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CYCLOADDITIONS WITH DICHLOROKETENE [1].

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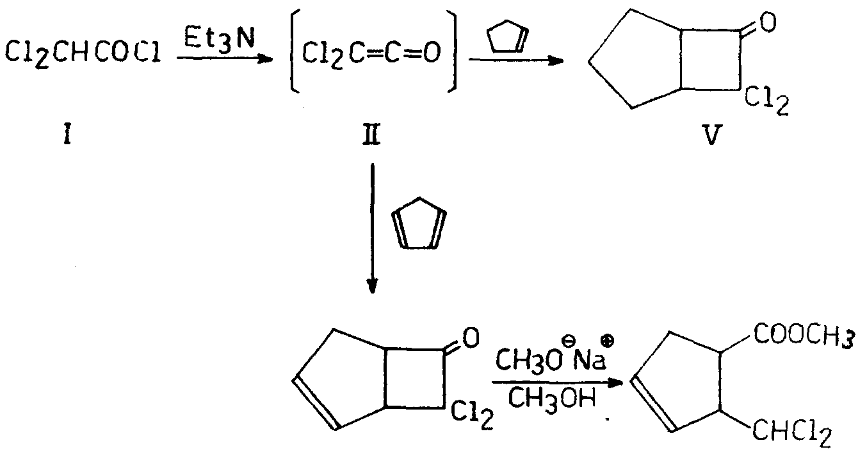
The activating effect of halogen substitution on a system of cumulated double bonds has been observed in several cases. Tetrachloro[2]- and tetrafluoroallenes[3] show a much stronger tendency to dimerize or polymerize than allene itself; ethylchloro[4]- or bromoketenes[5] polymerize in a few minutes even at -80°C. An attempt to prepare dichloroketene[4] by vacuum pyrolysis of mixed dichloromalonic-diphenylacetic anhydride lead to unidentified tars. These observations suggested to us that haloketenes could be specially effective in forming cyclobutanone derivatives by cycloaddition to unsaturated hydrocarbons. The exemples selected for this communication show this is indeed the case.

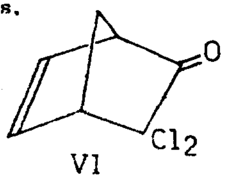
Dichloroketene II could be generated in situ by the dehydrohalogenation of dichloroacetylchloride I with triethylamine. Thus the dropwise addition of triethylamine (0.95 M.) into a refluxing pentane solution of dichloroacetylchloride (0.88 M.) and cyclopentadiene (2.62 M.) yielded 75 % of a colourless sweet smelling liquid[6], b.p. 71-73°/3 mm. n_D^{25} = 1,5136. (Anal.[7] Found: C, 47.28; H, 3.41; Cl, 39.85. Calcd. for $C_7H_6Cl_2O$: C, 47.49; H, 3.41; Cl, 40.06. Molec. W. (cryosc. in dioxane). Found : 181;

Calcd. : 177.03). The adduct appeared homogeneous on the basis of gas-liquid and thin-layer chromatography. It showed a strong absorption in the

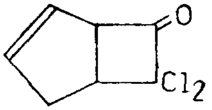


I II V III IV

infra-red (film) at 1807 cm^{-1} indicative of a four-membered ring ketone bearing α-halogen groups[8]. The weak absorption at 1608 cm^{-1} and the multiplet centered at τ 4.07 (2 H) are attributable to an olefinic double bond. In addition the proton magnetic resonance spectrum[9] exhibited two complex multiplets respectively at τ 5.57-6.12 (2 bridgehead tertiary H) and τ 7.17-7.48 (2 allylic methylene H). These data exclude structure VI (the 1,4 cycloadduct) from further consideration but do not allow to decide between III and VII, the two possible 1,2 adducts.

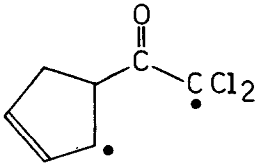


VI

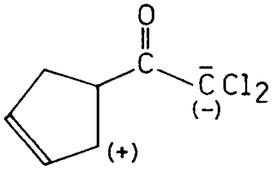


VII

This was done as follows: the four-membered ring could be easily opened on treatment of the adduct with methanolic sodium methoxide at -5°C. The resulting product (73 %), b.p. 118°5-119°5/11 mm. (Anal. Found: C, 45.90; H, 4.72; Cl, 33.77. Calcd. for $C_8H_{10}Cl_2O$: C, 45.95; H, 4.82; Cl, 33.92) presented infra-red absorptions at 1739 cm^{-1} (unconjugated ester) and 1620 cm^{-1} ($>C = C<$ stretching). The n.m.r. spectrum showed a complex signal (3 H) around τ 4.20 consisting of a doublet (τ 4.15, J=4 cps) due to the $-C\underline{H}Cl_2$ grouping and a multiplet corresponding to two olefinic protons; the characteristic signal for the methoxy group appeared at τ 6.29 (sharp singlet, 3 H). The β,γ position of the double bond with respect to the ester group could be excluded by the fact that no isomerisation to an α,β conjugated ester could be effected by means of strong basic or acidic reagents. These data indicated that the ester was best represented by structure IV. Hence we could safely assign structure III (with the double bond γ,δ to the carbonyl) to the dichloroketene-cyclopentadiene adduct. This result is consistent with the behaviour of other ketenes which react with conjugated dienes to form exclusively the 1,2 cycloadduct. The direction of addition cannot help for distinguishing between a diradical or an ionic mechanism: structure III is indeed expected from a ring closure involving either the most stable diradical VIII or the most stable ionic pair IX. Experiments designed to define the nature of the mechanism are now in progress.



VIII



IX

Dichloroketene could be also effectively trapped by an unactivated alkene such as cyclopentene. An adduct V, b.p. 70-72°/2.5 mm, n_D^{25} = 1.5000, was formed in 67 % yield which showed the correct elemental analysis (Found: C, 46.76; H, 4.60; Cl, 39.60. Cal cd. for $C_7H_8Cl_2O$: C, 46.95; H, 4.51; Cl, 39.61). The structural elucidation resulted from the spectral data: the infra-red spectrum exhibited a carbonyl band at 1807 cm^{-1} but no absorption in the olefinic region. The n.m.r. spectrum showed three complex multiplets centered respectively at τ 5.98, τ 6.61 and ca. τ 8.00 in the ratio 1:1:6.

This result contrasts strongly with the relative inertness of ketene and alkylsubstituted ketenes toward unactivated olefins[10].

Similar results have been obtained with other olefins and dienes and will be reported in the full publication.

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References.

1. This work was supported by the "Fonds pour la Recherche Scientifique Fondamentale Collective". Two of us (L.G. and R.M.) are indebted respectively to the F.N.R.S. and I.R.S.I.A. for the award of Fellowships.
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6. When this manuscript was in preparation, a report appeared (H. C. Stevens and al., Abstracts of the 150th Meeting of the American Chemical Society, Atlantic City, Sept. 1965, p. 62S) which described a tropolone synthesis from the dichloroketene-cyclopentadiene adduct.
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