

THE REACTION OF DICHLOROKETENE WITH 4-METHYLENE-*spiro*[2,4]HEPTANE

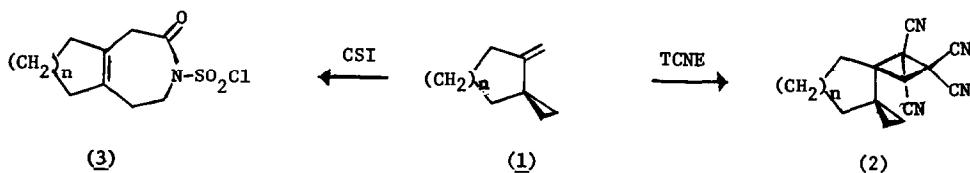
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Our studies of the cycloadditions between electron-rich homodienes of the *spiro*-vinylcyclopropane structure (1) and electron-deficient olefins indicated two distinctly different modes of addition. One mode, the [2+2]cycloaddition is manifested by tetracyanoethylene (TCNE) which affords the cyclobutane derivative (2)¹, and the second one, the [2+4]cycloaddition is displayed by N-chlorosulfonyl isocyanate (CSI) and involves the vinylcyclopropane unit, to form the 7-membered ring lactam (3)². Dichloroketene (DCK, Cl₂C=C=O) is as favorably constituted as CSI to play an antarafacial role as the π₂_a component in (nearly) concerted reactions^{3,4}. In view of this, we deemed it of interest to examine the reaction pattern between DCK and 4-Methylene-*spiro*-[2,4]heptane (1), and a brief account of such study is presented here.

A solution of (1) (10 mmoles) in pentane was mixed with two-fold excess of dichloroacetyl chloride and triethylamine under N₂ at 40°, setting an exothermic reaction. Glc separation (6'x1/4" column, 5% OV 17 on Gas chrom Q, 200°, 40 ml H₂/min.) afforded two isomeric products (30-35%) in a ratio 1:4. The major product (ret. time 26 min.), m.p. 69° (decom.) analyzed as a C₁₂H₁₂O₂Cl₄ bis-adduct, displaying an ester absorption band in the ir spectrum (KBr, 1775 cm⁻¹) and a conjugated polyenic uv absorption band at 272 mμ (EtOH, ε 14900).



The nmr spectrum (CDCl_3) indicate the presence of cyclopropane resonances at τ 9.15 (4H^{a} , m) multiplets at 8.55-7.90 (4H^{b}), 7.75-7.20 (2H^{c}), a triplet at 4.65 (1H^{d} , J 2Hz) and a singlet at 4.08 (1H^{e}). This is assigned the 4-(1,1-dichloro-2-dichloroacetoxy-allylidene)-*spiro*[2,4]heptane formulation (8) (Scheme 1).

The mass spectrum of (8) exhibits the parent molecular ion at m/e 328 (12% of the base peak) (with the expected isotopic ratios at 330, 332 and 334) and peaks at m/e 293 (M-Cl), 200 [$\text{M}-(\text{CHCl}_2\text{COOH})$] and 165 (base peak) corresponding to loss of a chlorine atom from the latter or a molecule of CHCl_2COOH from the former.

The minor product (r.t. 17 min.) which tends to decompose slowly even at 0° is assigned the 4-(3,3-dichloro-2-dichloroacetoxy-allyl)-*spiro*[2,4]hept-4-ene formulation (9) on the basis of : (i) its ir spectrum in neat, displaying intense peak at 1818 cm^{-1} ; (ii) its 60 MHz nmr spectrum in CCl_4 , indicating the presence of cyclopropane resonances at 9.55-8.65 (4H^{a} , m), and multiplets at 8.55-7.0 ($4\text{H}^{\text{b}}+2\text{H}^{\text{c}}$) and 4.40 (1H^{d}), and a singlet at 4.08 (1H^{e}) [identical with corresponding proton in (8)]; (iii) its low wavelength uv band at 217 m μ (in EtOH, ϵ 4300) indicative of deconjugation of the dienic system.

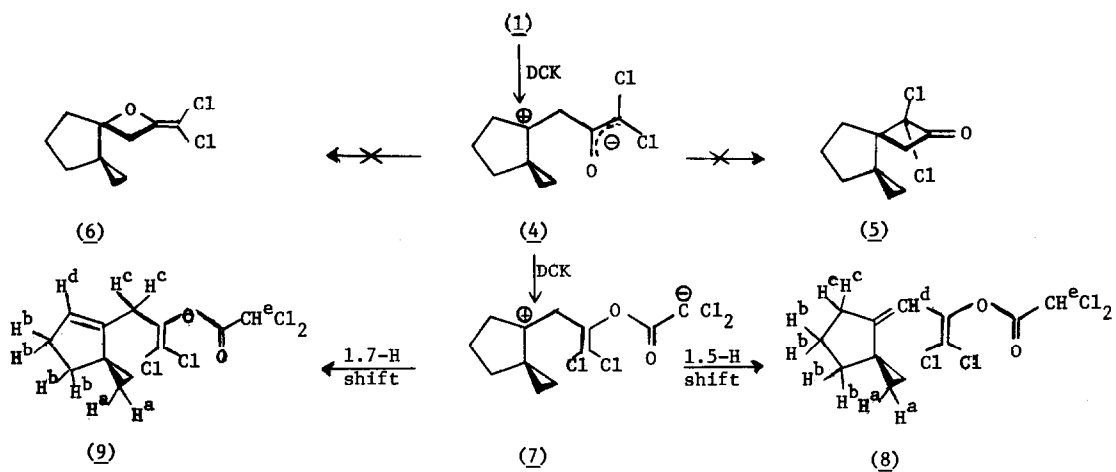
The mass spectrum of (9) indicates lower abundance of the molecular ion peak at m/e 328 (7.4% of the base peak at m/e 165) and similar cracking pattern to that of (8) (peaks at m/e 292 and 200) arising from the fragmentation of the molecular ion.

Mechanistically, the formation of (8) and (11) can be envisioned as arising from electrophilic attack of DCK on (1) to generate zwitterion (4) which reacts rapidly with an additional molecule of DCK to form a dipolar species (7) in which the charges on the polar heads are considerably separated.^{5,6,7} The collapse of (4) into the highly strained dispiro products (5) or (6) could not be observed. Zwitterion (7) is stabilized *via* two distinctly different modes of protropic shifts: 1,5 and 1,7 hydrogen migrations, to yield (8) and (9), respectively (Scheme 1).

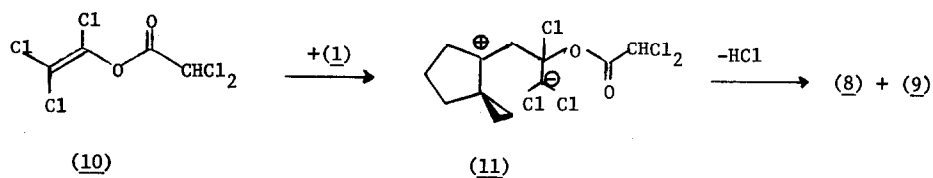
In view of the tendency of disubstituted acetyl halides to produce α -halovinyl esters under the influence of triethylamine^{8,9}, the formation of (8) and (9) can alternatively be envisioned as involving a reaction between trichlorovinyl dichloroacetate⁷ (10) and (1) to generate the zwitterion (11) which loses HCl to provide the open-chain adducts (Scheme 2).¹⁰

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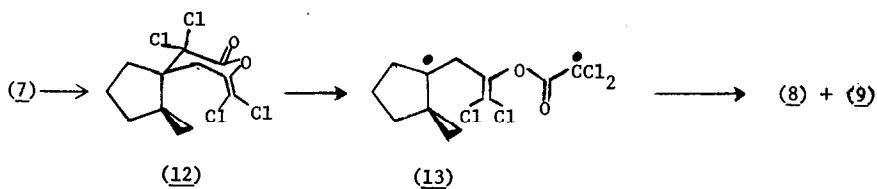
Scheme 1



Scheme 2



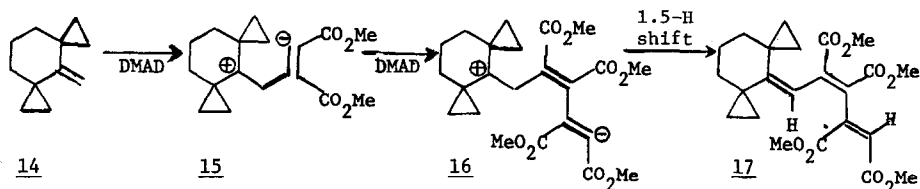
Scheme 3



A third alternative reaction mechanism is delineated in Scheme 3. It suggests that zwitterion (7) first collapses into (12) and then, *via* homolytic ring-opening and hydrogen shifts affords (8) and (9).

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