

Trichloroacetylation of Some Cyclic Enamines

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The pyrrolidine and morpholine enamines of cyclic ketones such as cyclohexanone and cyclopentanone were successfully diacetylated at α - and α' -positions with trichloroacetyl chloride using zinc catalyst. Morpholine enamines of the cyclic ketones gave acetylated morpholine in good yields besides the corresponding diacetylated cyclic enamines. When the same reactions were performed by using triethylamine without using zinc, monoacetylation products of the same enamines were synthesized.

Key words monoacetylation; diacetylation; cyclic enamine; trichloroacetyl chloride

The acylation of enamines derived from cyclic ketones is a well-established synthetic method for the synthesis of α -acylated carbonyl compounds.¹⁾ Enamine acylation with acid chlorides having no α -hydrogen atom appears to be a straightforward reaction at the enamine carbon. The enamine undergoes acylation to give the corresponding enamino ketone in a moderate yield, which then hydrolyses to 1,3-triketone (β -diketone). A number of β -diketones had been prepared *via* acylation of enamines.^{2–4)}

Besides the monoacylation of enamines, the diacylation of the same compounds at α - and α' -positions has been shown to be a possible reaction course,⁵⁾ however, we have rarely met α, α' -diacylated cyclic enamines in the literature which were synthesized by similar methods. The reaction of 1-(4-morpholino)cycloheptene with trifluoroacetic acid has been reported to give a diacetylated product, where more reactive enamines such as 1-(4-morpholino)cyclopentene has been reported to react even at low temperatures to give complicated reaction mixtures.⁶⁾

Acylation of enamines with acyl chlorides can not only take place on carbon but acylation on nitrogen is also observed. However, in contrast to the *N*-alkylated products, *N*-acylated products are not always stable so that *C*-acylation is generally the normal mode of the reaction.¹⁾

Herein we report diacylation reactions of pyrrolidine and morpholine enamines of cyclohexanone and cyclopentanone with trichloroacetyl chloride, in two different reaction medium, under the presence of zinc catalyst and by using triethylamine to prevent salt-formation, respectively.

In the present study, the first examples of bis(trichloroacetyl) cyclic enamines were synthesized by the reaction of cyclic enamines with trichloroacetyl chloride as acylating agent under the influence of zinc catalyst where the second acetyl attack was at the α' -position of the cyclic enamine. The diacetylation was probably due to the much greater reactivity of the trichloroacetyl chloride when compared to the reactivity of unsubstituted acyl chlorides used very frequently as acylating agents or it might be due to the presence of zinc which is not an usual catalyst in acylation reactions. Zinc is normally used in ketene formation reactions, however, we have unexpectedly obtained diacetylated products rather than substituted cyclobutanones over ketene formation, by using zinc catalyst. On the other hand, high yields are usually observed in ordinary acylation reactions when triethylamine is used as a base to prevent salt formation.⁷⁾ The attempts to realize the trichloroacetylation of the same enamines by using

triethylamine without using zinc gave monoacylation products as in the literature.

The reaction of 1-(1-pyrrolidinyl)cyclohexene (**1c**) with trichloroacetyl chloride using zinc catalyst yielded 2,6-di(trichloroacetyl)-1-(1-pyrrolidinyl)cyclohexene (**10**). Even though the product was isolated and characterized, it was quite unstable and subsequently hydrolyzed to the corresponding α, α' -triketone, 2,6-di(trichloroacetyl)cyclohexanone (**4**), when saturated NaHCO₃ solution was added. The less reactive morpholine enamine of cyclohexanone (**1a**) gave a better result than pyrrolidine enamine (**1c**) in enamine acylation under similar reaction conditions. A stable α, α' -diacetylated morpholine enamine, 2,6-di(trichloroacetyl)-1-(4-morpholino)cyclohexene (**2**), was successfully isolated and it resisted to hydrolysis during the same procedure. Compound **2** was hydrolyzed to **4** only by using 5 M NaOH solution under reflux condition. The single crystal X-ray analysis result of **2** was published elsewhere.⁶⁾ The reaction of compound **1a** yielded not only a diacetylated enamine (**2**) in 43% yield but a new product, *N*-(trichloroacetyl)morpholine (**3**), was obtained in 15% yield. Formation of the stable compound **3** is a good example to the acylation of enamines on nitrogen to yield *N*-acylated products. Compound **3** has been directly synthesized by the reaction of morpholine in chloroform with hexachloroacetone, in the literature.⁹⁾ In case of cyclopentanone enamines under the same reaction conditions, both the 1-(4-morpholino)cyclopentene (**1b**) and 1-(1-pyrrolidinyl)cyclopentene (**1d**) were converted directly to the corresponding triketone, 2,6-di(trichloroacetyl)cyclopentanone (**7**), in 45 and 55% yields, respectively. The reaction of compound **1b** also gave *N*-acetylated product, compound **3**, in 35% yield.

When the same enamines (**1a–d**) reacted with trichloroacetyl chloride under the presence of triethylamine without using zinc, new products, monoacylated enamines, were obtained. Monoacylation of compound **1a** gave 2-trichloroacetyl-1-(4-morpholino)cyclohexene (**5**) and 6-trichloroacetyl-1-(4-morpholino)cyclohexene (**6**) in 50 and 30% yields respectively as an isomeric mixture. Their properties were so similar that they could be hardly separated and isolated by means of HPLC technique. Even though the reaction of trichloroacetic anhydride in THF with 1-(4-morpholino)cyclohexene and triethylamine has been reported to give 2-trichloroacetyl cyclohexanone directly in the literature,¹⁰⁾ we were able to isolate monoacylated morpholine enamines of cyclohexanone (**5**, **6**) by our reaction. A similar reaction of **1b** also

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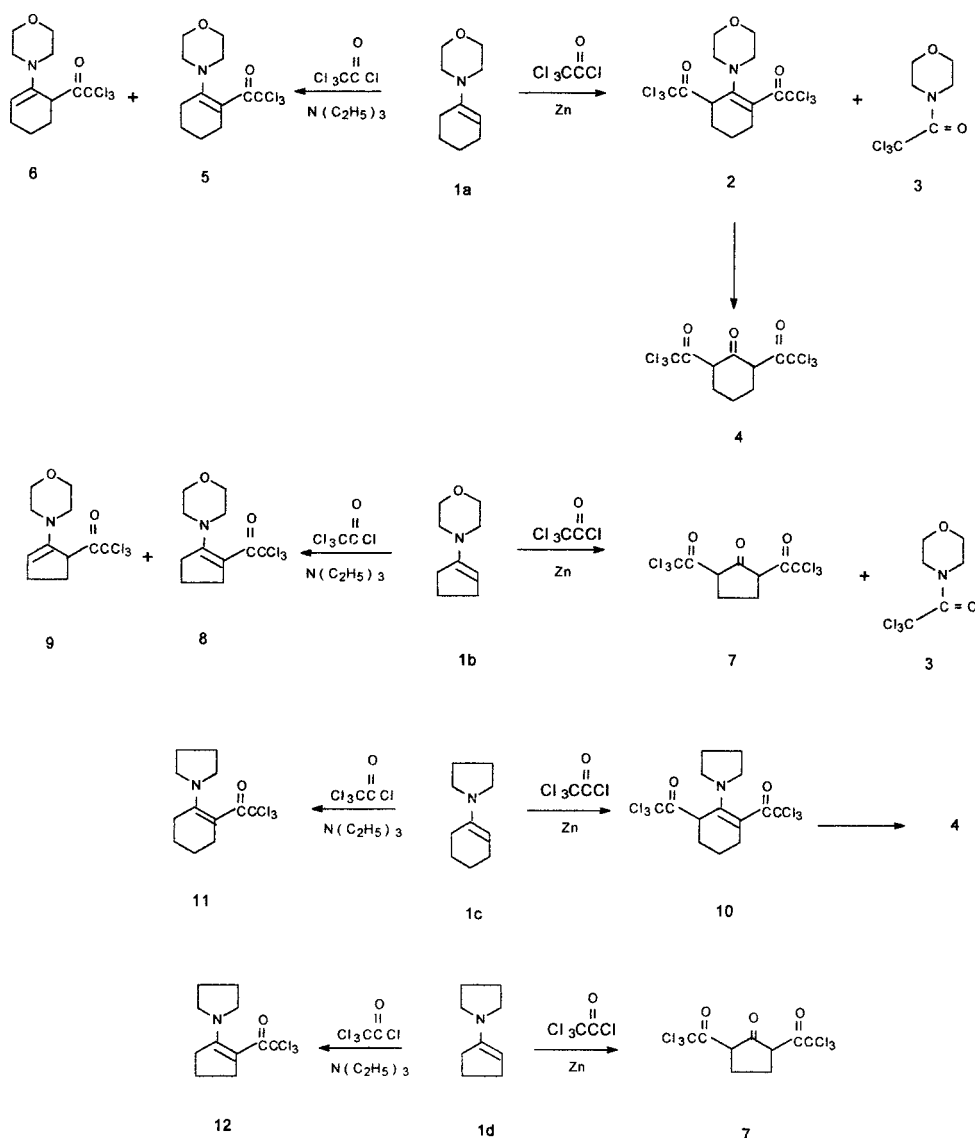


Fig. 1

gave an isomeric mixture composed of 2-trichloroacetyl-1-(4-morpholino)cyclopentene (**8**) and 5-trichloroacetyl-1-(4-morpholino)cyclopentene (**9**) in 40 and 30% yields respectively. However, each compound **1c** and **1d** gave only one isomer, 2-trichloroacetyl-1-(1-pyrrolidino)cyclohexene (**11**) and 2-trichloroacetyl-1-(1-pyrrolidino)cyclopentene (**12**) in higher yields, respectively. Thus, there were no trace of the second isomers, less conjugated structures, according to the HPLC measurements. This result might be due to the higher reactivity of pyrrolidiny enamines rather than morpholine enamines towards acyl chlorides. It was a surprising result that we were able to isolate monoacylated products of both pyrrolidine and morpholine enamines of cyclohexanone.

When the IR spectra of the diacylated products were compared, the absorption frequency of cyclohexanone carbonyl group of compound **4** was recorded at 1715 cm^{-1} , where the absorption band of the same group of cyclopentanone derivative (compound **7**) shifted to a higher stretching frequency (1740 cm^{-1}) due to angular strain of the cyclopentanone ring. The absorption frequency of a saturated aliphatic ketone at 1715 cm^{-1} is referred "normal".¹¹⁾

Changes in the environment of the carbonyl can either lower or raise the absorption frequency from this "normal" value. The trichloromethyl groups adjacent to the other two identical carbonyl groups in compounds **4** and **7** created inductive effect which reduced the length of the C=O bond and increased the frequency of absorption. Thus, the absorptions of the two similar carbonyl groups, in both cyclohexanone and cyclopentanone derivatives, shifted to higher frequencies, 1759 cm^{-1} and 1760 cm^{-1} , respectively. In the enamino derivatives of cyclohexanone (compounds **2** and **10**), a difference in the two carbonyl absorptions was observed because of a conjugation of the enamine double bond with one of the carbonyls. The resonance effect increased the C=O bond length and reduced the frequency of absorption. The unconjugated carbonyl absorption was recorded at its normal value (1760 cm^{-1} for compounds **2** and **10**) where the conjugated carbonyl absorption was observed at a lower frequency (1715 cm^{-1} for **2** and 1708 cm^{-1} for **10**) due to the resonance effect.

When the IR spectra of the monoacylated products were compared, there was also a good correlation between the

structures and the frequencies of the carbonyl bands. Even though the C=O stretching frequency of compound **6** was recorded at 1685 cm^{-1} , the same band of compound **5** appeared at 1640 cm^{-1} due to conjugation. The same result was observed in the IR spectra of compounds **8** and **9**. The C=O band of **9** was at 1680 cm^{-1} where the conjugated carbonyl band of **8** was shifted to 1630 cm^{-1} . The carbonyls of **11** and **12** were in conjugation with the enamine moiety so that C=O bands shifted to lower frequencies, 1624 and 1640 cm^{-1} , respectively.

The $^1\text{H-NMR}$ spectra supported the IR findings for both diacetylated and monoacetylated compounds. The methine protons adjacent to acyl carbonyls in all the diacetylated products appeared in the range between $\delta=4.20\text{--}4.70$. Not all but some monoacylation products, compounds **6** and **9**, gave characteristic peaks indicating the structures. These peaks arised from methine and vinylic protons of **6** and **9**. The vinylic proton of compound **6** appeared at $\delta=4.50\text{--}4.60$ where the same proton for compound **9** was observed at $\delta=4.60\text{--}4.80$. The methine proton adjacent to trichloromethyl carbonyl in compound **6** was observed at $\delta=4.20\text{--}4.30$ where the same proton belonging to compound **9** was at $\delta=4.30\text{--}4.40$.

Experimental

All reactions were performed under an atmosphere of nitrogen. Diethyl ether was dried over sodium-potassium alloy and freshly distilled prior to use. IR spectra were obtained on a Mattson 1000 FTIR spectrometer; absorption maxima are reported in wavenumbers (cm^{-1}). NMR spectra were recorded on a Bruker AC-200 (200 MHz) NMR spectrometer; CDCl_3 was the solvent and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts are reported in ppm (δ) downfield from the signal for TMS. The symbols s, t (triplet) and m (multiplet) are used to report the multiplicity of signals. $^{13}\text{C-NMR}$ spectra were recorded proton decoupled. GC-MS spectra were recorded on a 5890 Series Mass Selective Detector Combine System and gave a parent peak and other fragmentations in agreement with the proposed structures. HPLC measurements were performed by Agilent LCMSD, with a Phenomenex C-18 column using methanol-water (70%:30%) solvent mixture. The flow rate was 1 mm/min. Elemental analyses were determined on a LECO 932 CHNS-O elemental analyzer. Melting points were determined with an electrothermal melting point apparatus and were uncorrected. Trichloroacetyl chloride (from Aldrich) was freshly distilled before use and Zn was activated as described previously.¹² The morpholine and pyrrolidine enamines of cyclohexanone and cyclopentanone were prepared according to the literature procedures.^{3,13} Ether was dried by sodium-potassium alloy and purified by distillation prior to use.

General Procedure for the Diacetylation and Monoacetylation Reactions of Trichloroacetyl Chloride with Enamines A solution of freshly distilled trichloroacetyl chloride (17.8 mmol, 3.23 g) in 30 ml dry ether was added dropwise over a period of 1 h to a cooled mixture (in ice-salt bath) of activated zinc (8.9 mmol, 0.58 g) and appropriate enamine (17.8 mmol) in 50 ml anhydrous ether while stirring under nitrogen atmosphere. The reaction mixture was continued to stirring overnight then zinc chloride was removed by filtration and the solvent was evaporated under reduced pressure. The residue was dissolved in hexane, dried over MgSO_4 , filtered and then the solvent was evaporated.

The same reaction procedure was repeated only by replacing zinc with triethylamine and removing ammonium chloride instead of zinc chloride for the monoacetylation reactions.

2,6-Di(trichloroacetyl)-1-(4-morpholino)cyclohexene (2) and N-(Trichloroacetyl)morpholine (3) Trichloroacetyl chloride (17.8 mmol, 3.23 g), 1-(4-morpholino)cyclohexene (17.8 mmol, 2.97 g) and activated zinc (8.9 mmol, 0.58 g) were used. The column chromatography of the residue [silica gel, ethyl acetate-hexane (1:4)] afforded pure 1.77 g (43%) **2** as a pure yellow solid and 0.62 g (15%) **3** as a white solid respectively. Both **2** and **3** were then recrystallized from hexane solution separately.

Compound **2**: mp $125\text{--}126^\circ\text{C}$; MS m/z : 455 (M^+); IR (KBr): 1760 (C=O), 1715 (conjugated C=O), 1600 (C=C) cm^{-1} ; $^1\text{H-NMR}$: δ 4.40—4.50 (t, 1H, CHCO), 3.50—3.70 (t, 4H, NCH_2), 2.70—2.90 (t, 4H,

$\text{NCH}_2\text{CH}_2\text{O}$), 1.90—2.20 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.65—1.80 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$); $^{13}\text{C-NMR}$: δ 205 (C=O), 180 (conjugated C=O), 140 (C=C), 98 (CHCO), 78 (CCl_3), 65 (NCH_2), 50 ($\text{NCH}_2\text{CH}_2\text{O}$), 45 ($\text{CH}_2\text{--C=C}$), 35 (CH_2), 25 (CH_2). Calcd for $\text{C}_{14}\text{H}_{15}\text{Cl}_6\text{NO}_3$: C, 36.71; H, 3.29; N, 3.06. Found: C, 36.56; H, 3.26; N, 3.09.

Compound **3**: mp 83°C ; MS m/z : 231 (M^+); IR (KBr): 1680 (amide C=O) cm^{-1} ; $^1\text{H-NMR}$: δ 3.95—4.05 (t, 4H, NCH_2), 3.20—3.30 (t, 4H, $\text{NCH}_2\text{CH}_2\text{O}$); $^{13}\text{C-NMR}$: δ 168 (C=O), 78 (CCl_3), 65 (NCH_2), 44 ($\text{NCH}_2\text{CH}_2\text{O}$). Anal. Calcd for $\text{C}_6\text{H}_8\text{Cl}_3\text{O}_2$: C, 30.99; H, 3.46; N, 6.02. Found: C, 31.11; H, 3.47; N, 6.00.

2,6-Di(trichloroacetyl)cyclohexanone (4) Compound **2** was refluxed in 5 M NaOH solution for 2 h. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was recrystallized from hexane to give 1.33 g (90%) **4** as a pure white solid.

Compound **4**: mp 91°C ; MS m/z : 386 (M^+); IR (KBr): 1759 ($\text{Cl}_3\text{CC=O}$) and 1715 (cyclohexanone C=O) cm^{-1} ; $^1\text{H-NMR}$: δ 4.20—4.30 (t, H and H, 2CHCO), 2.20—2.50 (m, 4H, CHCH_2), 1.60—1.80 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$); $^{13}\text{C-NMR}$: δ 208 (C=O(CCl_3)), 185 (conjugated C=O), 100 (COCHCO), 78 (CCl_3), 44 (CH_2CH_2), 35 ($\text{CH}_2\text{CH}_2\text{CH}_2$). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{Cl}_6\text{O}_3$: C, 30.89; H, 2.07. Found: C, 31.14; H, 2.10.

Compound **4** was also obtained by stirring the mixture of compound **10** with a saturated NaHCO_3 solution.

2-Trichloroacetyl-1-(4-morpholino)cyclohexene (5) and 6-Trichloroacetyl-1-(4-morpholino)cyclohexene (6) Trichloroacetyl chloride (17.8 mmol, 3.23 g), 1-(4-morpholino)cyclohexene (17.8 mmol, 2.97 g) and triethylamine (17.8 mmol, 1.80 g) yielded **5** and **6** as an isomeric mixture. The HPLC afforded 1.38 g (50%) pure **5** and 0.83 g (30%) pure **6** as white solids respectively.

Compound **5**: mp $99\text{--}100^\circ\text{C}$; MS m/z : 311 (M^+); IR (KBr): 1640 (C=O), 1540 (C=C) cm^{-1} ; $^1\text{H-NMR}$: δ 3.50—3.60 (t, 4H, NCH_2), 3.30—3.40 (m, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 1.60—2.10 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$); $^{13}\text{C-NMR}$: δ 175 (C=O), 150 (C=C), 78 (CCl_3), 65 (NCH_2), 50 (2C, $\text{NCH}_2\text{CH}_2\text{O}$), 43 ($\text{CH}_2\text{C=C}$), 30 (CH_2), 25 (CH_2). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_3\text{NO}_2$: C, 46.34; H, 5.14; N, 4.50. Found: C, 46.65; H, 4.90; N, 4.21.

Compound **6**: mp $102\text{--}103^\circ\text{C}$; MS m/z : 311 (M^+); IR (KBr): 1685 (C=O), 1580 (C=C) cm^{-1} ; $^1\text{H-NMR}$: δ 4.50—4.60 (t, 1H, CH=C), 4.20—4.30 (t, 1H, CHCO), 3.40—3.60 (t, 4H, NCH_2), 3.00—3.20 (t, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 1.20—2.00 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$); $^{13}\text{C-NMR}$: δ 180 (C=O), 150 (C=C), 98 (CHCO), 78 (CCl_3), 65 (NCH_2), 50 ($\text{NCH}_2\text{CH}_2\text{O}$), 45 (CH_2), 35 (CH_2 , CH_2). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_3\text{NO}_2$: C, 46.34; H, 5.14; N, 4.50. Found: C, 46.02; H, 4.80; N, 4.05.

2,6-Di(trichloroacetyl)cyclopentanone (7) and N-(Trichloroacetyl)morpholine (3) The reaction of trichloroacetyl chloride (17.8 mmol, 3.23 g), 1-(4-morpholino)cyclopentene (17.8 mmol, 2.97 g) and activated zinc (8.9 mmol, 0.58 g) yielded **7** and **3** directly. Column chromatography of the residue [silica gel, ethyl acetate-hexane (1:9)] afforded 1.50 g (45%) **7** as an unstable white solid and 1.45 g (35%) **3** as a white solid respectively. Compound **7** was also obtained by the reaction of trichloroacetyl chloride (17.8 mmol, 3.23 g) and 1-(1-pyrrolidinyl)cyclopentene (17.8 mmol, 2.69 g) in 55% (1.84 g) yield.

Compound **7**: mp 111°C ; MS m/z : 372 (M^+); IR (KBr): 1760 ($\text{Cl}_3\text{C=O}$), 1740 (cyclopentanone C=O) cm^{-1} ; $^1\text{H-NMR}$: δ 4.30—4.40 (t, H and H, 2CHCO), 1.90—2.10 (m, 4H, CH_2CH_2); $^{13}\text{C-NMR}$: δ 210 (C=O(CCl_3)), 190 (C=O), 98 (CHCO), 78 (CCl_3), 45 (CH_2CH_2). Anal. Calcd for $\text{C}_9\text{H}_6\text{Cl}_6\text{O}_3$: C, 28.84; H, 1.61. Found: C, 28.75; H, 1.58.

2-Trichloroacetyl-1-(4-morpholino)cyclopentene (8) and 5-Trichloroacetyl-1-(4-morpholino)cyclopentene (9) Trichloroacetyl chloride (17.8 mmol, 3.23 g), 1-(4-morpholino)cyclopentene (17.8 mmol, 2.73 g) and triethylamine (17.8 mmol, 1.80 g) yielded **8** and **9** as an isomeric mixture. The HPLC afforded 1.06 g (40%) pure **8** and 0.79 g (30%) pure **9** as yellow solids respectively.

Compound **8**: mp $114\text{--}115^\circ\text{C}$; MS m/z : 297 (M^+); IR (KBr): 1630 (C=O), 1540 (C=C) cm^{-1} ; $^1\text{H-NMR}$: δ 3.30—3.40 (t, 4H, NCH_2), 2.70—2.80 (m, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 1.80—2.10 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$); $^{13}\text{C-NMR}$: δ 170 (C=O), 145 (C=C), 78 (CCl_3), 65 (NCH_2), 52 ($\text{NCH}_2\text{CH}_2\text{O}$), 43 ($\text{CH}_2\text{C=C}$), 33 (CH_2). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{Cl}_3\text{NO}_2$: C, 44.46; H, 4.71; N, 4.71. Found: C, 44.24; H, 4.38; N, 4.58.

Compound **9**: mp $117\text{--}118^\circ\text{C}$; MS m/z : 297 (M^+); IR (KBr): 1680 (C=O), 1600 (C=C) cm^{-1} ; $^1\text{H-NMR}$: δ 4.60—4.80 (t, 1H, CH=CH_2), 4.30—4.40 (t, 1H, CHCO), 3.60—3.70 (t, 4H, NCH_2), 3.40—3.50 (t, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.10—3.25 (m, 1H, CHCO), 1.80—2.00 (m, 4H, CH_2CH_2); $^{13}\text{C-NMR}$: δ 175 (C=O), 145 (C=C), 100 (CHCO), 78 (CCl_3), 67 (NCH_2), 52 ($\text{NCH}_2\text{CH}_2\text{O}$), 43 (CH_2), 35 (CH_2). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{Cl}_3\text{NO}_2$: C,

44.46; H, 4.71; N, 4.71. Found: C, 44.15; H, 4.40; N, 4.53.

2,6-Di(trichloroacetyl)-1-(1-pyrrolidinyl)cyclohexene (10) and 2,6-Di(trichloroacetyl)cyclohexanone (4) Trichloroacetyl chloride (17.8 mmol, 3.23 g), 1-(1-pyrrolidinyl)cyclohexene (17.8 mmol, 2.69 g) and activated zinc (8.9 mmol, 0.58 g) were used. The crude product was recrystallized from hexane to give 1.57 g (40%) **10** as an unstable yellow solid which subsequently hydrolyzed to compound **4** by the addition of NaHCO₃ solution.

Compound **10**: mp 158–160 °C; MS *m/z*: 439 (M⁺); IR (KBr): 1758 (C=O), 1643 (conjugated C=O), 1620 (C=C) cm⁻¹; ¹H-NMR: δ 4.60–4.70 (t, 1H, CHCO), 2.40–2.60 (t, 4H, NCH₂), 2.20–2.30 (m, 2H, CH₂C(CO)=C), 2.00–2.20 (m, 4H, NCH₂CH₂), 1.40–1.80 (m, 4H, CH₂CHCO and CH₂CH₂CH₂). ¹³C-NMR: δ 200 (C=O), 185 (conjugated C=O), 140 (C=C), 98 (CHCO), 78 (CCl₃), 58 (NCH₂), 45 (CH₂C=C), *Anal.* Calcd for C₁₄H₁₅Cl₃NO₂: C, 38.05; H, 3.42; N, 3.17. Found: C, 38.20; H, 3.21; N, 3.31.

2-Trichloroacetyl-1-(1-pyrrolidinyl)cyclohexene (11) Trichloroacetyl chloride (17.8 mmol, 3.23 g), 1-(1-pyrrolidinyl)cyclohexene (17.8 mmol, 2.69 g) and triethylamine (17.8 mmol, 1.80 g) were used. The crude product was recrystallized from hexane to give 3.30 g (63%) **11** as a pure white solid.

Compound **11**: mp. 85 °C; MS *m/z*: 295 (M⁺); IR (KBr): 1640 (C=O), 1550 (C=C) cm⁻¹; ¹H-NMR: δ 2.70–2.90 (t, 4H, NCH₂), 2.40–2.50 (t, 4H, NCH₂CH₂), 1.80–2.00 (m, 4H, CH₂CH₂CH₂CH₂), 1.50–1.70 (m, 4H, CH₂CH₂CH₂CH₂). ¹³C-NMR: δ 180 (C=O), 140 (C=C), 78 (CCl₃), 60 (NCH₂), 35 (NCH₂CH₂), 30 (CH₂), 25 (CH₂). *Anal.* Calcd for C₁₂H₁₆Cl₃NO: C, 48.81; H, 5.47; N, 4.75. Found: C, 48.50; H, 5.15; N, 4.39.

2-Trichloroacetyl-1-(1-pyrrolidinyl)cyclopentene (12) The reaction of trichloroacetyl chloride (17.8 mmol, 3.23 g) and 1-(1-pyrrolidinyl)cyclopentene (17.8 mmol, 2.69 g) and triethylamine (17.8 mmol, 1.80 g) were used. The crude product was recrystallized from hexane to give 2.75 g (55%) **12** as a pure yellow solid.

Compound **12**: mp 90 °C; MS *m/z*: 281 (M⁺); IR (KBr): 1624 (C=O), 1520 (C=C) cm⁻¹; ¹H-NMR: δ 2.90–3.00 (t, 4H, NCH₂), 2.50–2.65 (t, 4H, NCH₂CH₂), 1.90–2.00 (m, 4H, CH₂CH₂CH₂), 1.75–1.85 (m, 2H, CH₂CH₂CH₂); ¹³C-NMR: δ 175 (C=O), 145 (C=C), 78 (CCl₃), 60 (NCH₂), 40 (NCH₂CH₂), 30 (CH₂), 20 (CH₂). *Anal.* Calcd for C₁₁H₁₄Cl₃NO: C, 46.97; H, 5.02; N, 4.98. Found: C, 46.62; H, 4.65; N, 4.55.

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