Cycloaddition of Dichloroketene to Acetylenes. A Synthesis of Cyclobutenones[1]

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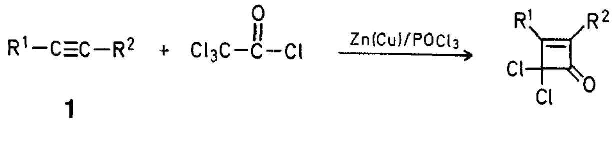
Despite the successful application of the dichloroketene cycloaddition to alkenes[2] there have been only scattered examples of the use of alkynes in these reactions[3,4].

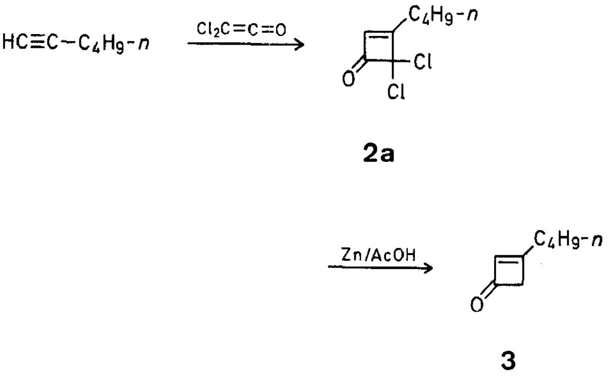
We wish to report that the cycloaddition of dichloroketene to acetylenes is a general and useful method for the synthesis of cyclobutenones **2**. Dichloroketene was generated *in situ*[5] from trichloroacetyl chloride with activated zinc in the presence of phosphoryl chloride and of an alkyne **1** at room temperature (Scheme **A**).



Scheme **A**

The reaction proceeds readily with mono- as well as with disubstituted acetylenes and eneynes react preferentially by cycloaddition to the triple bond (see Table). The yields of the dichlorocyclobutenones range between 32 and 85%. The major advantage of this procedure lies in the formation of cleaner products and in higher yields of the cyclobutenones **2**. For instance, in the absence of phosphoryl chloride the reaction of 1-hexyne with the ketene led to a mixture of products which was difficult to purify. Furthermore, the yield of **2d** by our method is much higher (85%) than as previously reported (12%)[4] when the ketene was generated by the reaction of dichloroacetyl chloride with triethylamine.

That the regiochemistry of the cycloaddition parallels that of alkenes was demonstrated by dechlorination of the dichlorocyclobutenone **2a** to the cyclobutenone **3** [^{1}H-N.M.R.: $\delta = 5.85$ (s, vinyl H); 3.13 ppm (s, CH_2)]; see Scheme **B**.



Scheme **B**

Dichlorocyclobutenones 2; General Procedure:

Trichloroacetyl chloride (24.4 mmol) and phosphoryl chloride (24.4 mmol) in anhydrous ether (10 ml) are added over a period of one hour to the acetylene **1** (12.2 mmol) and activated zinc[5] (36.6 mmol) in anhydrous ether (50 ml) with stirring and under nitrogen. The mixture is heated under reflux for 14 h, filtered on a pad of Celite, and the filtrate washed successively with water, sodium hydrogen carbonate solution, and saturated sodium chloride. After solvent removal, the product is purified at reduced pressure by bulb to bulb distillation or by chromatography over silica gel.

Table. Cycloaddition of Dichloroketene to Acetylenes **1**

Product	R^1	R^2	Yield [%]	m.p.	Molecular formula[a] or Lit. m.p.	^{1}H-N.M.R. δ [ppm]
2a	n-C_4H_9	H	77		$C_8H_{10}Cl_2O$ (193.1)	6.23 (s, 1H); 2.72 (t, 2H), 2.0–0.7 (m, 7H)
2b	C_2H_5	C_2H_5	62		$C_8H_{10}Cl_2O$ (193.1)	2.7 (q, 2H); 2.15 (q, 2H); 1.35 (t, 3H); 1.03 (t, 3H)
2c	C_6H_5	C_6H_5	32	121°	121°[6]	8.1, 7.8, 7.63 (3 br m)
2d	CH_3	CH_3	85		$C_6H_6Cl_2O$ (165.0)	2.20 (s, 3H); 1.73 (s, 3H)
2e	$H_2C\ \ C(CH_3)$	H	45		$C_7H_6Cl_2O$ (177.0)	6.30 (s, 2H); 5.93 (s, 1H); 2.10 (s, 3H)

[a] The microanalyses for the new compounds were in satisfactory agreement with the calculated values (C ±0.18, H ±0.06).

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[1] Cycloadditions; XXVII. For paper XXVI: see A. Hassner, L. Krepski, *J. Org. Chem.* **43**, 2879 (1978).

[2] W. T. Brady, *Synthesis* **1971**, 415.
L. Ghosez et al., *Tetrahedron* **27**, 615 (1971).
D. A. Bak, W. T. Brady, *J. Org. Chem.* **44**, 107 (1979) and literature cited therein.

[3] E. V. Dehmlow, *Chem. Ber.* **100**, 3829 (1967).
A. Krebs, H. Kimling, *Justus Liebigs Ann. Chem.* **1974**, 2074.
H. N. C. Wong et al., *Tetrahedron Lett.* **1976**, 2715.
D. Bellus et al., *Helv. Chim. Acta* **61**, 1784 (1978).

[4] H. Knoche, *Justus Liebigs Ann. Chem.* **722**, 232 (1969).

[5] A. Hassner, L. Krepski, *J. Org. Chem.* **43**, 2879 (1978).

[6] E. V. Dehmlow, *Chem. Ber.* **100**, 3829 (1967).

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