7e, 110355-26-5; **7f**, 110355-27-6; **7g**, 110355-28-7; **8a**, 7048-41-1; **8b**, 7048-42-2; **8c**, 58506-25-5; **8d**, 58506-24-4; **9a**, 110355-29-8; **9b**, 110355-30-1; **9c**, 110355-31-2; **9d**, 110355-32-3; **9e**, 110355-33-4; **9f**, 110355-34-5; **9g**, 110355-35-6; **10a**, 110355-36-7; **10b**, 110355-37-8; **10c**, 110355-38-9; nitromalonodialdehyde sodium salt, 34461-00-2; diethylene glycol ditosylate, 7460-82-4.

Supplementary Material Available: Tables of the anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and bond distances, angles, and torsion angles (6 pages); tables of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

An O → N Acyl Transfer. An Important Activation Step for a Formal Nucleophilic Substitution in a Cyclopropane Derivative

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Acylated (piperidinocyclopropyl)dimedone **8** proved to be a suitable starting material for smooth generation of a highly reactive cyclopropylidenedimedone species (**9**). The latter can be trapped in a [2 + 4] cycloaddition with enol ethers **14** leading to **15** or with methylene dihydrofuran derivatives **10** and **16** producing **11** and **17**. These latter adducts (**11** and **17**) isomerize to more stable furans **13** and **18**. Without a trapping reagent **9** is transformed to **10**; thus, compounds **11** or **13** can be prepared by simple heating of **8**. Derivatives **11**, **13**, **15**, **17**, and **18** can formally be regarded as the products of two consecutive nucleophilic substitutions starting from a cyclopropanone *N,O*-acetal **1**. In bicyclic compound **19**, steric reasons prohibited analogous reactions.

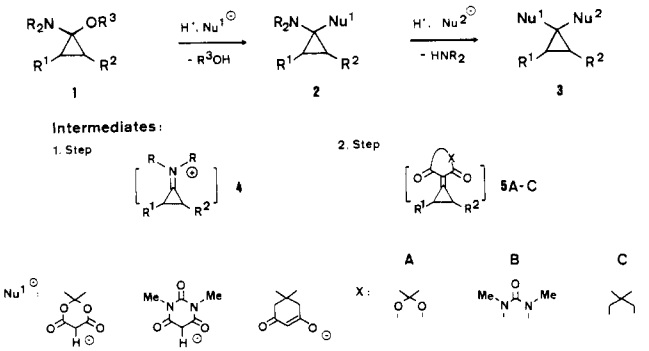
Introduction

Nucleophilic substitutions on cyclopropanes generally are characterized to be "notoriously difficult".[1] However, this is not correct for compounds of type **1**, in which the amino moiety promotes the nucleophilic substitution of the R^3O group by stabilizing the intermediate cyclopropyl cation **4**.[2,3] We could demonstrate (Scheme I) that with suitable nucleophiles Nu^1 **1** even acts as a starting material for a twofold nucleophilic substitution;[4] Meldrum's acid or barbituric acid as HNu^1 gave compounds **2**, in which the amino moiety may be displaced by further nucleophiles. Thus, nucleophiles Nu^2 as $^-CRR'$,[5-8] CN^-,[9] H^-,[9] RO^-,[9] or HO^-[10] reacted with **2**, forming cyclopropanes **3**. This second nucleophilic substitution is to be described as an elimination–addition sequence involving intermediates **5A** and **5B**.

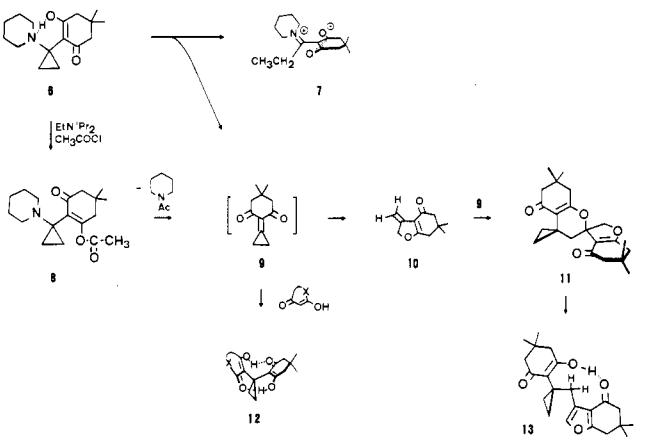
Nucleophiles Nu^1 derived from less strong CH acids (e.g., dimedone) so far allowed a twofold nucleophilic substitution in some exceptional cases only.[6,7] Whereas **6** could be synthesized from **1** ($R^1 = R^2 = H$, $R^3 = SiMe_3$[11]) and dimedone (step 1, Scheme I) without any problem,[6] a homoenamine ring opening[3] of **6** generating **7** interfered strongly with the nucleophilic substitution of the piperidino group in **6** to give **12** (step 2).[6] Thermolysis of **6** without added nucleophiles exclusively gave **7** as the product of a homoenamine ring opening.[6]

Ketene or isocyanates caused an acylation and a removal of the tertiary amino moiety in dialkylhydroxycyclopropylamines **1** ($R^3 = H$).[12] Cyclopropanone, which decomposed very quickly, was thereby formed in addition to the amide. We found that acylation of **6**, a vinylogous hydroxycyclopropylamine, also allows the removal of the amino moiety under smooth conditions, forming unexpected products of a nucleophilic substitution. An inter-

Scheme I



Scheme II



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fering homoenamine ring opening is not observed in this case.

Results and Discussion

Acylation of dimedone was reported to take place preferentially at the oxygen atom.[13] Analogously, reaction of **6** with acetyl chloride in dichloromethane at room temperature gave **8** in 72% yield (Scheme II). The ^1H and ^{13}C NMR spectra unequivocally established the presence of the *O*-acetyl group and the unchanged three-membered ring. Hindrance of the rotation of the two six-membered rings in **8** gave rise to broad unsplit signals for the cyclopropano group even in the ^{13}C NMR spectrum.

Upon heating, **8** decomposed by splitting off acetylpiperidine, which was characterized by its ^1H NMR spectrum. The decomposition was complete after $2^1/_2$ h of refluxing in dichloromethane; a mixture of **11** and **13** was thereby formed. The pure spiro compound **11** could be isolated in 44% yield. No other products besides acetylpiperidine, **11**, and **13** could be detected by observing the decomposition of **8** in $CDCl_3$ by ^1H NMR spectroscopy. Upon further heating, **11** isomerized quantitatively to the furan **13**. As chloroform was superior to dichloromethane for this step, pure **13** could be obtained directly in 66% yield by refluxing **8** in chloroform for 4 days.

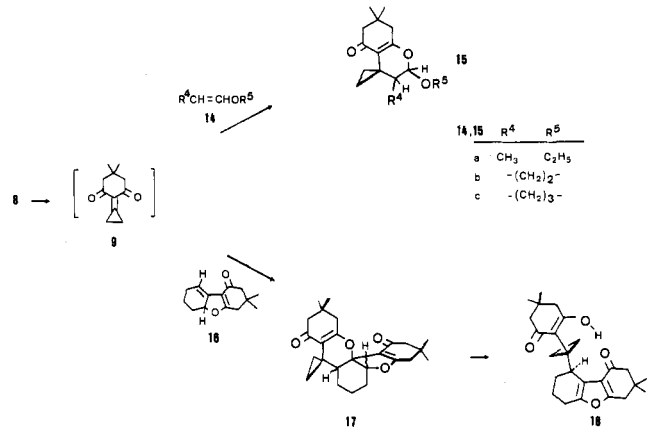
In the ^1H NMR, **11** shows six AB line systems for the methylene moieties of the six- and five-membered rings, four signal groups for the cyclopropane H atoms (ABMX system), and four methyl singlets as the consequence of the asymmetry. In **13** on the other hand a hydrogen bridge causes helical arrangements that are interconverted via a planar, nonchiral intermediate. As a consequence coalescence broadening is observed, especially for the signals of the cyclopropane H atoms and the noncyclic methylene group. The latter gives an AB system at −50 °C ($\nu_A - \nu_B$ = 46.8 Hz; J_{AB} = 13.9 Hz), which coalesces at 25 °C. From these values the activation energy for the helical inversion was calculated by the well-known approximation formula[14] to be 60.9 kJ/mol.

The ^{13}C NMR spectrum supports the structural assignments; it characteristically demonstrates the transformation of the spirodihydrofuran moiety of **11** (s, 86.0 ppm; t, 81.6 ppm) into the furan system of **13** (d, 140.9 ppm; s, 118 ppm).

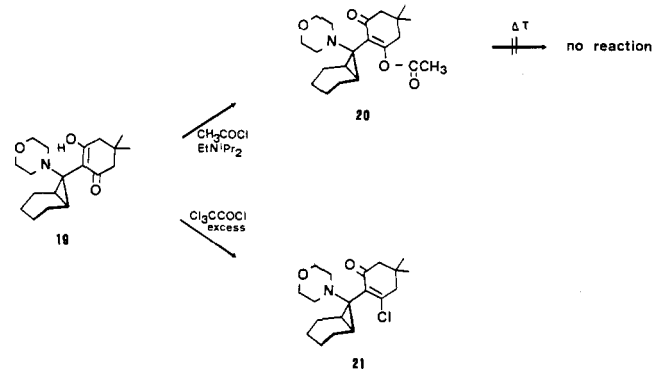
The decomposition of **8** starts with an O → N acyl transfer, elimination of the amino moiety as amide, and formation of the methylenecyclopropane **9**. Diacceptor substituted methylenecyclopropanes generally are unstable;[4] thus, **9** opens the three-membered ring to an allyl cation, which is attacked intramolecularly by the dimedone anion to form the methylenedihydrofuran **10**. **10** traps another molecule of **9** in a [4 + 2] cycloaddition leading to **11**. A β-elimination generating an aromatic furan system isomerizes **11** into **13**; traces of acid present in chloroform may thereby catalyze the isomerization. Since in addition to **11** **13** already was observed at an early stage of the reaction, an ene reaction between **9** and **10** to form **13** directly cannot be excluded.

The thermal decomposition of a (morpholinobicycloalkyl)dimedone derivative [e.g., **2C**, R^1, R^2 = $(CH_2)_3$ or $(CH_2)_9$] leads to a methylenedihydrofuran (e.g., **16**) as the stable end product.[15] Thus, the absence of a further bulky

Scheme III



Scheme IV



ring system obviously facilitates a subsequent cycloaddition of **9** and **10**.

The methylenecyclopropane **9** could also be trapped by other compounds possessing electron-rich CC double bonds. This was demonstrated by the decomposition of **8** in the presence of enol ethers **14** or the methylenedihydrofuran **16** (Scheme III). Thus, [4 + 2] cycloadducts **15a–c** were isolated in 64, 48, and 38% yields, respectively, from the reaction of **8** with enol ethers **14**. **16** as trapping reagent gave a mixture of [4 + 2] cycloadduct **17** and furan **18**, which could be separated to give the compounds in 25 and 37% yields, respectively. Upon further heating **17** isomerized completely to the more stable **18**.

The cycloadducts **15b** and **15c** proved to be pure stereoisomers; according to the small coupling constants of 3.8 Hz (**15b**) and 2 Hz (**15c**), the two heterocyclic ring systems are cis connected. A trans linkage of the two cycles causes a rigid system; the two hydrogen atoms at the bridgeheads, being in a trans diaxial position, should give values of about 8–12 Hz (e.g., derivatives with a 5,7-dioxabicyclo[4.4.0]dec-3-ene unit gave J = 1.5 Hz for a cis linkage and J = 8.8 Hz for a trans linkage[16]). The configuration of the polycyclic derivative **17** is unknown.

Nucleophilic substitution by amine acylation could not be performed with the bicyclic compound **19**. **19** was acylated to **20**; however, **20** proved to be stable upon heating to 160 °C (Scheme IV). Obviously, steric hindrance prevents the O → N acyl transfer in the bicyclic species. This is consistent with previous observations that in aminobicycloalkane derivatives a substituent could be displaced more easily from the exo than from the endo position.[4,17-19]

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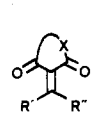
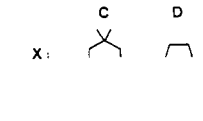
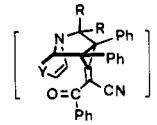
Use of trichloroacetyl chloride in order to increase the acylation power of the intermediate ester caused the formation of chloro compound **21** instead of an O → N acyl transfer. In this case, a nucleophilic displacement of the trichloroacetoxy group by chloride anion took place. ^1H and ^{13}C NMR spectra unequivocally proved the structures of **20** and **21**. Morpholino ^1H NMR signals of the ABXY type indicated the endo position[4,15,17-20] of the N heterocycle in **20** and **21**. Asymmetry as the consequence of a hindrance of the rotation of the *exo*-dimedone group was observed in the ^1H and ^{13}C NMR spectra for both compounds.

A [4 + 2] cycloaddition of enones and electron-rich olefins is a well-known method for the synthesis of pyrane derivatives;[21,22] methylenecycloalkanediones **22C**[23] and **22D**[24] successfully have been used in this sequence also.



22





23

A (benzoylcyanomethylene)cyclopropane intermediate **23** could be trapped by a [4 + 2] cycloaddition.[25] In this case, intermediate **23** was generated by an intramolecular cycloaddition of the corresponding methylenecyclopropene to pyridinium or thiazolium ylides.

Cyclopropylidenecycloalkanediones of type **5**, however, have a very strong tendency for ring opening and consequently are very unstable.[4] According to HMO calculations for methylenecycloalkanediones **22**,[26] the dimedone species **9** should be one of the most reactive and unstable representatives of this family of compounds. Therefore, acylation of **6** and reaction of **8** not only circumvent the disturbing homoenamine ring opening of **6**, but also serve as a basis for a smooth generation of **9**. Further investigations in progress already demonstrated that an acyl transfer is an important step to facilitate the nucleophilic displacement of the amino moiety in compounds of type **2**.

Experimental Section

2-(1-Piperidinocycloprop-1-yl)-5,5-dimethyl-3-oxocyclohex-1-en-1-yl Acetate (8). Acetyl chloride (0.28 mL, 4 mmol) and anhydrous dichloromethane (10 mL) sequentially were added at 20 °C to 2-(1-piperidinocycloprop-1-yl)-3-hydroxy-5,5-dimethylcyclohex-2-en-1-one (**6**[6]; 0.53 g, 2 mmol). The mixture was stirred for 5 min at 0 °C and then treated slowly with ethyldiisopropylamine (0.71 mL, 4.1 mmol). Stirring was continued for 5 min with ice cooling and 5 min after removal of the ice bath. Then the solution was extracted with a saturated aqueous solution of potassium dihydrogen phosphate (10 mL), the organic layer separated, and the aqueous phase extracted with dichloromethane (10 mL). Drying the dichloromethane solutions and evaporating the solvent under low pressure yielded a crystalline residue. The residue was dissolved in acetone (5 mL), water (1–2 mL) was added until the solution started to become cloudy, and then the mixture was stored at −18 °C for 20 h. Decantation of the solvent and washing the residue with an ice-cold mixture (1:1) of acetone–water (2 × 1 mL) gave colorless crystals of **8**: 0.44 g (72%); mp 89 °C; IR (KBr, cm^{-1}) 1760 (C=O), 1675, 1635 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 2.55 (s, 2 H), 2.52–2.41 (unstructured signal, 4 H, NCH_2), 2.30 (s, 2 H), 2.24 (s, 3 H), 1.51–1.24 (m, 6 H), 1.09 (s, 6 H), 0.89–0.80 and 0.55–0.46 (unstructured signals, 4 H); ^{13}C NMR ($CDCl_3$, 0 °C) δ 198.7, 167.7, 167.6, 123.1, 51.5, 42.7, 38.2, 32.3, 27.9, 26.6, 26.1, 24.2, 21.1, 14.7 (br t). Anal. Calcd for $C_{18}H_{27}NO_3$: C, 70.79; H, 8.91; N, 4.59. Found: C, 70.6; H, 8.90; N, 4.4.

Formation of 11 and 13 from 8. **8** (0.3 g, 1.15 mmol) was refluxed in 10 mL of anhydrous dichloromethane (**11**) or chloroform (**13**). Removal of the solvent in vacuo gave a residue, which was dissolved in 15 mL of acetone (**11**) or methanol (**13**). Water (ca. 1 mL) was added to the solution until it became cloudy. Storage for 3 days at −20 °C gave colorless crystals, which were filtered and washed with 5 mL of an ice-cold mixture (1:1) of water–acetone (**11**) or water–methanol (**13**).

2,3,6,7-Tetrahydro-6,6-dimethylbenzofuran-4(5*H*)-one-3-spiro-2′-[7′,8′-dihydro-7′,7′-dimethylchroman-5′(6′*H*)-one]-4′-spiro-1″-cyclopropane (11): reaction time 165 min; colorless needles; 0.18 g (44%); mp 160 °C; IR (KBr, cm^{-1}) 1640, 1615, 1590 (C=O, C=C); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.50 and 4.46 (AB system, J = 11.5 Hz, 2 H), 3.34 and 1.06 (AX system, J = 16 Hz, 2 H), 2.45 and 2.35 (AB system, J = 18 Hz, 2 H), 2.31 and 2.22 (AB system, J = 17 Hz, 2 H), 2.29 and 2.24 (AB system, J = 16 Hz, 2 H), 2.17 and 2.13 (AB system, J = 16 Hz, 2 H), 2.00–1.96 (m, 1 H), 1.31–1.26 (m, 1 H), 1.15 (s, 3 H), 1.11 (s, 3 H), 1.05 (s, 3 H), 1.02 (s, 3 H), 0.45–0.41 (m, 1 H), 0.36–0.32 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 196.6, 193.4, 180.5, 168.3, 113.2, 112.2, 86.0, 81.6, 52.2, 51.8, 43.3, 40.3, 38.1, 33.9, 31.3, 28.8, 28.6, 28.3, 27.4, 14.5 (t, J = 163 Hz), 13.3 (s), 7.8 (t, J = 164 Hz). Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.1; H, 7.91.

6,7-Dihydro-6,6-dimethyl-3-[[1-(3-hydroxy-5,5-dimethyl-1-oxocyclohex-2-en-2-yl)cycloprop-1-yl]methyl]benzofuran-4(5*H*)-one (13): reaction time 4 days; colorless needles; 0.27 g, (66%); mp 152 °C; IR (KBr, cm^{-1}) 3260 (OH), 1655, 1640, 1605 (C=O, C=C); ^1H NMR ($CDCl_3$, 200 MHz, 25 °C) δ 9.26 (s, 1 H), 7.09 (s, 1 H), 2.91 (br, 2 H), 2.73 (s, 2 H), 2.41 (s, 2 H), 2.35 (s, 2 H), 2.20 (s, 2 H), 1.14 (s, 6 H), 1.03 (s, 6 H), 0.73–0.16 (br, 4 H); ^{13}C NMR ($CDCl_3$) δ 197.8, 197.0, 173.2, 168.1, 140.9, 119.7, 118.6, 118.0, 52.1, 51.0, 42.3, 37.4, 35.4, 31.6, 28.1, 27.6, 12.3 (s), 10.0 (br t, J ~ 165 Hz). Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.2; H, 7.89.

3,4,5,6,7,8,8a,12,13,14a-Decahydro-3,3,12,12-tetramethyl-9*H*-benzofuro[2,3-*d*]xanthene-1(2*H*),10(11*H*)-dione-9-spiro-1′-cyclopropane (17) and 9-[1-(3-Hydroxy-5,5-dimethyl-1-oxocyclohex-2-en-2-yl)cycloprop-1-yl]-3,4,6,7,8,9-hexahydro-3,3-dimethyldibenzofuran-1(2*H*)-one (18). Acetoxy derivative **8** (0.61 g, 2 mmol) and dihydrofuran **16**[15] (0.44 g, 2 mmol) were refluxed in dichloromethane (15 mL) for 3 h. After the solvent was evaporated in vacuo, the residue was dissolved in methanol (20 mL); water (1–2 mL) was added until the solution started to become cloudy. **18** crystallized upon standing for 4 days at −20 °C; the colorless crystals were filtered off and washed with 5 mL of an ice-cold mixture (1:1) of methanol and water. **18**: 0.29 g (37%); mp 183 °C; IR (KBr, cm^{-1}) 3300 (OH), 1655, 1640, 1635, 1600, 1575 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 9.64 (s, 1 H), 3.15 (d, 1 H), 2.71 (s, 2 H), 2.65–1.26 (m, 6 H), 2.39 (s, 4 H), 2.20 (s, 2 H), 1.14 (s, 6 H), 1.07 (s, 3 H), 1.02 (s, 3 H), 0.91–0.81 (m, 1 H), 0.77–0.66 (m, 1 H), 0.37–0.27 (m, 1 H), 0.16–0.06 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 197.6, 196.2, 173.7, 166.0, 153.8, 119.6, 117.8, 114.0, 51.8, 51.6, 42.7, 37.4, 35.4, 34.6, 31.9, 28.8, 28.5, 28.2, 27.8, 26.5, 22.1, 18.6, 16.7 (s), 10.6 (t, J = 160 Hz), 8.2 (t, J = 162 Hz).

The remaining filtrate after the separation of **18** was treated with diaminoethane (3 mL) and water (10 mL) and extracted with pentane (2 × 10 mL). The combined pentane solutions were concentrated to a volume of 5 mL under low pressure and stored at 8 °C for 1 h to give **17** as a colorless precipitate, which was filtered off and washed with ice-cold pentane (5 mL). **17**: 0.20

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g (25%); mp 145 °C; IR (KBr, cm^{-1}) 1665, 1635, 1620, 1600 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 4.47 (t, 1 H), 2.41–2.15 (4 AB systems, 8 H), 2.15–0.91 (m, 9 H), 1.11 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H), 1.02 (s, 3 H), 0.35–0.20 (m, 2 H). Anal. Calcd for $C_{25}H_{32}O_4$: C, 75.73; H, 8.13. Found for **17**: C, 75.5; H, 8.04. Found for **18**: C, 75.5; H, 8.11;.

Transformation of 11 into 13 and 17 into 18. **11** (36 mg, 0.1 mmol) and **17** (40 mg, 0.1 mmol), respectively, were dissolved in deuteriochloroform (0.5 mL); each of the resultant solutions was heated in a sealed NMR tube to 60 °C for 4 days. The ^1H NMR spectra of the solutions were identical with the spectra of pure **13** and **18**, respectively.

Enol Ether Cycloadducts 15a–c. **6**[6] (0.53 g, 2 mmol) was dissolved in anhydrous methanol (10 mL), and the resultant mixture was treated with a 2 N methanolic solution of lithium methoxide (1 mL), and the resultant mixture was stirred at room temperature for 5 min. Methanol was removed as much as possible in vacuo (15 Torr); the residue was stirred in ether (20 mL), filtered, and washed with pentane (10 mL). The remaining white solid was dried under low pressure (0.001 Torr), added to anhydrous dichloromethane (10 mL), and treated with acetyl chloride (0.14 mL, 2 mmol) at 20 °C. Enol ether **14a–c** (20 mL) immediately was added. After refluxing dichloromethane and enol ether were removed in vacuo, the residue was treated with diaminoethane (6 mL) and water (20 mL) and extracted with pentane (2 × 20 mL). The pentane solutions were concentrated to 10 mL in vacuo and stored at −20 °C for 3 days. The crystalline **15** was filtered off and washed with ice-cold pentane (4 mL).

2-Ethoxy-7,8-dihydro-3,7,7-trimethylchroman-5(6*H*)-one-4-spiro-1-cyclopropane (15a): reaction time 3 h; 0.32 g (64%); mp 55 °C; IR (KBr, cm^{-1}) 1645, 1600 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 5.12 (X part of an ABX system, 1 H), 4.11 and 3.49 (AB part of an ABX_3 system, J_{AB} = 9.5 Hz, $J_{AX} = J_{BX}$ = 7 Hz, 2 H), 2.29 (s, 2 H), 2.15 (s, 2 H), 1.93–1.77 (m, 2 H), 1.56–1.40 (m, 2 H), 1.26 (t, 3 H), 1.05 (s, 6 H), 0.54–0.44 (m, 1 H), 0.34–0.25 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 196.4, 167.3, 112.0, 99.5, 64.4, 51.9, 42.6, 40.2, 30.9, 28.3, 27.4, 14.9, 12.8 (s), 12.4 (t, J = 163 Hz), 11.4 (t, J = 163 Hz). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.8; H, 8.81.

3,4,7,8,8a,9-Hexahydro-3,3-dimethylfuro[2,3-*b*]-5a*H*-chromen-1(2*H*)-one-9-spiro-1′-cyclopropane (15b): reaction time 5 h; 0.24 g (48%); mp 79 °C; IR (KBr, cm^{-1}) 1640, 1600 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 5.48 (d, J = 3.8 Hz, 1 H), 4.17 (H_A) and 3.95 (H_B) (AB part of an ABXY system, $J_{AB} = J_{AX} = J_{BX} = J_{BY}$ = 8.5 Hz, J_{AY} = 2.5 Hz, 2 H), 2.30 (s, 2 H), 2.28–2.21 (m, 1 H), 2.16 (s, 2 H), 2.10–1.73 (m, 2 H), 1.67–1.55 (m, 1 H), 1.22–1.15 (m, 1 H), 1.05 (s, 3 H), 1.04 (s, 3 H), 0.54–0.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 197.5, 167.8, 108.4, 100.1, 68.2, 52.1, 49.7, 42.7, 31.0, 28.5, 27.1, 26.2, 15.3 (t, J = 161 Hz), 13.8 (s), 9.0 (dd, J = 168, 158 Hz). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.3; H, 8.21.

3,4,5a,7,8,9a-Hexahydro-3,3-dimethyl-9*H*-pyrano[2,3-*b*]-10*H*-chromen-1(2*H*)-one-10-spiro-1′-cyclopropane (15c): reaction time 5 h; 0.20 g (38%); mp 85 °C; IR (KBr, cm^{-1}) 1655, 1600 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 5.39 (d, J = 2.6 Hz, 1 H), 3.92–3.65 (m, 2 H), 2.30 (s, 2 H), 2.21–2.11 (m, 1 H), 2.11 (s, 2 H), 1.70–1.35 (m, 5 H), 1.03 (s, 6 H), 1.12–0.87 (m, 1 H), 0.42–0.24 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 197.3, 168.1, 109.8, 97.3, 60.9, 51.9, 43.7, 42.3, 30.9, 28.2, 26.8, 24.3, 21.1, 18.8 (s), 15.2 (t, J = 163 Hz), 8.1 (t, J = 163 Hz). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.1; H, 8.32.

5,5-Dimethyl-2-(7-*endo*-morpholinobicyclo[4.1.0]hept-7-yl)-3-oxocyclohex-1-en-1-yl Acetate (20). Acetyl chloride (0.28 mL, 4 mmol) was added to a solution of morpholinobicycloheptyldimedone (**19**;[15] 0.64 g, 2 mmol) and ethyldiisopropylamine (1.04 mL, 6 mmol) in anhydrous dichloromethane (10 mL). The solution was stirred at 20 °C for 18 h. The reaction mixture was washed with a concentrated aqueous solution of potassium dihydrogen phosphate (10 mL), and the separated water layer was extracted with dichloromethane (10 mL). Drying the combined organic solutions (Na_2SO_4), removing the solvent in vacuo, and recrystallization of the residue from ether (10 mL) afforded pure **20**: 0.67 g (93%); mp 123 °C; IR (KBr, cm^{-1}) 1765, 1665, 1625 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 3.80–3.45 (m, 4 H), 2.91–2.08 (m, 4 H), 2.70 and 2.39 (AB system, J = 18 Hz, 2 H), 2.33 and 2.25 (AB system, J = 16 Hz, 2 H), 2.23 (s, 3 H), 1.91–1.39 (m, 6 H), 1.36–1.15 (m, 2 H), 1.15 (s, 3 H), 1.04 (s, 3 H), 0.94–0.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.5, 168.1, 167.7, 125.8, 67.9, 67.5, 52.1, 51.3, 43.1, 42.1, 32.7, 28.6, 27.8, 22.4, 21.8 (d, $^1J_{CH}$ = 163 Hz), 21.1, 19.6, 19.2. Anal. Calcd for $C_{21}H_{31}NO_4$: C, 69.78; H, 8.64; N, 3.87. Found: C, 69.7; H, 8.55; N, 3.8.

3-Chloro-5,5-dimethyl-2-(7-*endo*-morpholinobicyclo-[4.1.0]hept-7-yl)cyclohex-2-en-1-one (21). Morpholinobicycloheptyldimedone (**19**;[15] 0.64 g, 2 mmol) was stirred at 20 °C for 3 days in trichloroacetyl chloride (10 mL). Then the solution was added dropwise with stirring into an ice-cooled aqueous solution of potassium hydroxide (50 mL, 10% solution). Extraction with ether (3 × 20 mL), washing the ether with water (20 mL), stirring the ethereal phase with charcoal for 12 h, filtration, and removal of the solvent yielded a pale yellow oil. Crystallization from pentane (5 mL, −18 °C, 7 days) gave colorless **21**: 0.32 g (47%); mp 97 °C; IR (KBr, cm^{-1}) 1670, 1590 (C=O, C=C); ^1H NMR ($CDCl_3$) δ 3.79–3.44 (m, 4 H), 2.94–2.08 (m, 4 H), 2.73 and 2.66 (AB system, J = 18 Hz, 2 H), 2.37 and 2.22 (AB system, J = 16 Hz, 2 H), 1.97–1.41 (m, 6 H), 1.13 (s, 3 H), 1.01 (s, 3 H), 1.38–0.81 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 196.8, 156.8, 134.2, 67.8, 67.4, 52.0, 51.7, 51.3, 44.9, 32.9, 28.3, 27.7, 23.3 (d, $^1J_{CH}$ = 160 Hz), 23.1 (d, $^1J_{CH}$ = 160 Hz), 22.5, 22.4, 19.3, 19.2; mass spectrum, m/e 339 (2.2%) and 337 (7.6%) (M^+), 303, 302 (base). Anal. Calcd for $C_{19}H_{28}ClNO_2$: C, 67.54; H, 8.35; N, 4.15. Found: C, 67.6; H, 8.32; N, 4.1.

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