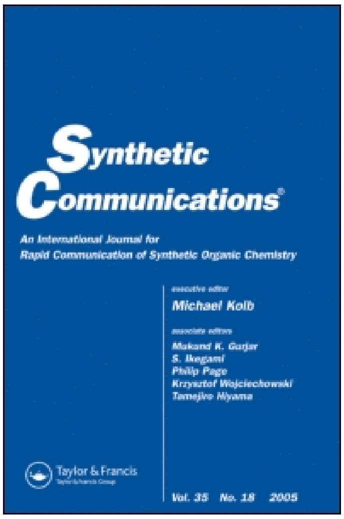

Synthetic Communications
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597304

Ultrasound Promoted Dichloroketene-Olefin Cycloadditions

Goverdhan Mehta[a]; H. Surya Prakash Rao[a]
[a] School of Chemistry, University of Hyderabad, Hyderabad, India

To cite this Article Mehta, Goverdhan and Rao, H. Surya Prakash(1985) 'Ultrasound Promoted Dichloroketene-Olefin Cycloadditions', Synthetic Communications, 15: 11, 991 — 1000
To link to this Article: DOI: 10.1080/00397918508076831
URL: http://dx.doi.org/10.1080/00397918508076831

SYNTHETIC COMMUNICATIONS, 15(11), 991-1000 (1985)

ULTRASOUND PROMOTED DICHLOROKETENE-OLEFIN CYCLOADDITIONS

Goverdhan Mehta* and H. Surya Prakash Rao

School of Chemistry, University of Hyderabad
Hyderabad 500134, India

ABSTRACT: We have observed that olefin-dichloroketene 2+2 cycloadditions are accelerated by ultrasonic irradiation. Short reaction times, good yields, ambient reaction conditions and use of ordinary bench-top zinc instead of activated zinc (Zn-Cu couple) are the significant advantages of this procedure.

The 2+2 cycloaddition of dichloroketene to reactive olefins is a versatile reaction that has figured prominently in the synthetic sequence leading to many natural[1] and unnatural products.[2] Since dichloroketene is a labile and reactive species, it is almost mandatory that it be generated _in situ_ by a convenient and efficient technique for effective deployment in synthesis. The two commonly used methods for generating dichloroketene are the dehalogenation of trichloroacetyl chloride by activated zinc and dehydrohalogenation of dichloroacetyl chloride with triethylamine.[3] Of the two, zinc dehalogenation method

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*To whom correspondence should be addressed.

0039-7911/85/1511-0991$3.50/0

appears to be widely employed procedure and many tactical modifications have been proposed to improve the yield of cycloaddition product and simplify the isolation procedure. These comprise of high dilution technique,[4] slow rate of addition of trichloroacetyl chloride to the activated zinc and olefin and the addition of phosphorous oxychloride along with trichloroacetyl chloride to the reaction mixture as scavenger for zinc chloride.[5] However, dichloroketene cycloadditions still take frustratingly long reaction times (an overnight period is unexceptional) and usually require large excess of the olefin.

In this report, we wish to record our observation that there is a significant rate enhancement in olefin-dichloroketene cycloaddition when reactions are carried out under ultrasonic irradiation (Fig.1). This finding agrees well with recent observations[6] that exposing heterogenous reactions to ultrasonic irradiations increases rate and efficiency of several reactions. It is, however, not clear whether this rate enhancement is due to cavitation effect or better agitation.[6g]

Our results with seven assorted mono- bi- and polycyclic olefins are summarised in Table 1. In all the cases, the reaction was more or less complete by the time addition of trichloroacetyl chloride

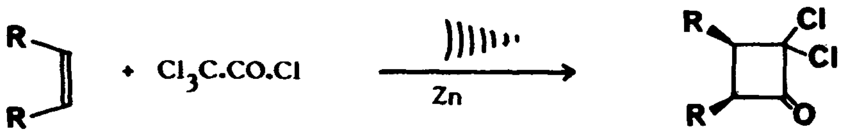
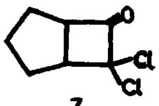
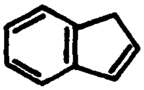
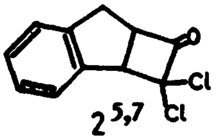
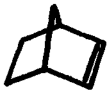
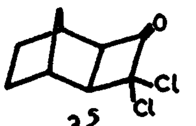
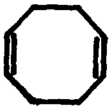
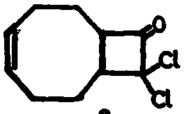
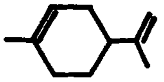
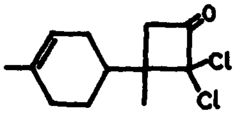
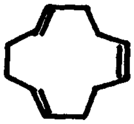
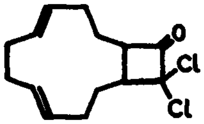
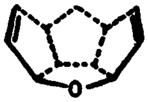
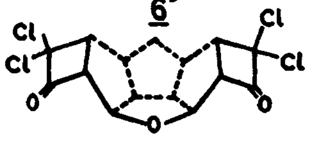


FIG. 1

Table 1

Olefin	Product	Yield %[a] (Reaction time in min.)[b]
	 $\underline{1}^{7}$	70 (20)
	 $\underline{2}^{5,7}$	80 (60)
	 $\underline{3}^{5}$	75 (45)
	 $\underline{4}^{8}$	70 (45)
	 $\underline{5}$	80 (20)
	 $\underline{6}^{9}$	90 (20)
	 $\underline{7}^{2c}$	45 (30)[c]

a. Yield refers to purified product; Yield of the crude product was higher.
b. Time for the completion of the reaction is not optimized.
c. 20% of mono-adduct was obtained.

ceased.[10] However, additional few minutes were given to ensure complete reaction. Significantly higher yields of the cycloaddition products were encountered in case of cyclopentene and 1,5-cyclooctadiene and no diadduct was formed in the later case.[5,7,8] The considerable short reaction times reported here result in cleaner products as dichloroketene polymerisation is minimised. Another notable feature of our procedure is that under ultrasound irradiation, commercially available zinc dust can be effectively used for dichloroketene cycloadditions. In the examples reported in Table 1, we found practically no difference in reaction time and yields whether the reaction was carried out with ordinary zinc or activated zinc (Zn-Cu couple).[5] Thus, good yields, shorter reaction times (~1 h), use of bench-top zinc dust and ambient reaction conditions are the advantages of this procedure, which we believe will find routine use for dichloroketene additions.

Experimental Section

Melting points were determined on a Buchi SMP-20 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer. All chemical shifts are reported in units relative to Me_4Si in $CDCl_3$ solution. In the ^{13}C NMR spectral data off resonance multiplicities are given in parentheses. Infrared spectra were recorded on Perkin-Elmer 293 spectrophotometer. All starting olefins were obtained from commercial sources or were available in the laboratory and were distilled or recrystallised before use.

Zinc dust purchased from Ranbaxy Laboratories Ltd., was used as supplied. Sonications were carried out in a common ultrasonic laboratory cleaner (Julabo USR3, 220V-50 Hz, 100 W, operating at 35 KHz) partially filled with water at ambient temp. (15-20°C).

General Procedure for Olefin-dichloroketene Cycloadditions: In a typical run, dry nitrogen filled, 100 ml, three-necked round bottomed flask filled with a nitrogen inlet and pressure equalising addition funnel was charged with (5 mmol-10 mmol) olefin, (10 mmol-15 mmol, 2 eq.) zinc dust and 50 ml of anhydrous ether. The flask was then partially submerged in the sonicator water bath in a place that produced maximum agitation. To this suspension (7.5 mmol-15 mmol, 1.5 eq.) of trichloroacetyl chloride in 25 ml anhydrous ether was added during 30 min period while sonication continued. Ice pieces were added occasionally to the water bath to maintain the temperature between 15-20°C. Reaction was usually complete within 60 min. After quenching with wet ether the reaction mixture was filtered through celite and the filtrate was washed with water (2 x 20 ml), saturated sodium bicarbonate solution (5x20 ml) and brine solution (20 ml). After drying the etherial solution over anhydrous Na_2SO_4 the solvent was removed. Purification of the crude dichlorocyclobutanone was effected by chromatography over a short (1.5 x 30 cm) column of silica gel and vacuum distillation or crystallisation.

7,7-Dichlorobicyclo[3.2.0]heptan-6-one (1): Reaction of 500 mg (7.34 mmol) cyclopentene, 980 mg (15 mmol) zinc dust and 2 g (1.22 ml, 11 mmol) trichloroacetyl chloride afforded 920 mg (70%) of the required compound after bulb to bulb distillation (bath temp. 90°C, 1.5 mm). IR (neat) 1800 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 4.0(t,1H), 3.32(t,1H), 2.36-2.0 (m,2H), 1.9-1.3(m,4H); ^{13}C NMR(CDCl$_3$) δ 199.14(s), 88.68(s), 62.29(d), 52.60(d), 30.71(t), 30.0(t), 25.80(t).

3,4-Benzo-66,-dichlorobicyclo[3.2.0]heptan-7-one (2): Reaction of 500 mg (4.3 mmol) indene, 562 mg (8.6 mmol) zinc dust and 1.17 g (0.72 ml, 6.45 mmol) trichloroacetyl chloride afforded 732 mg (80%) of the required compound after crystallisation from hexane, mp 78°C. IR (KBr) 1800 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.50-7.15(m,4H), 4.46-4.38(m, 2H), 3.30-3.08(m,2H); ^{13}C NMR (CDCl$_3$) δ 196.91(s), 143.31(s), 137.18(s), 129.04(d), 128.28(d), 127.28(d), 125.28(d), 88.71(s), 59.18(d), 58.87(d), 34.16(t).

4,4-Dichloro-exo-tricyclo[4.2.1.0^{2,5}]nonan-3-one (3): Reaction of 720 mg (7.64 mmol) norbornene, 1.03 g (15.3 mmol) zinc dust and 2.0 g (1.22 ml, 11 mmol) trichloroacetyl chloride afforded 1.15 g (75%) of the product after purification by bulb to bulb distillation (bath temp. 130°C, 0.1 mm): IR (neat) 1805 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.52(br d,1H), 2.84-2.6(m,3H), 1.71-1.0(m,6H); ^{13}C NMR (CDCl$_3$) δ 196.20(s), 87.30(s), 65.16(d), 53.89(d), 37.86(d), 34.70(d), 27.35(t), 26.36(t).

10,10-Dichlorobicyclo[6.2.0]dec-4-ene-9-one (4):[8] Reaction of 500 mg (4.62 mmol) 1,5-cyclooctadiene, 600 mg (9.17 mmol) zinc dust and

1.26 g (0.78 ml, 7.0 mmol) trichloroacetyl chloride afforded 1.16 g (70%) of the required product after bulb to bulb distillation (bath temp. 110°C, 0.1 mm). IR (neat) 1805 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.64(br s,1H), 3.88-3.52(m,1H), 3.2-2.8(m,1H), 2.6-1.8(m,8H); ^{13}C NMR ($CDCl_3$) δ 196.73(s), 130.33(d), 129.92(d), 88.0(s), 58.58(d), 49.66(d), 24.17(t), 25.36(t), 25.06(t), 24.12(t).

2,2-Dichloro-3-methyl-3 (4-methylcyclohex-3-enyl] cyclobutanone (5): Reaction of 500 mg (3.28 mmol) limonene, 430 mg (6.50 mmol) zinc dust and 900 mg (5 mmol, 0.55 ml) trichloroacetyl chloride resulted in 1.5 g (81%) of the mixture of diastereoisomers after bulb-to-bulb distillation (bath temp.120°C, 0.1 mm). Regiochemistry of the product was fixed on the basis of following spectral data: IR (neat) 1810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.38(br s,1H), 3.20, 3.16(d,1H), 2.62, 2.56(d,1H), 1.56(br s,3H), 2.4-1.2(m,7H), 1.14-1.12(s,3H); ^{13}C NMR ($CDCl_3$) δ 191.92 (s), 134.09, 133.14(s), 119.70(d), 92.29(s), 54.18, 53.18(t), 47.56(s), 40.18, 39.92(d), 30.64, 30.29(t), 27.06, 26.60(t), 25.18(t), 23.24(q), 18.49(q).

Cis-14,14-dichlorobicyclo[10.2.0]tetradeca-trans, trans-4,8-dien-13-one (6):[9] Reaction of 500 mg (3.08 mmol) trans, trans, cis-1,5,9-cyclododecatriene, 400 mg (6.1 mmol) zinc dust and 836 mg (0.51 ml, 4.62 mmol) trichloroacetyl chloride afforded 1.53 g (90%) of 6 after purification on silica gel column and bulb-to-bulb distillation (bath temp. 130°C, 0.5 mm). IR (neat) 1795 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.12

(m,4H), 3.62-3.32(m,1H), 2.98-2.64(m,1H), 2.4-1.2(m,12H); ^{13}C NMR ($CDCl_3$) δ 196.38(s), 131.98(d), 130.57(d), 130.21(d), 89.29(s), 58.18(d), 49.78(d), 32.40(t), 31.93(t), 30.70(t), 30.47(t), 26.59(t), 25.30(t).

(1R*, 2R*, 5R*, 6R*, 8S*, 9S*, 12S*, 14R*, 15S*)-3,3,11,11-Tetrachloro-7-oxahexacyclo[11.2.1.$0^{2,5}$.$0^{6,15}$.$0^{8,14}$.$0^{9,12}$]hexadecane-4,10-dione (7): Reaction of 50 mg (0.31 mmol) starting diene, 80 mg (1.22 mmol, 4 eq) zinc dust and 168 mg (100μ l, 0.93 mmol, 3 eq) trichloroacetyl chloride afforded 53 mg (45%) of the diadduct 7 after recrystallisation from dichloromethane-pet ether, mp 238-240°C (decomp). IR (KBr) 1810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.45(d,2H), 4.34, 3.46(ABq,2H), 3.3-2.8(m,4H), 2.66-2.1(m,2H), 1.95(m,1H), 1.4(m,1H); ^{13}C NMR ($CDCl_3$) δ 193.71(s), 89.17(d), 87.79(s), 67.54(d), 59.35(d), 56.09(d), 49.66(d), 39.59(t).

Acknowledgement: We thank CSIR and UGC for support under Special Assistance Programme in Organic Chemistry.

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10. In control experiments, using Zn-Cu couple[5] but no ultrasound irradiation, significantly longer reaction times (2-12 h) were required to complete the reaction.