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Unusual ring-chain tautomerism in bicyclo[4.2.0]octane derivatives

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ABSTRACT

A new type of ring-chain tautomerism, which consists of the reversible conversion of bicyclo[4.2.0]octane derivatives into trisubstituted enamines was found and studied by ^{1}H NMR spectroscopy. The starting materials were prepared by the stereoselective reaction of (*E*)-3,3,3-trichloro-1-nitropropene with cyclohexanone enamines.

Conjugated nitroolefins possess unique chemical reactivity in both nucleophilic and cycloaddition reactions because of their reactive double bond.[1] As a result, partially fluorinated nitroalkenes have attracted attention as excellent building blocks for the preparation of various R^F-containing compounds.[2] However, to the best of our knowledge, very little information is available on the reactivity of (*E*)-3,3,3-trichloro-1-nitropropene (**1**). There have been only a few papers describing examples of the Diels–Alder reaction,[3] 1,3-dipolar cycloaddition,[4] and Michael additions of *N*- and *O*-nucleophiles.[2e–g,5] Here we have examined the behaviour of **1** in reactions with three cyclohexanone enamines, **2a–c** with the purpose of studying the structures and tautomeric properties of the reaction products.

It is well known[6] that the first step of the reaction of nitroalkenes with enamines involves the diastereoselective formation of a new C–C bond in the resulting dipolar intermediate, the fate of which depends on the nature of the reactants, and it may lead to different products. The most common is a tri- or tetrasubstituted nitroalkylated enamine whose formation derives from abstraction of a proton by the carbanion. Alternatively, the ambident nitronate anion can react with the iminium carbon atom producing a cyclic compound, which can be either a cyclobutane (more rarely) or a 1,2-oxazine *N*-oxide (more frequently), as a result of a formal [2+2] or [4+2] cycloaddition reaction, respectively.[7] Very little is known concerning the nature of the substituents on the ring-chain tautomeric equilibria of these compounds. Only one case of tautomeric equilibria between 1,2-oxazine *N*-oxides derived from aminocycloalkenes and their corresponding trisubstituted enamines has been reported.[8] On the contrary, ring-opening of cyclobutane derivatives to give nitroalkylated enamines is regarded as irreversible.[9] This communication describes a new type of ring-chain tautomerism in CCl_3-containing bicyclo[4.2.0]octanes.

We have found that the reaction of CCl_3-nitropropene **1** with cyclohexanone enamines **2a–c** in dry hexane for 15 min at 10–15 °C, and for 0.5 h at room temperature results in the stereoselective formation of substituted bicyclo[4.2.0]octanes **3a–c**, as the products of kinetic control, in 61–76% yields.[10] Notably, cyclobutanes **3** contain four contiguous stereogenic centres, but only one diastereomer could be observed by ^{1}H NMR spectroscopy of the crude products. The stereochemistry of **3b** was confirmed unambiguously by X-ray crystal structure analysis (Fig. 1)[11] and is consistent with the literature data for related compounds.[12] The structures of **3a,c** were firmly established by comparison of their ^{1}H NMR spectra with those of **3b** in C_6D_6, which showed signals for the cyclobutane form only. The ^{1}H NMR spectra of **3** exhibited two downfield shifted signals assigned to H-7 (δ 3.76–3.81, dd, J = 9.8, 8.3 Hz) and H-8 (δ 4.83–4.90, d, J = 8.3 Hz); the assignment of all signals was achieved by using 2D HSQC and HMBC experiments.

When the reaction of nitroalkene **1** with enamines **2a,b** was performed in chloroform at ~20 °C for 3 h, trisubstituted *syn*-enamines **4a,b** were obtained in 48–53% yields. These compounds can also be prepared from bicyclo[4.2.0]octanes **3a,b** in chloroform in 50–53% yields. Irrespective of the preparation method, enamines

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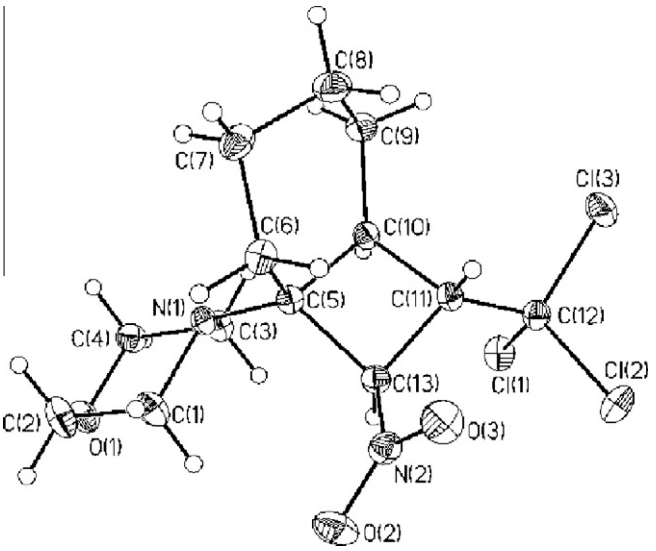


Figure 1. X-ray crystal structure of **3b** (ORTEP drawing, 50% probability level).

4a,b were always formed as one *syn*-diastereomer, the stereochemistry of which was proved by X-ray diffraction after isolation of **4b** as a single crystal (Fig. 2).[10,11] In the case of **3c**, only tetrasubstituted enamine **5c** was isolated under the same reaction conditions, while **5b** was prepared from **3b** at room temperature in two days. The conversion of the starting cyclobutanes **3b,c** into the tetrasubstituted enamines **5b,c** was quantitative, and the conditions were very mild. Only in one case, namely when the enamine was *N*-cyclohexenylmorpholine (**2b**), were both tri- and tetrasubstituted enamines **4b** and **5b** isolated in pure form.

Cyclobutanes **3** are sufficiently stable in the crystalline state and can be stored in a freezer (−10 °C), without deterioration, for a long time. However, in $CDCl_3$ at room temperature, these compounds exist as an equilibrium mixture of ring-chain tautomers **3** and **4**. Although the two isomers are stable in the solid state, upon dissolving either isomer in $CDCl_3$, it begins to convert into the other, and the process continues until an equilibrium mixture of **3** and **4** is reached. Opening of the cyclobutane ring **3** into trisubstituted enamines **4** and the reverse process occur via betaine **A**, and were

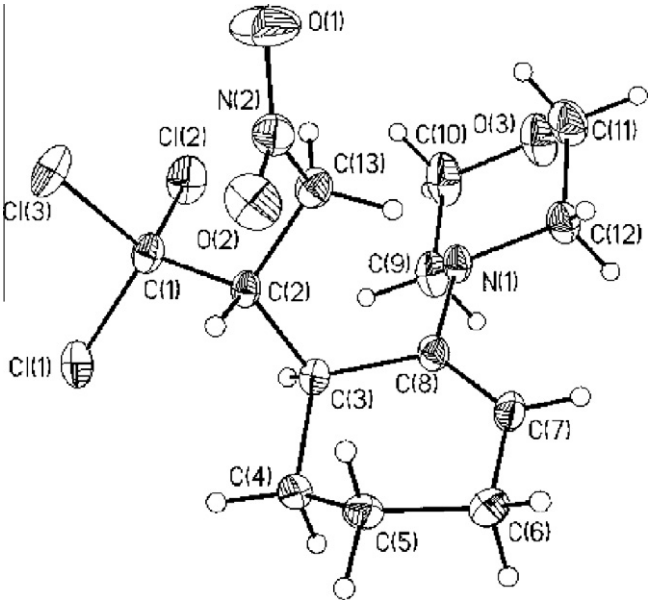


Figure 2. X-ray crystal structure of **4b** (ORTEP drawing, 50% probability level).

followed by monitoring the reaction by ^{1}H NMR spectroscopy at 25 °C. The proportions of the ring (**3**) and isomeric chain forms (**4** and **5**) in the tautomeric equilibria were determined by integration of the well-separated H-7 and H-8 (ring) and H-1 and H-2 (chain) proton signals in the ^{1}H NMR spectra.

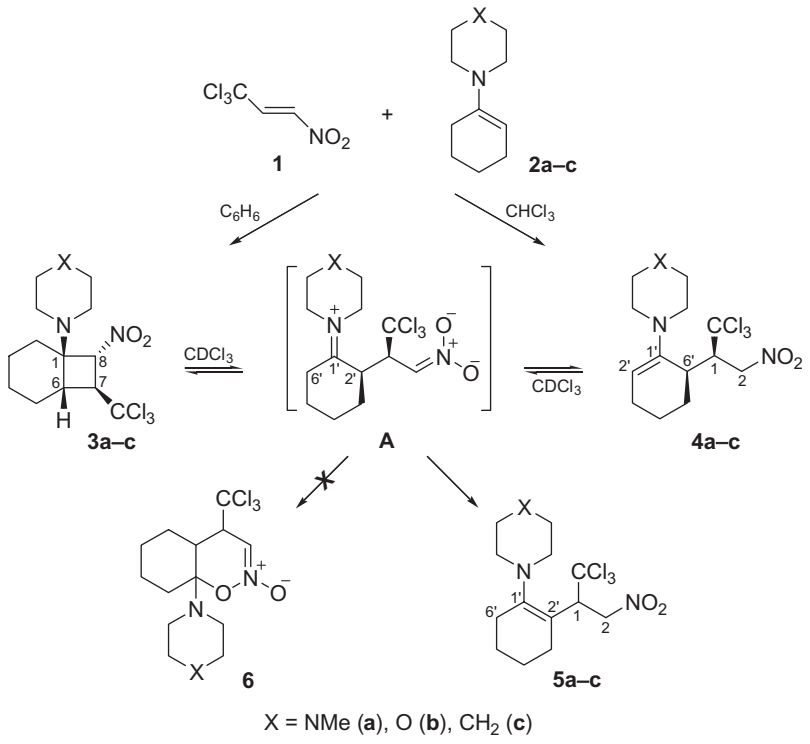
In the case of **3a**, the ratio **3a**:**4a** = 9:1 was recorded (2 min) after dissolving the crystals in $CDCl_3$. After 40 min, a 1:1 mixture of **3a** and **4a** was present, while after 3 h an equilibrium ratio of 1:4.5 was observed which remained unchanged for 24 h. Moreover, when the progress of the reaction was monitored by ^{1}H NMR spectroscopy over several weeks, we observed the appearance of a third product, indicating that under these conditions, compounds **3a** and **4a** irreversibly isomerize via dipolar intermediate **A** into the tetrasubstituted enamine **5a** (4% in seven days and 24% in 40 days). The predominant amount of **4a** in the final reaction mixture is due to the higher thermodynamic stability of the open form in comparison to cyclobutane **3a**. The same tautomeric mixture (**4a**:**3a** = 82:18 after 5 h) was obtained when the reaction was carried out on the pure *syn*-enamine **4a** (Scheme 1).

These results are of particular interest because reversible formation of a cyclobutane system from an acyclic enamine has not been described so far, and this is the first report of ring-chain tautomerism in cyclobutane derivatives. The ring-opening reaction is probably catalysed by traces of acid present in the deuterated chloroform. As would be expected, the nature of the solvent affects the state of this equilibrium. For instance, the equilibrium between tautomers **3a** and **4a** was almost completely shifted towards acyclic form **4a** immediately after dissolution of **3a** in CD_3OD.

Analogously, a 1:3.5 equilibrium mixture **3b** ⇆ **4b** was observed for the morpholino derivatives. In this case, ring-chain tautomerism was complicated by the appearance of tetrasubstituted enamine **5b**, while cyclobutane **3b** and trisubstituted enamine **4b** slowly disappeared during the course of the reaction. After 3 h at 25 °C, a third resonance signal for each proton from **5b** appeared (2%) and continued to grow until a ratio of **3b**:**4b**:**5b** = 16:40:44 (24 h) was observed. The irreversible stage **3b** ⇆ **4b** → **5b**, which caused the total shift of the ring-chain equilibrium towards the tetrasubstituted enamine **5b**, was complete within 48 h and gave **5b** as the sole reaction product. A similar equilibrium mixture was attained from the pure enamine **4b**, the conversion of which into **5b** was slower (for comparison, **4b**:**3b**:**5b** = 71:23:6 after 24 h).

As for the cyclobutane **3c**, there was a marked difference in its propensity towards ring-opening. ^{1}H NMR studies of **3c** in $CDCl_3$ indicated that this compound was less stable and underwent more rapid ring-opening to give the tri- and tetrasubstituted enamines **4c** and **5c**. The ^{1}H NMR spectrum of **3c** in $CDCl_3$, registered immediately after the compound had been dissolved (2 min), indicated a 2:3 mixture of **3c** and **4c**, while after 0.5 h a 1:5 ratio was observed. There was no subsequent change in the percentage tautomerism which remained unchanged for 3 h and only the content of the thermodynamically more stable tetrasubstituted enamine **5c** increased (3% in 1 h and 14% in 3 h). It should be noted that only decomposition products were detected in the ^{1}H NMR spectrum of **3c** after standing in $CDCl_3$ for 21 h.

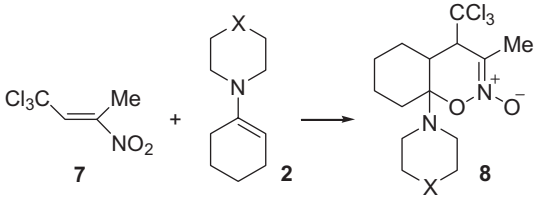
The main information for the characterization of enamines **5a–c** was obtained from ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of **5** showed no H-2′ vinyl proton signal and no H-6′ methine proton signal, a result consistent with the tetrasubstituted enamine structure. The most downfield shifted signal assigned to the H-1 methine proton of the side chain appeared as a doublet of doublets at δ 5.9–6.0 with J = 10.5 and 3.0 Hz. The remarkable shift of this signal compared with that of trisubstituted enamines (δ 3.6–3.7) can be explained by the influence of the double bond. Spectral studies of tetrasubstituted enamines **5a–c** in C_6D_6 and $CDCl_3$ showed that these compounds were stable and did not exhibit any tautomerism or isomerism.



Scheme 1.

It is important that while the reactions of enamines **2** with (*E*)-3,3,3-trichloro-1-nitropropene (**1**) gave [2+2] cycloaddition adducts **3** (cyclic nitronate form **6** was not found, Scheme 1), their reactions with (*E*)-1,1,1-trichloro-3-nitro-2-butene (**7**) under the same conditions gave no [2+2] cycloadducts at all. The latter reacted with **2** to give the [4+2] cycloaddition adducts, 3-methyl-4-trichloromethyl-1,2-oxazine *N*-oxides **8**, instead.[13] This observation indicated that the reactions of nitrobutene **7** with enamines **2** took an entirely different course as compared with the reactions of nitropropene **1**. The failure of the [2+2] cycloaddition reaction with **7** possibly results from the methyl group, which hinders the approach of the carbanion to the iminium carbon atom. In this case, steric interactions with the carbanionic centre become the deciding factor and nucleophilic attack of the ambident nitronate anion, which acts as an *O*-nucleophile, on the iminium carbon atom results in [4+2] heterocyclization to give 1,2-oxazine *N*-oxides **8** with the Me group at the 3-position (Scheme 2).

In conclusion, we have shown, for the first time, that the reaction of 3,3,3-trichloro-1-nitropropene with cyclohexanone enamines affords bicyclo[4.2.0]octanes or linear enamines depending on the reaction conditions. A new type of ring-chain tautomerism consisting of the reversible transformation of cyclobutane derivatives into trisubstituted enamines was found and studied by ^{1}H NMR spectroscopy. The ratios of the tautomeric forms involved in the equilibria of these systems are not strongly influenced by the nature of the amine. Further studies on the ring-chain and ring-ring tautomeric equilibria of related compounds are now in progress.



Scheme 2.

Acknowledgement

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10. *4-[(1R*,6S*,7S*,8R*)-8-nitro-7-(trichloromethyl)bicyclo[4.2.0]oct-1-yl]morpholine (**3b**).* Yield 72%, colourless crystals, mp 134–135 C (hexane–benzene, 1:2); IR (KBr) 1540, 1458, 1357 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 0.80–1.22 (m, 6H, $3CH_2$), 1.54–1.60 (m, 2H, CH_2), 2.17–2.22 (m, 2H, $N(CHH)_2$), 2.28 (ddt, 1H, H-6, J = 9.8, 6.3, 1.7 Hz), 2.38–2.42 (m, 2H, $N(CHH)_2$), 3.44 (ddd, 2H, $O(CHH)_2$, J = 10.8, 5.8, 3.3 Hz), 3.47 (ddd, 2H, $O(CHH)_2$, J = 10.8, 5.8, 3.3 Hz), 3.76 (dd, 1H, H-7, J = 9.8, 8.3 Hz), 4.83 (d, 1H, H-8, J = 8.3 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 1.2–2.1 (m, 8H, $4CH_2$), 2.6–2.7 (m, 3H, $N(CHH)_2$, H-6), 2.74–2.82 (m, 2H, $N(CHH)_2$), 3.68–3.75 (m, 4H, $O(CH_2)_2$), 3.87 (t, 1H, H-7, J = 9.1 Hz), 4.95 (d, 1H, H-8, J = 8.4 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ 20.5 (C-4), 21.0 (C-3), 22.3 (C-2), 24.3 (C-5), 36.5 (C-6), 47.1 (NCH_2), 54.3 (C-7), 64.1 (C-1), 67.3 (OCH_2), 83.7 (C-8), 99.8 (CCl_3). Anal. Calcd for $C_{13}H_{19}Cl_3N_2O_3$: C, 43.66; H, 5.35; N, 7.83. Found: C, 43.65; H, 5.51; N, 7.71.
*syn-4-[(1,1,1-Trichloro-3-nitroprop-2-yl)cyclohex-1-enyl]morpholine (syn-**4b**).* Yield 50%, colourless crystals, mp 101–102 °C; IR (KBr) 1648, 1558, 1383 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 1.33–1.54 (m, 3H, H-4′a, H-4′b, H-5′a), 1.73 (m, 1H, H-3′a), 1.83–1.90 (m, 2H, H-3′b, H-5′b), 2.06 (ddd, 2H, $N(CHH)_2$), J = 11.5, 5.8, 3.1 Hz), 2.53–2.60 (m, 3H, $N(CHH)_2$, H-6′), 3.32–3.42 (m, 4H, $O(CH_2)_2$), 3.62 (dt, 1H, H-1, J = 5.6, 4.4 Hz), 4.57 (dd, 1H, H-2a, J = 15.0, 4.4 Hz), 4.67 (dd, 1H, H-2′, J = 4.1, 3.5 Hz), 4.82 (dd, 1H, H-2b, J = 15.0, 5.6 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 1.55–2.20 (m, 6H, $3CH_2$), 2.51 (dt, 2H, $N(CHH)_2$, J = 11.7, 5.0 Hz), 2.87 (br q, 1H, H-6′, J = 3.5 Hz), 3.05 (dt, 2H, $N(CHH)_2$, J = 11.7, 5.0 Hz), 3.70 (t, 5H, $O(CH_2)_2$, H-1, J = 4.5 Hz), 4.84 (dd, 1H, H-2a, J = 15.1, 4.7 Hz), 5.04 (dd, 1H, H-2b, J = 15.1, 5.5 Hz), 5.08 (t, 1H, H-2′, J = 3.7 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ 17.1 (C-4′), 24.1 (C-3′), 30.5 (C-5′), 34.5 (C-6′), 50.6 (NCH_2), 61.2 (C-1), 67.0 (OCH_2), 75.6 (C-2), 103.0 (CCl_3), 112.6 (C-2′), 145.9 (C-1′). Anal. Calcd for $C_{13}H_{19}Cl_3N_2O_3$: C, 43.66; H, 5.35; N, 7.83. Found: C, 43.64; H, 5.22; N, 7.79.
*4-[2-(1,1,1-Trichloro-3-nitroprop-2-yl)cyclohex-1-enyl]morpholine (**5b**).* Yield 100%, yellow oil; IR (KBr) 1646, 1558, 1378 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.2–2.4 (m, 12H, $4CH_2$, $N(CH_2)_2$), 3.60–3.73 (m, 4H, $O(CH_2)_2$), 4.20 (t, 1H, H-2a, J = 10.7 Hz), 4.41 (dd, 1H, H-2b, J = 11.0, 3.0 Hz), 5.93 (dd, 1H, H-1, J = 10.5, 3.0 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 1.5–2.4 (m, 10H, $4CH_2$, NCH_2), 2.6–2.7 (m, 2H, NCH_2), 3.74 (br s, 4H, $O(CH_2)_2$), 4.76 (t, 1H, H-2a, J = 10.7 Hz), 4.98 (dd, 1 H, H-2b, J = 10.8, 3.0 Hz), 5.93 (dd, 1H, H-1, J = 10.3, 3.0 Hz).
11. *X-Ray diffraction study of compounds **3b** and **4b**.* Diffraction data were collected at 130 K (**3b**) and 150 K (**4b**) on an Xcalibur 3 automatic single-crystal diffractometer (graphite-monochromated MoKα radiation, ω-scans). The structures were solved by direct methods and refined by the full-matrix least-squares method using the SHELX-97 programme package.[14] The H atoms were located geometrically using the riding model. *Crystal data for* **3b**: $C_{13}H_{19}Cl_3N_2O_3$, M = 357.65, triclinic crystals, space group P-1, a = 8.5468(13), b = 9.1515(13), c = 11.0677(14) Å, α = 89.894(11), β = 80.635(12), γ = 65.478(14)°, V = 775.01(19) $Å^3$, Z = 2, ρ_{calcd} = 1.533 g/cm^3, μ = 0.602 mm^{-1}, $F(000)$ = 372. *Crystal data for* **4b**: $C_{13}H_{19}Cl_3N_2O_3$, M = 357.65, triclinic crystals, space group P-1, a = 8.8447(7), b = 9.0250(5), c = 11.8289(11) Å, α = 72.800(8), β = 74.919(7), γ = 62.058(8), V = 788.53(11) $Å^3$, Z = 2, ρ_{calcd} = 1.506 g/cm^3, μ = 0.591 mm^{-1}, $F(000)$ = 372. Crystallographic data for compounds **3b** (CCDC deposition number 809202) and **4b** (CCDC deposition number 809203) have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.
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