occur during this distillation and in the receiver pot. To avert this, the distillation can be carried out at aspirator pressure, collecting the less pure product in a dry ice trap and diluting it *at least* to a 33% solution with CH_2Cl_2 chloride. Hydroquinone is also added as a stabilizer: NMR, two symmetrical multiplets at δ 0·47 (4H) and 0·73 (4H) and a singlet at 6·13 ppm (2H); IR, *inter alia*, (12 mm, gas phase) at 3080, 3010, 1014, 933, 876 and 737 cm^{-1}; λ_{max} (EtOH) 203 mμ (ε 5·72 × 10^3). Calc. for C_8H_{10}:C, 90·50; H, 9·50. Found: C, 90·35; H, 9·60%). Ozononlysis of **4** in MeOH following the procedure of Bailey,[16] followed by oxidation of the ozonide by performic acid results in > 80% yield of bicyclopropyl-l, l′-dicarboxylic acid[17]: NMR, two symmetrical multiplets at δ 0·62 [4H] and 1·01 [4H] and a broad singlet at 12·7 ppm [2H]. (Calc. for $C_8H_{10}O_4$: C, 56·46; H, 5·92. Found: C, 56·34; H, 6·00%).

Dispiro[2.0.2.2]*octane* (**2b**). Upon addition of a small quantity of hydroquinone to 0·50 g methylenecyclopropane,[18] the mixture was sealed in a pyrex tube (~3 ml) and heated in a tube furnace at 240–245° for 48 hr. 20% Dimer was formed amd was separated from the mixture by Vacuum line transfer of volatile materials followed by GLPC of the residue using a ¼″ × 10′ column, 10% carbowax (30 M) on Chromosorb P: NMR, two symmetrical multiplets at δ 0·16 (4H) and 0·27 (4H) and a singlet at 2·18 ppm (4H); IR (CCl_4), 2932 (s), 2833 (w), 1412 (m), 1013 (s), 1000 (s), and 873 (s) cm^{-1}; MS (70 eV), *m/e* 108 (p), 94, 80 and 66. (Calc for C_8H_{12}: C, 88·82; H, 11·18. Found: C, 88·57; H, 11·14%).

2,2-*Dibromo*-3,3-*dimethylmethylenecyclopropane*.[20] 29·8 g of $CHBr_3$ was added to a slurry of 3-methyl-1,2-butadiene[19] (6 g) and 13·5 g of tBuOK in 100 ml hexane over a period of 100 min while maintaining a temp. of −6 –0°. After standing at room temp overnight, the soln was diluted with 80 ml H_2O, the organic layer sepd. and the aq. layer extracted with ether. Drying, evapn and fractionation gave 13·7 (64%) of the dibromide (b.p. 60–70°/23 mm).

2-*Bromo*-3,3-*dimethylmethylenecyclopropane*.[20] 2,2-Dibromo-3,3-dimethylmethylenecyclopropane (13·7 g) was reduced using the procedure of Kuivila to yield 5·05 g of the bromide (55%).

2,2-*Dimethylmethylenecyclopropane* (**5**).[20] The 2-bromo-3,3-dimethylmethylenecyclopropane (5 g) was reduced using the method of Kuivila to give 0·92 of **5** (36%).

Pyrolysis of 2,2-*Dimethylmethylenecyclopropane* (**5**). In the pyrolyses of **5**, with or without added hydroquinone, at temperatures from 210 to 245° and for times from 4 to 82 hr, *no* detectable dimeric products were formed. GLPC indicated that no appreciable amount of material boiling over 80° was produced, (other than polymeric).

Tetraspiro[3.0.3.0.2.0.2.0]*tetradecane* (**2e**). Cyclopropylidene cyclobutane* was sealed in a pyrex tube and pyrolyzed at 210° for 4 hr. Small amounts of volatile materials were removed on the vacuum line and 2e was purified by GLPC using the carbowax (20 m) column at 170°. NMR, two symmetrical multiplets at δ 0·20 (4H) and 0·40 (4H) and a complex broad group of peaks between 1·3 and 2·3 ppm (12 H). (Calc. for $C_{14}H_{20}$: C, 89·4; H, 10·6. Found: C, 89·33; H, 10·69%).

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