36. Cyclobut-2-enones from Alkynes *via* Dichlorocyclobut-2-enones[1])

by **Adrian A. Ammann, Max Rey,** and **André S. Dreiding***

Organisch-Chemisches Institut der Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich

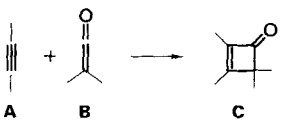
(15.XII.86)

The [2 + 2]-cycloaddition of dichloroketene (prepared *in situ* from CCl_3COCl and Zn(Cu)) with three alkynes **1a–c** to form 2,3-dimethyl- (**2a**), 2,3-diethyl- (**2b**) and 3-butyl-4,4-dichlorocyclobut-2-enone (**2c**) proceeds rapidly in the absence of $POCl_3$. The primary products **2a–c** rearrange *in situ* to the 2,4-dichlorocyclobut-2-enones **3a–c** under the influence of $ZnCl_2$ produced during the reaction. $ZnCl_2$ converts both **2a** and **3a** into a 4:6 equilibrium mixture of the two; this isomerization does not occur with LiCl. The Cl-atoms of both **2a,b** and **3a,b** and of **2c** may reductively be removed with Zn(Cu) in AcOH/pyridine to afford the alkylcyclobutenones **4a–c**. Without pyridine, this reduction gives *ca.* 1:1 mixtures of the double-bond isomers **4** and **5** in low yields. The cyclobutenones **2c** and **4c** may be deuterated by CD_3COOD in the presence of pyridine. D-Atom is introduced into **2c** at C(4) and at C(γ), and into **4c** at C(2) and C(4). A mechanism for this deuteration is considered, which does not involve a cyclobutadienolate **7**, but rather a cyclobutenolate of type **8**. The reductions of **2** and **3** to **4** might also pass through the same type of intermediate **8**.

1. Introduction. – Cycloaddition of acetylenes **A** to ketenes **B** *(Scheme 1)* might be a direct and general approach to cyclobut-2-enones **C**; however, non-activated acetylenes react well only with special ketenoids[2]). Among reactive ketenes, dichloroketene is often preferred because the two Cl-atoms are replaceable by H-atoms. When generated from trichloroacetyl chloride with Zn(Cu), dichloroketene has been reported [3–5] to add to acetylenes in good yields, particularly in the presence of $POCl_3$ [3] [5], but the reductive removal of the Cl-atoms from these cycloadducts had not been achieved reliably[3]). We report a reexamination of some of these reactions, and thereby present a convenient two-step procedure for the preparation of alkylcyclobut-2-enones **4**.

2. Addition of Dichloroketene to Alkynes. – When we added dichloroketene, prepared *in situ* by dehalogenation of CCl_3COCl with Zn(Cu), to 2-butyne (**1a**), 3-hexyne (**1b**), and 1-hexyne (**1c**), we found as products not only the reported [3] 4,4-dichlorocyclobutenones

Scheme 1

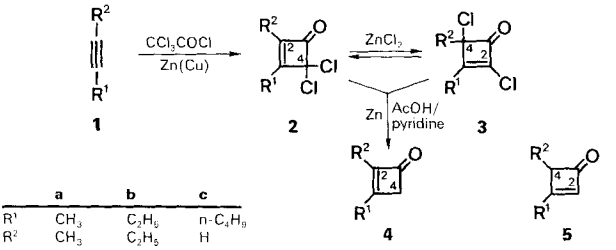


[1]) In part taken from the Ph.D. thesis of *A.A.A.*, University of Zürich, 1986.

[2]) Especially reactive ketenoids are keteniminium salts [1] and ketenes bearing electronegative substituents [2].

[3]) While this reduction was reported [5] to prove the structure of the cycloadduct from dichloroketene and 1-hexyne, it was later found [3] 'to be a difficult task', possibly due to 'unfavorable formation of cyclobutadienyl-oxide anion or radicals'.

Scheme 2



2a–c, but also the 2,4-dichlorocyclobutenones **3a–c** *(Scheme 2)*. Using the conditions of *Hassner* and *Dillon* [3], *i.e.* in the presence of $POCl_3$, the reaction in the **a** and **c** series was worked up after 17–50 h, when the ratios **2**/**3** were 42:58 (**a**: after 17 h) and 70:30 (**c**: 50 h), respectively. Monitoring the course of these two cycloadditions by GC (see *Exper. Part*) showed the primary products to be **2a**,**c** and the secondary ones **3a**,**c**; it also showed the reactions to be half-completed after *ca.* 3 h in the **a**, and after *ca.* 6 h in the **c** series. Contrary to what had been reported in [3] [5], we found $POCl_3$ not to be advantageous for the cycloaddition. In the absence of $POCl_3$, the reaction in the **a**, **b**, and **c** series could be worked up with 50–90% yield after 8–15 min, and the ratios **2**/**3** were 80:20 (**a**: after 15 min), 35:65 (**b**: 15 min), and 100:0 (**c**: 8 min), respectively. Monitoring the course of this reaction without $POCl_3$ in the **a** series showed it to be half-completed after < 2 min. Our monitoring data also indicated that the reaction of dichloroketene with the acetylenes **1**, in the absence of $POCl_3$, could be stopped at a point where **2** was predominant besides only traces of **3**, and that this was the case after a short time. Thus, almost pure **2a** was obtained after 7 min, and **2c** was the only product after 8 min.

The secondary products **3a–c** of this cycloaddition must have been formed from the primary ones **2a–c** by a $ZnCl_2$-induced allylic migration of a Cl-substituted species. A S_N2' attack of halide anion had been reported [6] with 4,4-dihalo-3-phenylcyclobutenones and lithium halide in boiling acetone. Under these conditions with LiCl, we found the 4,4-dichlorocyclobutenone **2a** to remain unchanged. However, in the presence of $ZnCl_2$ in refluxing Et_2O, a 4:6 equilibrium mixture **2a**/**3a** was reached both from **2a** and **3a**.

The structures of **2a–c** and 3**a–c** were assigned on the basis of their spectral properties *(Table)*.

We were anxious to have good criteria for the differentiation between the isomers **2** and **3** (*cf.* also [6]). In the **c** series, the ^{1}H-NMR spectra are conclusive (H–C(2) of **2c**: 6.30 (*t*, J = 1,5); H–C(4) of **3c**: 5.25 (*s*)). In the **a** and **b** series, however, the ^{1}H-NMR-spectra of **2** and **3** are too similar, but the UV, IR, and ^{13}C-NMR spectra show characteristic differences: Because of the Cl-atom at C(2), the UV maxima of **3** are shifted by *ca.* +10 nm with respect to those of **2**, and the separation of the IR bands for C=O and C=C in **3a**,**b** is larger (*ca.* 190 cm^{-1}) [7] than in **2a**,**b** (*ca.* 150 cm^{-1}). The H-atom at C(2) or C(4) disturbs this correlation in the case of **3c** and **2c**. The ^{13}C-NMR chemical shifts of C(2) in **3a**,**b** are shifted by *ca.* −20 ppm with respect to those of **2a**,**b**.

3. Reduction of Dichlorocyclobut-2-enones. – The two Cl-atoms were removed from the dichlorocyclobutenones with Zn(Cu) in AcOH/pyridine 4:1 (*cf.* [8]; *Scheme 2*). Of the two double-bond isomers **4** and **5** which could be the products of these reductions in the **a** and **b** series, only **4** was formed; the same isomer **4** resulted from both **2** and **3**. Thus, **2a** afforded **4a** (62%), **2c** gave **4c** (57%), and **3a** also led to **4a** (60%) (for other syntheses of

Table. *Some Spectroscopic Data of 4,4-Dichlorocyclobutenones* **2a–c** *and 2,4-Dichlorocyclobutenones* **3a–c**

		UV	IR		^{1}H-NMR		^{13}C-NMR				
		λ_{max} (ε)	C=O	C=C	R^1	R^2	C(1)	C(2)	C(3)	C(4)	R^1/R^2
	**a**	223 (8600)	1790	1645[a])	2.28 (*s*)[a])	1.85 (*s*)[a])	181.3	147.9	175.8	92.2	9.4, 8.0[a])
	b	224 (8900)	1785	1630[a])	2.75 (*q*)	2.30 (*q*)	181.6	152.3	178.6	91.8	19.4, 17.2, 10.9, 10.8
					1.40 (*t*)[a])	1.20 (*t*)[a])					
	c	219 (8200)	1800	1585[a])	2.70 (*t*, *J* = 7.5)	6.20 (*t*, *J* = 1.5)[a])	[b])				
					1.9–1.2 (*m*)						
2					0.95 (*t*)[a])						
	**a**	231 (7900)	1805	1615	2.25 (*s*)	1.80 (*s*)	182.4	129.3	178.4	80.5	22.1, 9.7
	b	235 (8300)	1800	1610	2.70 (*q*, *J* = 7.5)	2.20 (*q*, *J* = 7.5)	182.7	128.8	181.3	84.7	29.6, 20.0, 10.1, 9.9
					1.40 (*t*, *J* = 7.5)	1.05 (*t*, *J* = 7.5)					
	c[c])	230 ([b]))	1805	1610	2.8–2.6 (*m*)	5.25 (*s*)	[b])				
					1.9–1.2 (*m*)						
3					1.0 (*t*, *J* = 6)						

[a]) These are values of our own measurements which agree with those given in [3], except for the case of **2b**, where the values given in [3] (IR (neat): 1800, 1605. ^{1}H-NMR: 2.7 (*q*); 2.15 (*q*); 1.35 (*t*); 1.03 (*t*); no UV and ^{13}C-NMR) are closer to our values for **3b**.

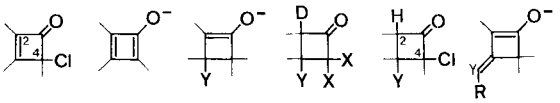
[b]) This was not measured.

[c]) This sample contained 10% of **2c**.

4a and **4c**, see [9] and [10], resp.). Furthermore, a mixture **2b**/**3b** was reduced to yield only **4b** (70%). In the absence of pyridine, *i.e.* in pure AcOH, the Zn(Cu) reductions of **3a**,**b** produced *ca.* 1:1 mixtures of the two double-bond isomers **4** and **5** in much lower yields (**a**: 17%; **b**: 33%).

Thus, the method of choice for the preparation of alkylcyclobut-2-enones **4**, according to our experience, is the Zn(Cu) dechlorination of CCl_3COCl in the presence of alkynes **1** under conditions which ensure a maximum yield of **2**/**3**, followed by Zn(Cu) reduction of the mixture in AcOH/pyridine.

4. Mechanistic Considerations and Deuteration. – α-Haloketones are usually considered to pass through enolates during reductive removal of the halogen atoms. In the case of a 4-chlorocyclobut-2-enone **6**, such an intermediate would be a cyclobutadienolate **7**, expected to be energetically unfavorable (see also *Footnote 3*). Indeed, no D-atom could be incorporated into **4** by a usual enolate-forming procedure: When **4c** was treated with $LiN(i\text{-}Pr)_2$ in THF and then with D_2O, only non-deuterated **4c** was recovered (26%), indicating that no cyclobutadienolate **7** had been formed under these conditions or else that it was destroyed before being subjected to D_2O.



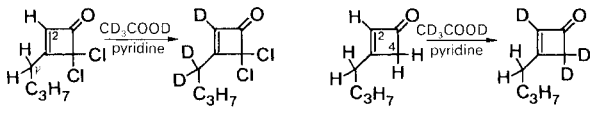
6 **7** **8** **9** **10** **11**

Y pyridinium, AcO or Cl
X = Cl or H

In the presence of (D_5)pyridine, however, we found a rapid D-incorporation with CD_3CO_2D into **2c** and **4c**: The H-atoms at C(2) and C(4) of **4c** and the H-atoms at C(2) and C(γ) of **2c** were replaced by D-atoms at room temperature giving D_3-**4c** and D_3-**2c**, respectively *(Scheme 3)*. The isolated deuterated compounds D_3-**2c** and D_3-**4c** were converted back to **2c** and **4c** on treatment with AcOH/pyridine. In the absence of pyridine, this H/D exchange did not take place.

To avoid the invokation of a cyclobutadienolate **7**, we suggest that these D-exchanges proceed by a rapid *Michael* addition and elimination of pyridine *via* the cyclobutenolate anion **8** during the process of deuteration and deprotonation. Since no intermediate (especially also none of type **9**) could be detected by monitoring the H/D-exchange by ^{1}H-NMR, this mechanism implies the elimination of HY from **10** to be more rapid than its addition to **2** or **4**.

Scheme 3



2c D_3-**2c** **4c** D_3-**4c**

The same type of mechanism could apply to the Zn reductions of **2** and **3**, in which case the enolate **8** would be formed by attack of Zn on the Cl-atom at C(4) of the intermediate **10**. Since the reduction also took place in the absence of pyridine (see above), it seems that AcO^- and/or Cl^- is able to replace pyridine as a *Michael* donor. The reduction of **3a** and **3b** in AcOH alone may remain under kinetic control when it yields the *ca.* 1:1 mixture **4a**/**5a** and **4b**/**5b**, respectively; the function of pyridine would then be to induce thermodynamic control *via* the intermediate **8** to afford the more stable **4a** and **4b**. Indeed, allowing a solution of the *ca.* 1:1 mixture **4b**/**5b** in AcOH/pyridine 4:1 to stand at 40–50° for *ca.* 1 h changed the ratio **4b**/**5b** to 98:2.

The D-replacement of the H-atoms at C(γ) (on the side chain) in **2c**, but not in **4c**, might be due to an enhancement of the enolization tendency of the H-atoms at C(γ) caused by the inductive effect of the two Cl-atoms at C(4) in **2c** (compare **4c**: 2 H-atoms at C(4)). The H/D exchange at the γ-position in **2c** would involve the linear dienolate **11**.

This work was supported by the *Swiss National Science Foundation* and by *Sandoz AG*, Basel.

Experimental Part

1. General. – See [12]. In addition: The alkynes were commercially available and distilled before use. The Et_2O was dried over Na with benzophenone-ketyl as indicator. Zn(Cu) was prepared according to [11]. Some of the reaction courses were monitored in separate assays by taking occasionally aliquots from the reaction mixture, diluting them with Et_2O, shaking with H_2O, and injecting the org. layer into an anal. gas chromatograph (*SE-54*, 0.25 mm × 25 m, 50–100°). Yields determined by GC were obtained by using dodecane as an internal standard. ^{1}H-NMR and ^{13}C-NMR spectra: *Varian-EM-390* or *-XL-200* and *Bruker-AM-400* spectrometer, resp.; intensities are not reported if in agreement with the given interpretation.

2. Addition of Dichloroketene to Alkynes. – 2.1. *General Procedures.* 2.1.1. *Procedure A, in the Presence of $POCl_3$.* The reaction was performed according to [3], but was continued for the time needed to monitor the rearrangement **2**→**3**.

2.1.2. *Procedure B, in the Absence of $POCl_3$.* A soln. of CCl_3COCl in 10 ml of dry Et_2O was added within 3–5 min to a mixture of the alkyne and Zn(Cu) in 50 ml of dry Et_2O in a flask equipped with a dry-ice condenser. When the reaction started (often spontaneously; occasionally brief heating was required) as seen by the boiling Et_2O, the flask was cooled in a manner that left the Et_2O refluxing. When the envisaged result (*Criterion a*, maximum total yield; *Criterion b*, optimal yield of unrearranged product while minimum yield of rearranged product) had been achieved as indicated by a separate monitoring experiment, the reaction was stopped (time mentioned in each case) by pouring the mixture on ice. The separated Et_2O layer was washed with sat. $NaHCO_3$ soln. and dried ($MgSO_4$). Evaporation at reduced pressure left a dark oil which was treated with hexane to precipitate some tarry materials. The yellow oil left after evaporation of the hexane was bulb-to-bulb distilled to afford a pure mixture (GC) of the dichlorocyclobutenones **2** and **3**, separable by LC.

2.2. *4,4-Dichloro-2,3-dimethyl-* (**2a**) *and 2,4-Dichloro-3,4-dimethylcyclobut-2-enone* (**3a**). 2.2.1. *Procedure A.* The reaction of 3.74 g (20.6 mmol) of CCl_3COCl, 4.44 g (28.9 mmol) of $POCl_3$, 325 mg (6 mmol) of 2-butyne (**1a**), and 1.17 g (18 mmol) of Zn(Cu) was stopped after 17 h, when no further changes occurred (for monitoring see below). Distillation at 60–70°/1 Torr gave 880 mg (89%) of a 42:58 mixture **2a**/**3a** (GC) as a colorless liquid ([3]: 85% **2a**). Separation by LC (hexane/2% AcOEt) gave a 1st fraction of pure **3a** as a colorless liquid. UV (EtOH): 231 (7900). IR (film): 1805*s* (C=O), 1615*s* (C=C), 670*s*. ^{1}H-NMR (90 MHz, $CDCl_3$): 2.25, 1.80 (2*s*, 2 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 182.4 (*qq*, J = 6.5, 1.4, C=O); 178.4 (*qq*, J = 7.6, 4.2, C(3)); 129.3 (*qq*, J = 6.1, 1.3, C(2)); 80.5 (*qq*, J = 4.8, 3.6, C(4)); 22.1 (*q*, J = 130, CH_3); 9.7 (*q*, J = 130, CH_3). Anal. calc. for $C_6H_6Cl_2O$ (165.02): C 43.68, H 3.67, Cl 42.97; found: C 43.82, H 3.70, Cl 42.60.

The 2nd fraction contained pure **2a** as as colorless oil, which solidified on standing, m.p. 42.5–43.5° ([13]: 44.5° (from pentane)). UV (EtOH): 223 (8600). IR (film; *cf.* also [3]): 1790*s* (C=O), 1645*s* (C=C), 835*s*, 785*s*, 645*s*. ^{1}H-NMR: as in [3]. ^{13}C-NMR (50.4 MHz, $CDCl_3$): 181.3 (*qq*, J = 5.1, 1.5, C=O); 175.8 (*qq*, J = 7.5, 6.0, C(3)); 147.9 (*qq*, J = 7.5, 5.0, C(2)); 92.2 (*q*, J = 4.5, C(4)); 9.4 (*q*, J = 130, CH_3); 8.0 (*q*, J = 130, CH_3). Anal. calc. for $C_6H_6Cl_2O$ (165.02): Cl 42.97; found: Cl 42.70 (C, H as in [3]).

Monitoring by anal. GC showed the following yields [%] of **2a**/**3a** (reaction time [h] in parentheses): 9:1 (1), 21:2 (2), 54:7 (3), 61:19 (4), 58:33 (5), 52:41 (6), 42:56 (17).

2.2.2. *Procedure B.* The reaction of 1.19 g (22 mmol) of **1a**, 4.60 g (70 mmol) of Zn(Cu), and 8.00 g (44 mmol) of CCl_3COCl, kept at moderate reflux by occasional cooling with an ice bath, according to *Criterion a* for 15 min (for monitoring see below). Distillation at 60–70°/1 Torr gave 2.52 g (69%) of a 4:1 mixture **2a**/**3a** (GC) as a colorless liquid. Separation by LC (hexane/2% AcOEt) yielded from the 1st fraction pure **3a** as colorless liquid and from the 2nd fraction pure **2a** as a colorless oil, which solidified on standing.

Monitoring by anal. GC showed the following yields [%] of **2a**/**3a** (reaction time [h] in parentheses): 72:0 (2), 73:8 (7), 69:10 (10), 65:24 (30), 54:39 (60).

Another experiment where the reaction was allowed to reflux according to *Criterion b* for only 7 min afforded, after distillation, 2.28 g (63%) of a 96:4 mixture **2a**/**3a**.

2.3. *4,4-Dichloro-2,3-diethyl-* (**2b**) *and 2,4-Dichloro-3,4-diethylcyclobut-2-enone* (**3b**). *Procedure B.* A mixture of 2.00 g (24.4 mmol) of 3-hexyne (**1b**), 4.77 g (73.2 mmol) of Zn(Cu), and 8.87 g (48.8 mmol) of CCl_3COCl was allowed to reflux according to *Criterion a* for 15 min (time chosen by assuming analogy to the monitoring of *Exper. 2.2.2*). Distillation at 60–70°/0.1 Torr gave 4.06 g (86%) of a 35:65 mixture **2b**/**3b** (GC) as a colorless liquid. LC (hexane/2% AcOEt) yielded from the 1st fraction pure **3b** as a colorless liquid. UV (EtOH): 235 (8300). IR (film): 1800*s* (C=O), 1610*s* (C=C). ^{1}H-NMR (90 MHz, $CDCl_3$): 2.70, 2.20 (2*q*, *J* = 7.5, 2 CH_2); 1.40, 1.05 (2*t*, *J* = 7.5, 2 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 182.7 (*tt*, *J* = 5.7, 1.7, C=O); 181.3 (*ttq*, *J* = 8.0, 5.0, 2.5, C(3)); 128.8 (*qq*, *J* = 7.5, 5.0, C(2)); 84.7 (*ttq*, *J* = 8.0, 3.9, 2.8, C(4)); 29.6, 20.0 (2*tq*, *J* = 130, 4.8, 2 CH_2); 10.1, 9.9 (2*qt*, *J* = 130, 4.3, 2 CH_3). Anal. calc. for $C_8H_{10}Cl_2O$ (193.07): C 49.77, H 5.22, Cl 36.73; found: C 50.16, H 5.52, Cl 36.40.

The 2nd fraction contained pure **2b** as a colorless liquid. UV (EtOH): 224 (8900). IR (film): 1785*s* (C=O), 1630*s* (C=C), 850*s*. ^{1}H-NMR (90 MHz, $CDCl_3$): 2.75, 2.30 (2*q*, *J* = 7.5, 2 CH_2); 1.40, 1.20 (2*t*, *J* = 7.5, 2 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 181.6 (*tt*, *J* = 6.0, 1.5, C=O); 178.6 (*ttq*, *J* = 10.5, 7.5, 5.3, C(3)); 152.3 (*tqq*, *J* = 11.0, 5.5, 1.0, C(2)); 91.8 (*t*, *J* = 4.0, C(4)); 19.4, 17.2 (2*tq*, *J* = 128, 4.3, 2 CH_2); 10.9, 10.8 (2*qt*, *J* = 128, 5.1, 2 CH_3). Anal. calc. for $C_8H_{10}Cl_2O$ (193.07): C 49.77, H 5.22, Cl 36.73; found: C 50.03, H 5.40, Cl 36.45.

2.4. *3-Butyl-4,4-dichloro-* (**2c**) *and 3-Butyl-2,4-dichlorocyclobut-2-enone* (**3c**). 2.4.1. *Procedure A.* Using the same amounts of reagents as reported in [3], the reaction was allowed to go arbitrarily for 50 h ([3]: 4–14 h). At that time, a significant amount of **3c** had appeared: 2.27 g (86%) of a 7:3 mixture **2c**/**3c** (GC) as a colorless liquid ([3]: 77% of **2c**). Separation by LC (hexane/2% AcOEt) yielded, in addition to **2c**, 90%-enriched **3c**.

3c: UV (EtOH): 230. IR (film): 1805*s* (C=O), 1610*s* (C=C). ^{1}H-NMR (90 MHz, $CDCl_3$): 5.25 (*s*, H–C(4)); 2.8–2.6 (*m*, CH_2(1')); 1.9–1.2 (*m*, 2 CH_2); 1.0 (*t*, *J* = 6, CH_3).

Monitoring by anal. GC showed the following yields [%] of **2c**/**3c** (reaction time [h] in parentheses): 20:0 (0.5), 31:0 (1), 41:0 (2.5), 49:0 (6), 71:3 (21), 71:7 (29), 58:25 (50).

2.4.2. *Procedure B.* The reaction of 2.00 g (24.4 mmol) of **1c**, 4.76 g (73 mmol) of Zn(Cu), and 8.88 g (48.8 mmol) of CCl_3COCl was started by warming in a hot air stream and allowed to go without cooling according to *Criterion b* for 8 min only (time chosen by assuming analogy to the monitoring of *Exper. 2.2.2*). Distillation at 70–80°/0.01 Torr afforded 2.40 g (51%) of pure **2c** as a colorless liquid. UV (EtOH): 219 (8200). IR and ^{1}H-NMR: in agreement with [3]. Anal. calc. for $C_8H_{10}Cl_2O$ (193.07): Cl 36.73; found: Cl 36.50 (C, H as in [3]).

3. Isomerization of the Dichlorocyclobut-2-enones 2a and 3a. – 3.1. *Isomerization of* **2a**. A soln. of 94 mg of pure **2a** and 19 mg of dodecane (internal standard) in 6 ml of dry Et_2O was refluxed in the presence of 82 mg of dry $ZnCl_2$. The reaction was monitored by anal. GC showing the following yields [%] of **2a**/**3a** (reaction time [h] in parentheses): 90:10 (0.5), 68:32 (2), 53:47 (4), 46:53 (5), 43:55 (6), 41:57 (7), 40:58 (9).

An attempt was made to isomerize **2a** by the procedure described in [6]: A soln. of 166 mg of **2a** and 32 mg of dodecane (internal standard) in 7 ml of a soln. of LiCl in acetone, in the presence of undissolved LiCl, was refluxed for 17 h. Monitoring by GC showed no decrease in the amount of **2a**.

3.2. *Isomerization of* **3a**. A soln. of 89 mg of pure **3a** and 23 mg of dodecane (internal standard) in 6 ml of dry Et_2O was refluxed in the presence of 74 mg of dry $ZnCl_2$. Monitoring by anal. GC showed the following yields of **2a**/**3a** (reaction time [h] in parentheses): 3:98 (0.5), 10:91 (2), 29:71 (4), 37:63 (5), 40:60 (6), 39:61 (7), 40:60 (8).

4. Reduction of Dichlorocyclobut-2-enones 2a, 3a, 2c, and 2b/3b with Zn(Cu) in AcOH/Pyridine. – 4.1. *General Procedure.* To a stirred soln. of dichlorocyclobutenone (1 mmol/ml) in AcOH/pyridine 4:1 [8], 5 mol-equiv. of Zn(Cu) were added in portions within *ca.* 20 min, thereby allowing the temp. to reach to 50–60°. After 5 h at 50–60° (GC control of product formation), Et_2O was added and the soln. separated from the insoluble material. The org. layer was washed with H_2O, 1N HCl, sat. $NaHCO_3$ soln., and dried ($MgSO_4$). The solvent was distilled off over a 5-cm *Vigreux* column at normal pressure. Bulb-to-bulb distillation of the residue gave the pure cyclobutenone **4**.

4.2. *2,3-Dimethylcyclobut-2-enone* (**4a**). 4.2.1. *Reduction of* **2a**. From 830 mg (5 mmol) of **2a**, 300 mg (62%) of **4a** was collected at 50–60°/15 Torr as a colorless liquid (*cf.* [9], no properties given). UV (EtOH): 231 (7500). IR (film): 1755*s* (C=O), 1645*s* (C=C). ^{1}H-NMR (90 MHz, $CDCl_3$): 3.0–3.2 (*m*, 2 H–C(4)); 2.1–2.2 (*m*, CH_3–C(3)); 1.6–1.7 (*m*, CH_3–C(2)). Anal. calc. for C_6H_8O (96.13): C 74.97, H 8.39; found: C 74.79, H 8.49.

4.2.2. *Reduction of* **3a**. From 330 mg (2 mmol) of **3a**, under the same conditions, 115 mg (60%) of **4a** were collected at 50–60°/15 Torr as a colorless liquid.

4.3. *2,3-Diethylcyclobut-2-enone* (**4b**). From 965 mg (5 mmol) of a 1:2 mixture **2b**/**3b**, 436 mg (70%) of **4b** were collected at 50–60°/1 Torr as a colorless liquid. UV (EtOH): 233 (7600). IR (film): 1760*s* (C=O), 1635*s* (C=C). ^{1}H-NMR (200 MHz, $CDCl_3$): 3.06–3.08 (*m*, CH_2(4)); 2.58, 2.06 (2*q*, *J* = 7.6, 2 CH_2); 1.20, 1.09 (2*t*, *J* = 7.6, 2 CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$, PND, DEPT): 189.6 (C(1)); 172.7 (C(3)); 148.0 (C(2)); 48.6 (dn, CH_2(4)); 22.8, 16.4 (dn, 2 CH_2); 11.6, 10.4 (up, 2 CH_3). Anal. calc. for $C_8H_{12}O$ (124.18): C 77.38, H 9.74; found: C 75.16, H 10.00.

4.4. *3-Butylcyclobut-2-enone* (**4c**). From 965 mg (5 mmol) of **2c**, 351 mg (57%) of **4c** were collected at 50–60°/1 Torr as a colorless liquid ([10]: 35–60°/1 Torr). UV (EtOH): 225 (9200). IR- and ^{1}H-NMR agreed with those of [10].

5. Reduction of Dichlorocyclobut-2-enones 3a and 3b with Zn(Cu) in AcOH without Pyridine. – 5.1. *General Procedure.* These reactions were performed in analogy to *Exper. 4.1*, but without pyridine; the Zn(Cu) was added within 10 min to a soln. of **3** in AcOH (0.3 mmol/ml) at 50°.

5.2. *Mixture of 2,3-Dimethyl-* (**4a**) *and 3,4-Dimethylcyclobut-2-enone* (**5a**). From 193 mg (1.17 mmol) of **3a**, after 5 h at 50°, 19 mg (17%) of a *ca.* 1:1 mixture (by GC and ^{1}H-NMR) **4a**/**5a** were collected at 60–70°/15 Torr as a colorless liquid. ^{1}H-NMR (90 MHz, $CDCl_3$): all signals of **4a** and in addition (intensity ratio *ca.* 1:1) the following signals of **5a**: 5.80 (*s*, H–C(2)); 3.40 (*q*, *J* = 7, H–C(4)); 2.1–2.2 (split *s*, partially covered CH_3); 1.20 (*d*, *J* = 7, CH_3).

5.3. *Mixture of 2,3-Diethyl-* (**4b**) *and 3,4-Diethylcyclobut-2-enone* (**5b**). From 193 mg (1 mmol) of **3b**, after 2½ h at 50°, 41 mg (33%) of a *ca.* 1:1 mixture (by GC and ^{1}H-NMR) **4b**/**5b** were collected at 50–60°/1 Torr as a colorless liquid. The spectra showed all signals of **4b** and in addition (intensity ratio *ca.* 1:1) the following signals of **5b**: IR (film): 1585*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.90–5.91 (*m*, H–C(2)); 3.41 (*t*, *J* = 5.7, H–C(4)); 2.45–2.60 (*m*, partially covered, 2 CH_2–C(3)); 1.58–1.74 (*m*, CH_2(4)); 1.23, 0.96 (2*t*, *J* = 7.4, CH_3).

6. Isomerization of a 1:1 Mixture 4b/5b in AcOH/Pyridine. – A soln. of 23 mg of a 1:1 mixture **4b**/**5b** in 0.5 ml of AcOH/pyridine 4:1 was kept at 40–50°. Following the isomerization by GC (without internal standard) showed the following ratios **4b**/**5b** (reaction time [min] in parentheses): 85:15 (15), 97:3 (60), 98:2 (120).

7. Deuteration of 2c and 4c in CD_3CO_2D/(D_5)Pyridine. – 7.1. *3-(1′,1′-D_2)Butyl-4,4-dichloro(2-D)cyclobut-2-enone* (D_3-**2c**). A soln. of 25 mg of **2c** in 0.4 ml of CD_3CO_2D showed no changes in the ^{1}H-NMR after standing for 2 h at r.t. One h after the addition of 0.2 ml of (D_5)pyridine, the signal at 6.45–6.50 ppm (*m*, H–C(2)) had decreased by 50% and the one at 2.65–2.85 ppm (*m*, CH_2–C(3)) by *ca.* 85%. The *s* at 13.5 ppm of CD_3CO_2H integrated for 1.8 H. After 3 d, D_3-**2c** was isolated as described for **4** in *Exper. 4.1*. IR (film): 2320*w*, 1795*s* (C=O), 1560*s* (C=C), 720*s*. ^{1}H-NMR (90 MHz, $CDCl_3$): 6.20 (*s*, 0.1 H, H–C(2)); 2.5–2.8 (*m*, 0.1 H, CH_2(1′); 1.3–1.8 (*m*, 4 H, 2 CH_2); 0.9–1.1 (*m*, 3 H, CH_3).

After standing in AcOH/pyridine for *ca.* 1 d, D_3-**2c** was converted back to **2c** (by ^{1}H-NMR and IR).

7.2. *3-Butyl(2,4,4-D_3)cyclobut-2-enone* (D_3-**4c**). The ^{1}H-NMR of 25 mg of **4c** in 0.4 ml of CD_3CO_2D showed no changes after 2 h. One h after the addition of 0.2 ml of (D_5)pyridine, the 2 *s* at 5.90 (H–C(2)) and 3.10 ppm (CH_2(4)) had decreased by *ca.* 90%. The *s* at 13.2 ppm of CD_3CO_2H integrated for 2.5 H. After *ca.* 3 d, no further changes had occurred, and D_3-**4c** was isolated as described in *Exper. 4.1*. IR (film): 2220*w*, 1760*s* (C=O), 1560*s* (C=C). ^{1}H-NMR (90 MHz, $CDCl_3$): 5.90 (*s*, 0.1 H, H–C(2)); 3.10 (*s*, 0.2 H, 2 H–C(4)); 2.60 (*t*, *J* = 7.5, CH_2–C(3)); 1.2–1.7 (*m*, 4 H, 2 CH_2); 0.9–1.1 (*m*, 3 H, CH_3).

After standing in AcOH/pyridine for *ca.* 1 d, D_3-**4c** was converted back to **4c** (by ^{1}H-NMR and IR).

7.3. *Attempted Deuteration of* **4c** *with LiN(i-Pr)$_2$/D_2O.* To a stirred soln. of 51 mg (0.5 mmol) of (i-Pr)$_2$NH in 7 ml of dry THF, 0.5 mmol of BuLi in hexane was added at –10°. After 15 min, the mixture was cooled to –65°, and a soln. of 62 mg (0.5 mmol) of **4c** in 0.7 ml of dry THF was added within 10 min. After stirring for 30 min, 27 mg (1.5 mmol) of D_2O was added, the mixture allowed to warm to 0°, treated with more D_2O (0.2 ml), and warmed to r.t. The soln. was diluted with Et_2O, washed with H_2O, dried ($MgSO_4$), and concentrated. Bulb-to-bulb distillation at 50–60°/1 Torr yielded 16 mg (26%) of non-deuterated (by IR and ^{1}H-NMR) **4c**.

REFERENCES

[1] C. Schmit, S. Sahraoui-Taleb, E. Differding, G.C. Dehass-De Lombaert, L. Ghosez, *Tetrahedron Lett.* **1984,** *25,* 5043.
[2] D.C. England, C.G. Krespan, *J. Org. Chem.* **1970,** *35,* 3308; P.L. Fishbein, H.W. Moore, *ibid.* **1985,** *50,* 3226; M.D. Gheorg, C. Draghici, L. Stanescu, M. Avram, *Tetrahedron Lett.* **1976,** 2715.
[3] A. Hassner, J. Dillon jr., *J. Org. Chem.* **1983,** *48,* 3382.
[4] R.L. Danheiser, H. Sard, *Tetrahedron Lett.* **1983,** *24,* 23.
[5] A. Hassner, J. Dillon jr., *Synthesis* **1979,** 689.
[6] M.C. Caserio, H.E. Simmons, A.E. Johnson, J.D. Roberts, *J. Am. Chem. Soc.* **1960,** *82,* 3102.
[7] E. Pretsch, T. Clerc, J. Seibel, W. Simon, 'Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden', Springer, Heidelberg, 1976, p. 125.
[8] M. Rey, U.A. Huber, A.S. Dreiding, *Tetrahedron Lett.* **1968,** 3583.
[9] R.L. Danheiser, St.K. Gee, H. Sard, *J. Am. Chem. Soc.* **1982,** *104,* 7670.
[10] H.H. Wasserman, J.U. Piper, E.V. Dehmlow, *J. Org. Chem.* **1973,** *38,* 1451; B. Corbel, J.M. Decesare, T. Durst, *Can. J. Chem.* **1978,** *56,* 505; T. Takeda, T. Tsuchida, K. Ando, T. Fujiwara, *Chem. Lett.* **1983,** 549.
[11] L.R. Krepski, A. Hassner, *J. Org. Chem.* **1978,** *43,* 3173.
[12] D.A. Jackson, M. Rey, A.S. Dreiding, *Helv. Chim. Acta* **1983,** *66,* 2330.
[13] H. Knoche, *Liebigs Ann. Chem.* **1969,** *722,* 232.