

36. Cyclobut-2-enones from Alkynes *via* Dichlorocyclobut-2-enones¹⁾

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

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

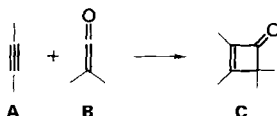
(15.XII.86)

The [2 + 2]-cycloaddition of dichloroketene (prepared *in situ* from CCl_3COCl and $\text{Zn}(\text{Cu})$) 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 $\text{Zn}(\text{Cu})$ 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 ketenoids²⁾. Among reactive ketenes, dichloroketene is often preferred because the two Cl-atoms are replaceable by H-atoms. When generated from trichloroacetyl chloride with $\text{Zn}(\text{Cu})$, 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 reliably³⁾. 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 $\text{Zn}(\text{Cu})$, 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

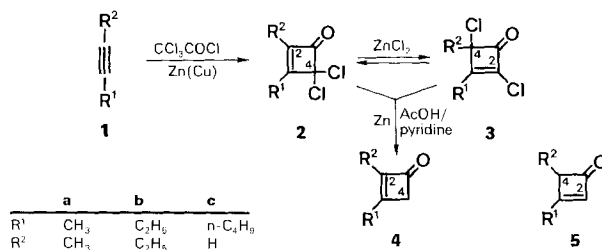


¹⁾ In part taken from the Ph.D. thesis of A.A.A., University of Zürich, 1986.

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.

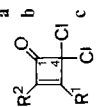
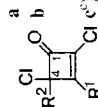
The secondary products **3a-c** of this cycloaddition must have been formed from the primary ones **2a-c** by a ZnCl_2 -induced allylic migration of a Cl-substituted species. A $\text{S}_{\text{N}}2'$ attack of halide anion had been reported [6] with 4,4-dihalo-3-phenylcyclobutenones and lithium halide 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 **3a-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 $^1\text{H-NMR}$ spectra are conclusive ($\text{H-C}(2)$ of **2c**: 6.30 (*t*, $J = 1.5$); $\text{H-C}(4)$ of **3c**: 5.25 (*s*)). In the **a** and **b** series, however, the $^1\text{H-NMR}$ -spectra of **2** and **3** are too similar, but the UV, IR, and $^{13}\text{C-NMR}$ 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 $^{13}\text{C-NMR}$ 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 $\text{Zn}(\text{Cu})$ in $\text{AcOH}/\text{pyridine}$ 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		R ²	¹³ C-NMR				
	λ _{max} (ε)	C=O	C=C	R ¹		C(1)	C(2)	C(3)	C(4)	R ¹ /R ²
 2	a	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	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
	c	1800	1585 ^{a)}	1.40 (t) ^{a)} 2.70 (t, J = 7.5) 1.9-1.2 (m) 0.95 (t) ^{a)}	1.20 (t) ^{a)} 6.20 (t, J = 1.5) ^{a)}	b)				
 3	a	1805	1615	2.25 (s)	1.80 (s)	182.4	129.3	178.4	80.5	22.1, 9.7
	b	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
	c ^{c)}	1805	1610	1.40 (t, J = 7.5) 2.8-2.6 (m) 1.9-1.2 (m) 1.0 (t, J = 6)	1.05 (t, J = 7.5) 5.25 (s)	b)				

^{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.

¹H-NMR: 2.7 (q); 2.15 (q); 1.35 (t); 1.03 (t); no UV and ¹³C-NMR) are closer to our values for **3b**.

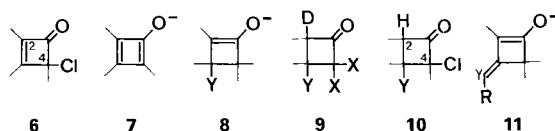
^{b)} This was not measured.

^{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_2COCl 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 $\text{LiN}(\text{i-Pr})_2$ 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 .

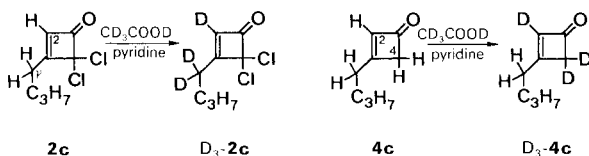


Y = pyridinium, AcO or Cl
X = Cl or H

In the presence of (D_5)pyridine, however, we found a rapid D-incorporation with $\text{CD}_3\text{CO}_2\text{D}$ 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 invocation 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 $^1\text{H-NMR}$, this mechanism implies the elimination of HY from **10** to be more rapid than its addition to **2** or **4**.

Scheme 3



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**.

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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 \times 25 m, 50–100°). Yields determined by GC were obtained by using dodecane as an internal standard. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ 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** \rightarrow **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): 1805s (C=O), 1615s (C=C), 670s. $^1\text{H-NMR}$ (90 MHz, CDCl_3): 2.25, 1.80 (2s, 2 CH_3). $^{13}\text{C-NMR}$ (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 $\text{C}_6\text{H}_6\text{Cl}_2\text{O}$ (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 a 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]): 1790s (C=O), 1645s (C=C), 835s, 785s, 645s. $^1\text{H-NMR}$: as in [3]. $^{13}\text{C-NMR}$ (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 $\text{C}_6\text{H}_6\text{Cl}_2\text{O}$ (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): 1800s (C=O), 1610s (C=C). $^1\text{H-NMR}$ (90 MHz, CDCl_3): 2.70, 2.20 (2q, $J = 7.5$, 2 CH_2); 1.40, 1.05 (2t, $J = 7.5$, 2 CH_3). $^{13}\text{C-NMR}$ (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 (2tq, $J = 130$, 4.8, 2 CH_2); 10.1, 9.9 (2qt, $J = 130$, 4.3, 2 CH_3). Anal. calc. for $\text{C}_8\text{H}_{10}\text{Cl}_2\text{O}$ (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): 1785s (C=O), 1630s (C=C), 850s. $^1\text{H-NMR}$ (90 MHz, CDCl_3): 2.75, 2.30 (2q, $J = 7.5$, 2 CH_2); 1.40, 1.20 (2t, $J = 7.5$, 2 CH_3). $^{13}\text{C-NMR}$ (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 (ttq, $J = 11.0$, 5.5, 1.0, C(2)); 91.8 (t, $J = 4.0$, C(4)); 19.4, 17.2 (2tq, $J = 128$, 4.3, 2 CH_2); 10.9, 10.8 (2qt, $J = 128$, 5.1, 2 CH_3). Anal. calc. for $\text{C}_8\text{H}_{10}\text{Cl}_2\text{O}$ (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): 1805s (C=O), 1610s (C=C). $^1\text{H-NMR}$ (90 MHz, CDCl_3): 5.25 (s, H–C(4)); 2.8–2.6 (m, $\text{CH}_2(1')$); 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 $^1\text{H-NMR}$: in agreement with [3]. Anal. calc. for $\text{C}_8\text{H}_{10}\text{Cl}_2\text{O}$ (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): 1755s (C=O), 1645s (C=C). ¹H-NMR (90 MHz, CDCl₃): 3.0–3.2 (*m*, 2 H–C(4)); 2.1–2.2 (*m*, CH₃–C(3)); 1.6–1.7 (*m*, CH₃–C(2)). Anal. calc. for C₆H₈O (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): 1760s (C=O), 1635s (C=C). ¹H-NMR (200 MHz, CDCl₃): 3.06–3.08 (*m*, CH₂(4)); 2.58, 2.06 (*2q*, *J* = 7.6, 2 CH₂); 1.20, 1.09 (*2t*, *J* = 7.6, 2 CH₃). ¹³C-NMR (50 MHz, CDCl₃, PND, DEPT): 189.6 (C(1)); 172.7 (C(3)); 148.0 (C(2)); 48.6 (dn. CH₂(4)); 22.8, 16.4 (dn, 2 CH₂); 11.6, 10.4 (up, 2 CH₃). Anal. calc. for C₈H₁₂O (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 ¹H-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 ¹H-NMR) **4a/5a** were collected at 60–70°/15 Torr as a colorless liquid. ¹H-NMR (90 MHz, CDCl₃): 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 CH₃); 1.20 (*d*, *J* = 7, CH₃).

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 ¹H-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): 1585m. ¹H-NMR (200 MHz, CDCl₃): 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 CH₂–C(3)); 1.58–1.74 (*m*, CH₂(4)); 1.23, 0.96 (*2t*, *J* = 7.4, CH₃).

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 CD₃CO₂D/(D₅)Pyridine. – 7.1. *3-(1',1'-D₂) Butyl-4,4-dichloro(2-D)cyclobut-2-enone (D₃-2c)*. A soln. of 25 mg of **2c** in 0.4 ml of CD₃CO₂D showed no changes in the ¹H-NMR after standing for 2 h at r.t. One h after the addition of 0.2 ml of (D₅)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*, CH₂–C(3)) by *ca.* 85%. The *s* at 13.5 ppm of CD₃CO₂H integrated for 1.8 H. After 3 d, D₃-**2c** was isolated as described for **4** in *Exper. 4.1*. IR (film): 2320w, 1795s (C=O), 1560s (C=C), 720s. ¹H-NMR (90 MHz, CDCl₃): 6.20 (*s*, 0.1 H, H–C(2)); 2.5–2.8 (*m*, 0.1 H, CH₂(1')); 1.3–1.8 (*m*, 4 H, 2 CH₂); 0.9–1.1 (*m*, 3 H, CH₃).

After standing in AcOH/pyridine for *ca.* 1 d, D₃-**2c** was converted back to **2c** (by ¹H-NMR and IR).

7.2. *3-Butyl(2,4,4-D₃)cyclobut-2-enone (D₃-4c)*. The ¹H-NMR of 25 mg of **4c** in 0.4 ml of CD₃CO₂D showed no changes after 2 h. One h after the addition of 0.2 ml of (D₅)pyridine, the 2 *s* at 5.90 (H–C(2)) and 3.10 ppm (CH₂(4)) had decreased by *ca.* 90%. The *s* at 13.2 ppm of CD₃CO₂H integrated for 2.5 H. After *ca.* 3 d, no further changes had occurred, and D₃-**4c** was isolated as described in *Exper. 4.1*. IR (film): 2220w, 1760s (C=O), 1560s (C=C). ¹H-NMR (90 MHz, CDCl₃): 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, CH₂–C(3)); 1.2–1.7 (*m*, 4 H, 2 CH₂); 0.9–1.1 (*m*, 3 H, CH₃).

After standing in AcOH/pyridine for *ca.* 1 d, D₃-**4c** was converted back to **4c** (by ¹H-NMR and IR).

7.3. *Attempted Deuteration of 4c with LiN(i-Pr)₂/D₂O*. To a stirred soln. of 51 mg (0.5 mmol) of (i-Pr)₂NH 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 D₂O was added, the mixture allowed to warm to 0°, treated with more D₂O (0.2 ml), and warmed to r.t. The soln. was diluted with Et₂O, washed with H₂O, dried (MgSO₄), and concentrated. Bulb-to-bulb distillation at 50–60°/1 Torr yielded 16 mg (26%) of non-deuterated (by IR and ¹H-NMR) **4c**.

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