Addition of Twisted 1-Thioacyl-2,2-diaminoethylenes to Dimethyl Acetylenedicarboxylate. Formation and Ring Opening of Thiopyran-4-spiro-2'-(1',3'-diazacyclanes)

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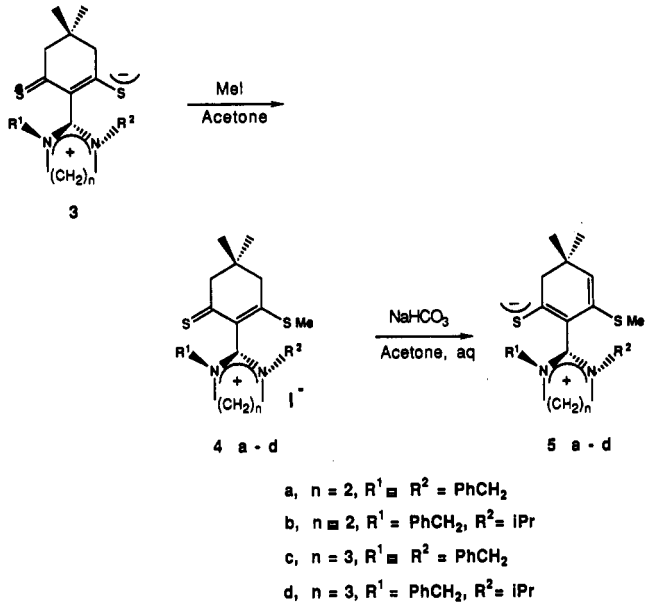
Reaction of 1,3-dialkyl-2-(4,4-dimethyl-2,6-dithioxocyclohexylidene)imidazolidines and -hexahydropyrimidines (twisted push-pull ethylenes, **3**) with methyl iodide followed by treatment with base leads smoothly to *S*-methyl derivatives, which are betaines with a 1,4-dipole and an electron-rich 1,3-butadiene system (**5**). These compounds react with DMAD to give dihydrobenzothiopyranspiroimidazolidine and -hexahydropyrimidine derivatives **7** in high yields. The spiro compounds rearrange in acid medium or on chromatography on silica gel to compounds, which we previously incorrectly described as "folded ethylenes" A but which are now shown to be 4-(2-aminoethyl)amino- or 4-(3-aminopropyl)aminothiopyran derivatives **11**. The 4-amino groups of **11** are twisted out of the thiopyran plane by the flanking substituents, and the barrier to rotation through the plane was found by NMR bandshape analysis to be 17.8 kcal/mol for the (2-aminoethyl)amino and 16.9 kcal/mol for the (3-aminopropyl)amino group. A 1:2 adduct of **5** and DMAD which we also previously incorrectly described as a folded ethylene (B), was shown to be an aminomaleic ester derivative **12** formed by addition of the NH group of **11** to DMAD.

Introduction

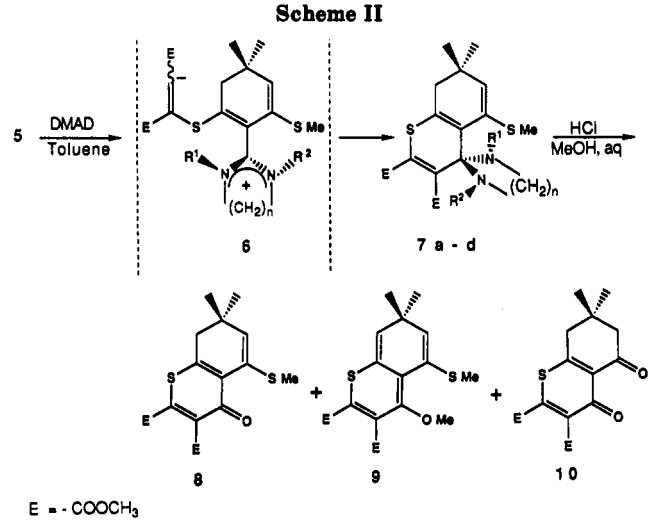
It has been shown that push-pull ethylenes (**1**) with sterically demanding donor (D) and acceptor (A) groups are twisted about the double bond. The D-C-C-A torsional angle is a function of both steric and electronic factors.[2] The torsion is facilitated by efficient stabilization of a negative charge in the A^1-C-A^2 part and of a positive charge in the D^1-C-D^2 part. Venkatesan and co-workers[3] have shown by X-ray crystallography that a number of push-pull ethylenes with D^1, D^2 = MeS, SMe; MeS, NMe_2; Me_2N, NMe_2, or $MeN(CH_2)_nNMe$ (n = 2 or 3) are twisted at the double bond with the largest twist angle (80.8°) found for **3a** (Scheme I).[3b] Recently, a twist angle of 84° has been reported for 1,3-diisopropyl-2-(diacetylmethylene)imidazolidine,[4a] and the twist angle 85° has been found for **3c**.[4b] Formulas like **2** are inadequate to describe the structures of these highly twisted compounds, which are better represented as betaines (**3**, Scheme I). Several push-pull ethylenes with lower twist angles due to less severe steric effects have also been described.[2,3] The $A^1A^2C^1$-C^2 and C^1-$C^2D^1D^2$ parts are in general found to be planar.

In the course of an investigation of the steric and electronic effects of thioxo groups as acceptor groups in push-pull ethylenes,[3d,5] we have studied the nucleophilic reactivity of the [S-C-C-C-S]$^-$ moiety in **3**.

Scheme I



Scheme II



(1) On leave of absence from P.C.S.I.R., Karachi, Pakistan.

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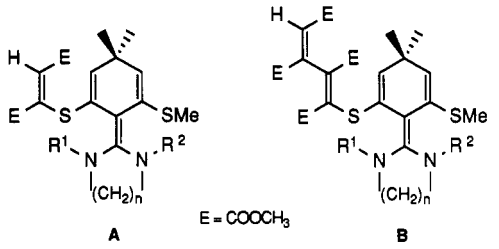
In a preliminary communication[6] we reported the reaction of compounds **3** with methyl iodide and on the subsequent facile deprotonation of the resulting methiodides **4** to the enethiol ethers **5** (Scheme I). Compounds **5** were found to add to one and two molecules of dimethyl acetylenedicarboxylate (DMAD) to give products, which were formulated as A and B and described as "folded



ethylenes" with antipyramidal double bond carbon atoms. The reactions were believed to be initiated by addition of **5** to one molecule of DMAD to give the betain **6** (Scheme II) with a vinyl anion, which could abstract a proton from the neighboring CH_2 group to give A in a reaction reminiscent of that leading to **5**. In the presence of excess DMAD, **6** was believed to add to a second molecule of this reagent and give B after inter- or intramolecular proton transfer. The proposed structures A were supported by ^1H and ^{13}C NMR spectra, by the appearance of two stereoisomers when $R^1 \neq R^2$, and by the observation through temperature-dependent NMR spectra of a dynamic process exchanging diastereotopic nuclei ($\Delta G^{\ddagger}$ 17–18 kcal/mol) and interpreted as an inversion of the pyramidal carbon atoms.

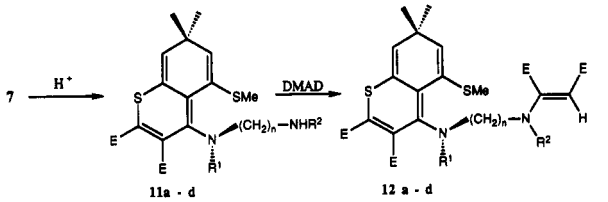
However, as is discussed here, continued studies of these reactions have shown that our previous interpretation[6] is incorrect. The alleged "folded ethylenes" have in fact been identified as thiopyran derivatives formed by ring opening of spiro compounds **7** obtained in the initial addition of **5** to DMAD. The spiro compounds were unobserved in our earlier experiments because they are unstable on TLC analysis and chromatographic workup of the reaction mixtures.

Results and Discussion

Compounds **3** are strong nucleophiles and react readily with methyl iodide to form amidinium iodides **4** (Scheme I), in which the sulfur-containing chromophore is a vinylogous methyl dithiocarboxylate. Compounds **4** are rapidly and nearly quantitatively deprotonated to the betaines **5** by sodium bicarbonate in water–acetone solution. Compounds **5** are twisted, as shown by the nonequivalence of prochiral nuclei in ^1H and ^{13}C spectra. Compound **5a** shows one AB pattern for the four benzylic protons and an AA'BB' pattern for the imidazolidine ring protons, both unchanged at +180 °C, indicating a free energy barrier to passage through the untwisted state higher than 28 kcal/mol. A recent X-ray crystallographic study of **5c**[4b] has shown the twist angle at the C^1–C^2 bond to be 72.5°.

Compounds **5** are electron-rich 1,3-dienes but are also 1,4-dipoles, and their reactions with dienophiles/dipolarophiles are of interest. Reaction of **5** with dimethyl acetylenedicarboxylate (DMAD) in a 1:1 ratio in toluene led to 1,4-dipolar additions, giving the spiro compounds **7** in high yields (Scheme II).

Scheme III



The addition of **5** to DMAD to give **7** has parallels in the additions of vinylogous thioamides[7-10] and thioacylketene *N,S*-acetals[11] to electrophilic alkenes and alkynes with formation of dihydrothiopyran and thiopyran derivatives, respectively. The former may become fully unsaturated by elimination of the amine component.[8] Similar reactions leading to spiro compounds have been observed between cyclic thioacylketene mercaptals and enamines.[12]

The general structure of the spiro compounds **7** follows from their NMR spectra (supplementary material, Table II). All four compounds show the resonance of a tetrasubstituted carbon atom in the range δ 76.9–81.3 due to the spiro carbon atom. Compounds **7a** and **7c** with equal N substituents give singlet *C*-methyl proton resonances, indicating a time-average plane of symmetry through the cyclohexadiene ring, and compounds **7b** and **7d** with unequal N substituents give two equally intense singlets. The benzylic methylene proton resonances of **7a–d** appear as single AB patterns, and the isopropyl methyl resonances in **7b** and **7d** are pairs of doublets. These two compounds are chiral, and **7b** (but not **7d**) cuold be resolved by chromatography on microcrystalline triacetylcellulose.[5a,13]

When the spiro compounds **7** were refluxed with aqueous methanolic HCl, three products of hydrolysis/methanolysis were formed (Scheme II): the thiopyran-4-one **8**, the corresponding enol ether **9**, and the dione **10**. The formation of all these compounds is in keeping with the aminal structures of compounds **7**.

However, when the spiro compounds **7a–d** are left in ethanolic HCl at room temperature, or when they are subjected to chromatography on silica, the main products (**11a–d**, Scheme III) are isomers of **7** with NMR spectra which indicate a total lack of symmetry elements (supplementary material, Table III). The ^{13}C spectra show that the spiro carbon atom has been changed to an unsaturated one (δ 126–136). Compounds **7b** and **7d**, with different N substituents, give pairs of isomeric products $\mathbf{11b_1}/\mathbf{11b_2}$ and $\mathbf{11d_1}/\mathbf{11d_2}$, which have the same color and very similar chromatographic behavior. All compounds give two broadened singlets for the *C*-methyl protons, and **11a** and **11c** give two separate resonances, an AB pattern, and a singlet for the benzylic methylene protons. The benzylic methylene resonances of $\mathbf{11b_1}$, $\mathbf{11b_2}$, $\mathbf{11d_1}$, and $\mathbf{11d_2}$ all appear as AB patterns, and most of their isopropyl methyl ^1H and all of the ^{13}C resonances show nonequivalent methyl groups. The NCH_2 groups are nonequivalent in all compounds, and several compounds show nonequiva-

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lent protons in the individual methylene groups. The presence of a 1,4-cyclohexadiene ring is verified by the two vinylic proton resonances in the range δ 5.5–5.8 with a four-bond coupling of 1.5–1.6 Hz. Coupled ^{13}C spectra show coupling of the corresponding vinylic carbon nuclei to the *C*-methyl protons, establishing the positions of the vinylic protons.

Compounds **11** must contain the dihydrobenzo[*b*]thiopyran skeleton found in the spiro compounds **7**, since hydrolysis with dilute aqueous methanolic HCl gave nearly quantitative yields of the thiopyran-4-one **8**. This leads to a 4-aminothiopyran structure for compounds **11**, created by opening the 1,3-diazacyclane ring in **7** (Scheme III). The amino group must be rotated out of the plane of the thiopyran ring to explain the nonequivalences observed.

The benzylic methylene ^1H resonances of **11a** and **11c** appear as one AB pattern and one singlet, likewise the NCH_2 resonances of the ethylenediamine/trimethylenediamine residues appear as one triplet and one more complex multiplet. In each case the group displaying the larger shift difference between diastereotopic protons is most likely the one nearest to the thiopyran ring. The isomer pairs **11b**$_1$/**11b**$_2$ and **11d**$_1$/**11d**$_2$ are explained by opening of the imidazolidine/hexahydropyrimidine ring in **7b** and **7d** either at NiPr or at NCH_2Ph. The observed slow exchange of the diastereotopic nuclei can be ascribed to slow rotation of the $R^1N(CH_2)_nNHR^2$ group through the thiopyran ring plane. The free energy barrier to this exchange is higher for **11a** (17.8 kcal/mol) than for **11c** (16.9 kcal/mol). The difference may be due to the larger conformational freedom of the longer alkane chain in **11c** in the transition state.

The opening of the diazacyclane rings in the spiro compounds **7** is probably initiated by N-protonation, followed by breaking of the N^+HC (spiro) bond and abstraction of a proton from the cyclohexadiene methylene group. The agent in the latter step may be another molecule **7**, which thereby propagates the reaction.

No great energy difference between the isomers **11d**$_1$ and **11d**$_2$ is expected, and reversibility of the ring opening of the spiro compounds should lead to exchange **11d**$_1$ ⇌ **11d**$_2$. However, no new signals were observed after heating a sample of **11d**$_1$ (the least abundant of the isomers formed from **7d**) in toluene-d_8 to 185 °C for 1 h in an NMR tube sealed under vacuum.

As mentioned in ref 6, reaction of compounds **5** with excess DMAD leads to diadducts, which were expected to be formed by reaction of the vinyl anion **6** with DMAD and were given the structure B. However, in view of the new structures assigned to compounds **11** and the observation of vinylic carbon resonances at δ 83–85 in the spectra of the diadducts, indicating an enamine moiety, structure **12** seems reasonable for the diadducts. This structure probably arises by addition of the NH group of **11** to DMAD, an assumption, which was confirmed by mixing equivalent quantities of **11a** and DMAD to give quantitative yield of **12a** after 0.5 h at ambient temperature. In the first experiment the reaction mixture, probably containing **7** and excess DMAD, was subjected to column chromatography. Rearrangement of **7** to **11** should have occurred on the column, followed by addition to DMAD to give **12**. The aminomaleic ester configuration (*E*) in **12** is assumed by analogy with a similar adduct, for which the *E* configuration has been demonstrated by NOE experiments.[14] The vinylic and methylene ^1H resonances of all compounds **12** appear broadened at ambient temperature but sharpen at +50 °C. No splittings could be observed at low temperature, and probably the compounds are involved in a conformational process with a strongly biased equilibrium and a barrier in the range 12–14 kcal/mol. A likely candidate to this process is the hindered rotation about the enamino C–N bond, since the barrier to this rotation in ethyl 3-(dimethylamino)acrylate is 13.9 kcal/mol.[15]

Compounds **9**, **11**, and **12** all have rather similar UV spectra with weak bands in the ranges 430–460 and 356–380 nm, and stronger bands in the regions 265–281 and 238–244 nm. These spectra are characteristic for the common chromophore in these compounds.

Experimental Section

Preparation of the dithiones **3a**[3d] and **3d**[5a] has been described before. The analogues **3b** and **3c** were prepared by similar methods.

1-Benzyl-3-isopropyl-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)imidazolidine (the dioxygen analogue of **3b**) was obtained in 89% yield by reaction of 2-[bis(methylthio)methylene]-5,5-dimethylcyclohexane-1,3-dione[16] with 1 equiv of *N*-benzyl-*N'*-isopropyl-1,2-diaminoethane in boiling DMF (1 h), colorless crystals, mp 161–163 °C after recrystallization from toluene/petroleum ether: ^1H NMR (300 MHz, $CDCl_3$) δ 1.03 (3 H, s), 1.07 (3 H, s), 1.21 (6 H, d, *J* = 6.8 Hz), 2.26 (4 H, s), 3.57–3.72 (4 H, AA'BB'), 3.98 (1 H, sept, *J* = 6.8 Hz), 4.37 (2 H, s), 7.23–7.33 (5 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1 [(CH_3)$_2$CH], 28.6, 28.9 [(CH_3)$_2C$], 31.6 [(CH_3)$_2C$], 41.0 (CH_2N), 45.5 (CH_2N), 48.8 [(CH_3)$_2$CH], 50.7 (CH_2CO), 51.4 (CH_2Ph), 95.5 [(O=C)$_2C$], 128.2, 128.6, 129.0, 134.4 (Ph), 168.1 (CN_2), 191.0 (C=O); MS [70 eV] *m/z* (relative intensity) 340 (9, M^+), 323 (8), 297 (10), 256 (8), 249 (30), 132 (19), 105 (19), 91 (100), 84 (40), 56 (22), 43 (35); UV [EtOH, λ nm (ε)] 265 (22 500), 248 sh (17 800), 206 (8900).

Reaction of this compound with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson's reagent)[17] in 1,2-dimethoxyethane (dried over CaH_2) under argon at ambient temperature gave **1-benzyl-3-isopropyl-2-(4,4-dimethyl-2,6-dithioxocyclohexylidene)imidazolidine (3b)** in 82% yield as orange prisms, mp 185–187 °C, after recrystallization from toluene. Dimethoxyethane gives a homogeneous solution, from which the product separates as crystals. Use of this solvent instead of refluxing toluene raised the yield of **3a** from 44[3d] to 82%: ^1H NMR (300 MHz, $CDCl_3$) δ 1.02 (3 H, s), 1.03 (3 H, s), 1.24 (6 H, d, *J* = 6.7 Hz), 2.77 (4 H, s), 3.54–3.75 (4 H, AA'BB'), 3.85 (1 H, sept., *J* = 6.7 Hz), 4.33 (2 H, s), 7.26–7.39 (5 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3 [(CH_3)$_2$CH], 27.6, 27.9 [(CH_3)$_2C$], 33.8 [(CH_3)$_2C$], 41.3 (CH_2N), 46.0 (CH_2N), 48.8 [(CH_3)$_2$CH], 51.5 (CH_2Ph), 57.8 (CH_2C=S), 129.5 [(S=C)$_2C$], 128.3, 128.7, 129.4, 133.7, (Ph), 168.7 (CN_2), 205.9 (C=S); MS [70 eV] 372 (9, M^+), 357 (3), 339 (38), 329 (7), 281 (20), 132 (16), 105 (30), 91 (100), 84 (52), 56 (45), 44 (100).

Reaction of 2-[bis(methylthio)methylene]-5,5-dimethylcyclohexane-1,3-dione with 1 equiv of *N,N'*-dibenzyl-1,3-diaminopropane in boiling DMF (1 h) gave **1,3-dibenzyl-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hexahydropyrimidine** (dioxygen analogue of **3c**) in 86% yield, mp 214–216 °C, after recrystallization from toluene: ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (6 H, s), 1.86 (2 H, quint), 2.22 (4 H, s), 3.22 (4 H, tr), 4.62 (4 H, s), 7.25–7.35 (10 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5 [(NCH_2)$_2$CH$_2$], 29.0 [(CH_3)$_2$C], 31.6 [(CH_3)$_2C$], 44.4 (CH_2N), 50.4 (CH_2CO), 57.6 (CH_2Ph), 101.9 [(O=C)$_2C$], 128.0, 128.5, 128.9, 134.7 (Ph), 164.8 (CN_2), 190.2 (C=O); MS [70 eV] 402 (6, M^+), 385 (9), 311 (16), 146 (20), 118 (9), 91 (100), 55 (10), 41 (35); UV (EtOH) 272 (21 000), 229 (24 000).

The bis-thionation of this compound was performed in 1,2-dimethoxyethane with 2,4-bis[4-(methylthio)phenyl]-1,3,2,4-dithiadiphosphetane 2,4-disulfide, which was obtained in high yield

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by refluxing a toluene solution of thioanisole with P_4S_{10}. The new reagent (yellow crystals, mp 155–175 °C) is somewhat more stable and easier to handle than the methoxy analogue.

1,3-Dibenzyl-2-(4,4-dimethyl-2,6-dithioxocyclohexylidene)hexahydropyrimidine (3c) was obtained in 86% yield as orange crystals, mp 207–209 °C, after recrystallization from toluene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (6 H, s), 1.97 (2 H, quint), 2.81 (4 H, s), 3.16 (4 H, tr), 4.62 (4 H, s), 7.27–7.50 (10 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0 [$(NCH_2)_2CH_2$], 28.2 [$(CH_3)_2C$], 33.9 [$(CH_3)_2C$], 44.2 (NCH_2), 57.0 (CH_2Ph), 58.0 ($CH_2C{=}S$), 128.3, 128.8, 130.1, 133.9 (Ph), 135.3 [$(S{=}C)_2C$], 166.0 (CN_2), 205.2 ($C{=}S$); MS [70 eV] 434 (4, M^+), 401 (10), 343 (4), 310 (5), 295 (6), 146 (9), 118 (8), 104 (7), 91 (100), 70 (30), 65 (15), 56 (8), 41 (35); UV (EtOH) 490 (31), 419 (50 800), 350 (660), 264 (6500), 226 (26 000).

The methiodides **4a–d** were all obtained in quantitative yield by reaction between equimolar amounts of **3**, dissolved in dry acetone, and methyl iodide. The products were isolated by evaporation and characterized by ^{1}H and ^{13}C NMR spectra (supplementary material, Table I): UV (**4d**, EtOH) 370 (22 000), 270 sh (4200), 219 (26 500).

1,3-Dibenzyl-2-[2-(methylthio)-4,4-dimethyl-6-thioxocyclohex-2-enylidene]imidazolidine (5a) precipitated in 98% yield on addition of a 5% aqueous $NaHCO_3$ solution (20 mL) to a solution of **4a** (0.01 mol) in acetone (30 mL) as yellow prisms, mp 162–164 °C, after recrystallization from toluene: ^{1}H NMR ($CDCl_3$) δ 1.05 (6 H, s), 2.34 (3 H, s), 2.67 (2 H, s), 3.48–3.63 (4 H, AA'BB'), 4.55 (2 H, d, J = 14.7 Hz), 4.60 (2 H, d, J = 14.7 Hz), 4.98 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 14.7 (q), 27.7 (q), 33.5 (s), 45.6 (t), 51.5 (t), 55.0 (t), 105.4 (s), 120.4 (d), 128.6 (s), 169.3 (s), 174.9 (s); MS [70 eV] 434 (8, M^+), 419 (9), 401 (10), 387 (7), 352 (5), 295 (7), 281 (8), 149 (6), 132 (12), 121 (4), 117 (6), 105 (20), 91 (100), 77 (10), 65 (20), 56 (13), 44 (72); UV (EtOH) 330 (7600), 287 sh (6500), 242 (17 300). Elemental analysis: C, H, N, S.

1-Benzyl-3-isopropyl-2-[2-(methylthio)-4,4-dimethyl-6-thioxocyclohex-2-enylidene]imidazolidine (5b) was obtained by the same procedure in 73% yield, yellow prisms, mp 153–155 °C, after recrystallization from toluene–petroleum ether: ^{1}H NMR ($CDCl_3$) δ 1.02 (3 H, s), 1.03 (3 H, s), 1.24 (3 H, d, J = 6.7 Hz), 1.38 (3 H, d, J = 6.7 Hz), 2.27 (3 H, s), 2.61 (2 H, s), 3.51–3.89 (4 H, m), 4.08 (1 H, sept, J = 6.7 Hz), 4.48 (1 H, d, J = 15.0 Hz), 4.57 (1 H, d, J = 15.0 Hz), 4.91 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 14.9 (q), 19.9 (q), 20.9 (q), 27.7 (q), 28.3 (q), 33.6 (s), 45.8 (t), 48.9 (t), 51.3 (t), 51.3 (d), 55.0 (t), 106.0 (s), 120.3 (d), 128.5 (s), 168.7 (s), 173.4 (s); MS [16 eV] 386 (100, M^+), 371 (72), 353 (80), 339 (40), 91 (11), 84 (12), 44 (36).

1,3-Dibenzyl-2-[2-(methylthio)-4,4-dimethyl-6-thioxocyclohex-2-enylidene]hexahydropyrimidine (5c) was obtained in 84% yield, mp 169–171 °C, after recrystallization from toluene–petroleum ether: ^{1}H NMR ($CDCl_3$) δ 0.93 (6 H, s), 1.86 (2 H, quint), 2.27 (3 H, s), 2.56 (2 H, s), 3.13 (4 H, t), 4.70 (2 H, d, J = 14.7 Hz), 4.78 (2 H, d, J = 14.7 Hz), 4.85 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 14.6 (q), 19.6 (t), 28.2 (q), 33.6 (s), 44.2 (t), 54.8 (t), 56.9 (t), 112.3 (s), 119.8 (d), 128.9 (s), 165.4 (s), 170.9 (s); MS [70 eV] 448 (5, M^+), 433 (4), 415 (10), 309 (4), 295 (6), 146 (10), 118 (8), 104 (4), 91 (100), 65 (10), 56 (12), 41 (25). Elemental analysis: C, H, N, S.

1-Benzyl-3-isopropyl-2-[2-(methylthio)-4,4-dimethyl-6-thioxocyclohex-2-enylidene]hexahydropyrimidine (5d) was obtained in 96% yield, mp 163–165 °C, after recrystallization from toluene: ^{1}H NMR ($CDCl_3$) δ 1.00 (3 H, s), 1.03 (3 H, s), 1.25 (3 H, d, J = 6.9 Hz), 1.43 (3 H, d, J = 6.9 Hz), 1.91–2.19 (2 H, m), 2.28 (3 H, s), 2.59 (2 H, s), 3.12–3.46 (4 H, m), 4.46 (1 H, sept, J = 6.9 Hz), 4.71 (1 H, d, J = 14.5 Hz), 4.76 (1 H, d, J = 14.5 Hz), 4.87 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 14.6 (q), 19.5 (t), 19.6 (q), 21.1 (q), 27.9 (q), 28.7 (q), 33.6 (s), 38.6 (t), 45.0 (t), 53.7 (d), 56.7 (2 C, t), 112.9 (s), 119.4 (d), 128.9 (s), 164.1 (s), 167.8 (s); MS [70 eV] 400 (13, M^+), 385 (8), 367 (32), 353 (14), 237 (7), 146 (6), 118 (6), 98 (13), 91 (100), 70 (15), 56 (27), 41 (32). Elemental analysis: C, H, N, S.

2,3-Bis(methoxycarbonyl)-7,8-dihydro-5-(methylthio)-7,7-dimethyl-1',3'-dibenzyl-4*H*-benzo[*b*]thiopyran-4-spiro-2'-imidazolidine (7a). DMAD (0.001 mol in 10 mL of dry toluene) was added slowly with efficient stirring under N_2 to a solution of **5a** (0.001 mol in 50 mL of dry toluene) during 1 h at room temperature. After a further 1 h, the solution was concentrated to give an oil as residue, which recrystallized on standing at −18 °C. Pale yellow solid, 93% yield, mp 80–81 °C, after recrystallization from toluene: ^{1}H NMR ($CDCl_3$) δ 1.09 (6 H, s), 2.27 (3 H, s), 2.27 (2 H, s), 2.91–3.16 (4 H, AA'BB'), 3.87 (3 H, s), 3.91 (3 H, s), 3.92 (2 H, d, J = 13.3 Hz), 4.09 (2 H, d, J = 13.3 Hz), 5.35 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 16.7 (q), 26.5 (q), 31.8 (s), 44.6 (t), 47.9 (t), 52.2 (t), 52.6 (q), 53.0 (q), 81.3 (s), 123.1 (d), 126.5 (s), 127.8 (s), 129.1 (s), 133.8 (s), 136.1 (s), 162.8 (s), 169.4 (s); MS [17 eV] 576 (9, M^+), 561 (27), 529 (42), 517 (85), 485 (14), 434 (80), 419 (20), 410 (55), 395 (30), 387 (29), 366 (35), 337 (12), 239 (100), 210 (15), 134 (12), 120 (35), 111 (40), 91 (45), 84 (30), 49 (40); MS [CI-NH_3] 577 (100, M^+ + 1); UV (EtOH) 342 (4500), 276 (5700), 232 (14 300). Elemental analysis: C, H, N, S.

A similar reaction with **5b** gave a quantitative yield of **7b**, pale yellow crystals, mp 92–95 °C, after recrystallization from toluene–petroleum ether: ^{1}H NMR ($CDCl_3$) δ 0.90 (3 H, s), 0.99 (3 H, d, J = 6.5 Hz), 1.06 (3 H, s), 1.12 (3 H, d, J = 6.5 Hz), 2.01 (1 H, d, J = 15.0 Hz), 2.16 (3 H, s), 2.29 (1 H, d, J = 15.0 Hz), 2.75–3.34 (4 H, m), 3.23 (1 H, sept, J = 6.5 Hz), 3.75 (3 H, s), 3.77 (1 H, d, J = 14.0 Hz), 3.88 (1 H, d, J = 14.0 Hz), 5.21 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 17.0 (q), 21.6 (q), 21.7 (q), 25.4 (q), 28.1 (q), 31.9 (s), 44.6 (t), 45.6 (t), 47.6 (t), 47.9 (d), 52.0 (t), 52.5 (q), 53.0 (q), 80.1 (s), 124.6 (d), 124.6 (s), 125.6 (s), 126.1 (s), 126.4 (s), 134.1 (s), 163.3 (s), 169.2 (s); MS [16 eV] 528 (5, M^+), 513 (25), 481 (20), 469 (32), 386 (35), 353 (18), 191 (15), 158 (17), 132 (25), 126 (30), 111 (26), 105 (20), 100 (30), 94 (75), 91 (50), 90 (55), 85 (60), 48 (80), 44 (100); UV (EtOH) 346 (6050), 279 (7500), 230 (16 800); CD (EtOH, Δε) 367 (+0.64), 297 (−1.07), 232 (+1.85).

In the same way, **7c** was obtained in quantitative yield from **5c**, pale yellow crystals, mp 125–126 °C, after recrystallization from toluene-petroleum ether: ^{1}H NMR ($CDCl_3$) δ 0.92 (6 H, s), 2.18 (2 H, s), 2.24 (3 H, s), 2.53–2.67 (2 H, m), 2.67–2.93 (4 H, m), 3.75 (2 H, d, J = 13.6 Hz), 3.85 (2 H, d, J = 13.6 Hz), 3.86 (3 H, s), 3.86 (3 H, s), 5.27 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 17.3 (q), 21.3 (t), 26.5 (q), 31.8 (s), 42.9 (t), 44.9 (t), 52.9 (q), 53.1 (q), 55.8 (t), 77.4 (s), 125.2 (s), 126.5 (d), 127.1 (s), 130.4 (s), 134.2 (s), 135.4 (s), 162.7 (s), 171.2 (s); MS [CI-NH_3] 591 (55, M^+ + 1), 160 (100); [70 eV] 590 (2), 575 (5), 543 (8), 517 (15), 447 (70), 415 (100), 401 (30), 323 (20), 148 (16), 111 (40), 91 (70), 62 (70), 48 (100), 44 (93). Elemental analysis: C, H, N, S.

The same reaction with **5d** gave a quantitative yield of **7d**, mp 126–127 °C after recrystallization from toluene. ^{1}H NMR (C_6D_6) δ 0.74 (3 H, s), 0.83 (3 H, s), 1.24 (3 H, d, J = 6.4 Hz), 1.44 (3 H, d, J = 6.4 Hz), 1.80 (1 H, d, J = 14.9 Hz), 2.04 (3 H, s), 2.27 (1 H, d, J = 14.9 Hz), 2.41–2.92 (2 H, m), 2.95–3.05 (4 H, m), 3.25 (1 H, sept, J = 6.4 Hz), 3.25 (3 H, s), 3.57 (3 H, s), 4.08 (1 H, d, J = 14.4 Hz), 4.23 (1 H, d, J = 14.4 Hz), 5.10 (1 H, s); ^{13}C NMR (C_6D_6) δ 16.8 (q), 19.0 (q), 21.5 (q), 21.9 (t), 24.1 (q), 28.8 (q), 31.9 (s), 36.8 (t), 43.5 (t), 44.3 (t), 49.4 (d), 52.4 (q), 52.5 (q), 56.1 (t), 76.9 (s), 126.2 (s), 126.7 (d), 128.5 (s), 128.8 (s), 135.0 (s), 135.0 (s), 163.1 (s), 170.6 (s); MS [CI-NH_3] 543 (100, M^+ + 1), 164 (30). Elemental analysis agrees with $C_{29}H_{38}N_2O_4S_2 + 2H_2O$.

Formation of 4-Aminothiopyrans 11 and Diadducts 12. The spiro compounds **7** on chromatography on silica gel underwent ring opening to give the 4-aminothiopyrans **11**. In some cases the chromatography was performed directly on the reaction mixture from **5** and DMAD. The stated yields are the isolated ones, often considerably lower than the total yields because of overlapping of chromatographic bands. Ring opening also occurred in dilute ethanolic HCl solution, but because of extensive formation of byproducts this was not found to be a suitable preparative method.

Dimethyl 4-[*N*-Benzyl-*N*-[2-(benzylamino)ethyl]-amino]-5-(methylthio)-7*H*-7,7-dimethylbenzo[*b*]thiopyran-2,3-dicarboxylate (11a) was isolated in 13% yield as a brownish-yellow, semisolid material when a reaction mixture of equimolar amounts of **5a** and DMAD in CH_2Cl_2 was subjected to flash chromatography[18] on silica gel with heptane followed by toluene and an increasing proportion of ethyl acetate. This compound could not be obtained crystalline, but its purity was ascertained by TLC and ^{1}H and ^{13}C NMR spectroscopy: ^{1}H NMR ($CDCl_3$) δ 1.05 (3 H, s), 1.08 (3 H, s), 2.26 (3 H, s), 2.66 (2 H, t), 3.15 (2 H, AB part of ABX_2 system), 3.51 (3 H, s), 3.70 (2 H, s), 3.78 (3 H, s), 4.21 (1 H, d, J = 14.2 Hz), 4.33 (1 H, d, J = 14.2 Hz), 5.56

(18) Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

(1 H, d, J = 1.5 Hz), 5.67 (1 H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 17.1 (q), 29.3 (q), 40.7 (s), 47.9 (t), 51.6 (t), 52.5 (q), 52.7 (q), 53.8 (t), 58.6 (t), 124.0 (s), 124.3 (s), 126.5 (s), 126.6 (s), 131.8 (s), 135.5 (d), 138.0 (s), 140.7 (d), 162.5 (s), 167.4 (s); MS [17 eV] 576 (42, M^+), 575 (51), 529 (18), 517 (87), 434 (25), 239 (40), 148 (17), 85 (50), 84 (80), 49 (100); UV (EtOH) 440 (1500), 356 (2250), 269 (10000), 208 (19000).

The 1-isopropyl-3-benzyl analogue **11b** was obtained as a mixture of **11b$_1$** and **11b$_2$** when subjecting **7b** to flash chromatography on silica gel. Only **11b$_1$** could be isolated as a brownish-yellow, semisolid material after repeated chromatography, but the ^{1}H NMR data for **11b$_2$** could be obtained from a 2:1 mixture of **11b$_1$** and **11b$_2$**. **11b$_1$**: ^{1}H NMR ($CDCl_3$) δ 1.08 (3 H, s), 1.14 (3 H, s), 1.156 (3 H, d, J = 6.4 Hz), 1.165 (3 H, d, J = 6.4 Hz), 2.29 (3 H, s), 2.75 (2 H, t), 2.95 (1 H, sept, J = 6.4 Hz), 3.26 (2 H, t), 3.63 (3 H, s), 3.80 (3 H, s), 4.14 (1 H, d, J = 12.7 Hz), 4.33 (1 H, d, J = 12.7 Hz), 5.61 (1 H, d, J = 1.6 Hz), 5.69 (1 H, d, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 17.2 (q), 20.77 (q), 20.83 (q), 29.36 (q), 29.41 (q), 41.1 (s), 44,3 (t), 49.1 (d), 49.9 (t), 52.9 (q), 53.2 (q), 58.8 (t), 123.4 (s), 125.0 (s), 127.5 (s), 128.2 (s), 131.1 (s), 136.6 (d), 137.1 (s), 141.4 (d), 163.2 (s), 168.3 (s). **11b$_2$**: ^{1}H NMR ($CDCl_3$) δ 0.92 (3 H, d, J = 6.9 Hz), 0.94 (3 H, d, J = 6.9 Hz), 1.10 (3 H, s), 1.11 (3 H, s), 2.33 (3 H, s), 2.9–3.3 (4 H, m), 3.80 (3 H, s), 3.81 (3 H, s), 4.41 (1 H, sept, J = 6.9 Hz), 4.23 (1 H, d, J = 12.7 Hz), 4.30 (1 H, d, J = 12.7 Hz), 5.65 (1 H, d, J = 1.6 Hz), 5.72 (1 H, d, J = 1.6 Hz); MS [**11b$_1$**, 16 eV] 528 (70, M^+), 513 (88), 481 (34), 469 (30), 455 (35), 428 (62), 422 (38), 386 (25), 324 (34), 117 (31), 99 (100), 94 (75).

Dimethyl 4-[*N*-benzyl-*N*-[3-(benzylamino)propyl]-amino]-5-(methylthio)-7*H*-7,7-dimethylbenzo[*b*]thiopyran-2,3-dicarboxylate (11c) was obtained in 57% yield as a brownish-yellow, semisolid material when the reaction mixture from equimolar quantities of **5c** and DMAD in CH_2Cl_2 was subjected to flash chromatography on silica gel with ethyl acetate with an increasing proportion of methanol as eluent: ^{1}H NMR ($CDCl_3$) δ 1.02 (3 H, s), 1.10 (3 H, s), 1.82 (2 H, m), 2.26 (3 H, s), 2.56 (2 H, t), 2.99 (2 H, AB part of ABX_2 system), 3.56 (3 H, s), 3.74 (2 H, s), 3.77 (3 H, s), 4.11 (1 H, d, J = 13.7 Hz), 4.21 (1 H, d, J = 13.7 Hz), 5.57 (1 H, d, J = 1.5 Hz), 5.59 (1 H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.9 (q), 28.5 (t), 29.2 (q), 29.3 (q), 40.4 (s), 47.2 (t), 50.6 (t), 52.4 (q), 52.5 (q), 56.3 (t), 58.6 (t), 123.8 (s), 125.6 (s), 126.6 (s), 132.0 (s), 135.2 (d), 136.2 (s), 138.0 (s), 139.3 (d), 162.4 (s), 167.1 (s); MS [CI-NH_3] 591 (100, M^+ + 1), 575 (4), 559 (17), 547 (28), 533 (42), 501 (30), 433 (18), 411 (19), 309 (18), 281 (18), 269 (22), 255 (43), 196 (75), 165 (55), 146 (72), 122 (70); high-resolution MS (M^+ – 15) found 575.2041, calcd for $C_{32}H_{35}N_2O_4S_2$ 575.2038.

The *N*-isopropyl-*N'*-benzyl analogues **11d$_1$** and **11d$_2$** were obtained in a total yield of 56% and in a ratio of 1:8 when the above reaction was repeated with **5d** and DMAD. Purified isomers were obtained as brownish-yellow, semisolid materials after repeated chromatographic separations on silica gel with ethyl acetate–methanol as eluent. **11d$_1$**: 1.01 (3 H, s), 1.10 (3 H, s), 1.34 (6 H, d, J = 6.5 Hz), 2.01 (2 H, quint), 2.28 (3 H, s), 2.77–3.12 (4 H, m), 3.20 (1 H, sept, J = 6.5 Hz), 3.60 (3 H, s), 3.61 (3 H, s), 4.04 (1 H, d, J = 13.8 Hz), 4.13 (1 H, d, J = 13.8 Hz), 5.57 (1 H, d, J = 1.6 Hz), 5.62 (1 H, d, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 17.1 (q), 19.0 (q), 19.1 (q), 25.0 (t), 29.3 (q), 29.4 (q), 40.4 (s), 47.2 (t), 49.4 (d), 50.6 (t), 52.8 (q), 52.9 (q), 58.1 (t), 123.9 (s), 125.1 (s), 127.0 (s), 127.1 (s), 132.1 (s), 136.0 (d), 137.6 (s), 140.2 (d), 167.2 (s), 168.3 (s); MS [16 eV] 542 (2, M^+), 527 (15), 323 (24), 114 (12), 100 (100), 91 (9), 84 (22), 49 (45), 36 (28); high-resolution MS (M^+ – 15) found 527.2036, calcd for $C_{28}H_{35}N_2O_4S_2$ 527.2038. **11d$_2$**: ^{1}H NMR ($CDCl_3$) δ 0.98 (3 H, s), 1.02 (6 H, d, J = 6.3 Hz), 1.08 (3 H, s), 1.77 (2 H, quint), 2.24 (3 H, s), 2.51 (2 H, t), 2.77 (1 H, sept, J = 6.3 Hz), 2.92 (2 H, AB part of ABX_2 system), 3.55 (3 H, s), 3.74 (3 H, s), 4.07 (1 H, d, J = 13.7 Hz), 4.15 (1 H, D, J = 13.7 Hz), 5.53 (1 H, d, J = 1.6 Hz), 5.56 (1 H, d, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 17.0 (q), 22.61 (q), 22.65 (q), 25.9 (t), 29.1 (q), 29.3 (q), 40.5 (s), 45.4 (t), 48.5 (d), 50.8 (t), 52.5 (q), 52.6 (q), 58.5 (t), 123.9 (s), 125.7 (s), 126.0 (s), 126.8 (s), 132.1 (s), 135.3 (d), 137.9 (s), 139.4 (d), 162.5 (s), 167.6 (s); MS [CI-NH_3] 543 (100, M^+ + 1), 511 (22), 485 (13), 455 (18).

Of the diadducts, **12a**, **12c**, and **12d** could be isolated by flash chromatography on silica gel of the reaction mixtures from the corresponding compounds **5** and two molar proportions of DMAD in CH_2Cl_2. Small amounts of the monoadducts **11** were eluted after the diadducts. No attempt was made to isolate **12b**. Only one isomer of **12d** has been isolated.

Dimethyl 4-[*N*-benzyl-*N*-[2-[*N*-benzyl-*N*-[1,2-bis(methoxycarbonyl)vinyl]amino]ethyl]amino]-5-(methylthio)-7*H*-7,7-dimethylbenzo[*b*]thiopyran-2,3-dicarboxylate (12a) was obtained in 62% yield as a red solid, mp 62–64 °C: ^{1}H NMR ($CDCl_3$) δ 1.03 (3 H, s), 1.08 (3 H, s), 2.27 (3 H, s), 3.10–3.36 (4 H, m), 3.56 (3 H, s), 3.59 (3 H, s), 3.79 (3 H, s), 3.86 (3 H, s), 4.07 (1 H, d, J = 13.1 Hz), 4.14 (1 H, d, J = 13.1 Hz), 4.21 (2 H, s), 4.71 (1 H, s), 5.60 (1 H, d, J = 1.5 Hz), 5.64 (1 H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 17.2 (q), 29.1 (q), 29.3 (q), 40.9 (s), 49.2 (t), 49.3 (t), 50.5 (q), 52.4 (q), 52.6 (q), 52.7 (q), 54.0 (t), 58.8 (t), 85.1 (d), 123.9 (s), 125.3 (s), 128.2 (s), 129.0 (s), 135.8 (s), 136.7 (d), 137.5 (s), 140.8 (d), 154.4 (s), 162.4 (s), 165.8 (s), 167.2 (s), 168.5 (s); MS [CI-NH_3] 719 (78, M^+ + 1), 383 (56), 295 (50), 274 (45), 252 (35), 164 (100), 147 (35), 134 (28), 120 (22), 105 (51); high-resolution MS (M^+ – 15) found 703.2142, calcd for $C_{37}H_{39}N_2O_8S_2$ 703.2148; UV (EtOH) 430 sh (3300), 378 (3500), 281 (31000), 238 (1700), 204 (32300). Elemental analysis: C, H, N, S.

Equimolar amounts of **5a** (0.018 g) and DMAD (0.005 g) in dry toluene (20 mL) showed nearly complete conversion to **12a** after a few minutes (TLC). After 30 min the mixture was evaporated, and a ^{1}H NMR spectrum of the residue in $CDCl_3$ showed only resonances of **12a**. The analogue **12c** was obtained as a red, semisolid mass in 73% yield: ^{1}H NMR ($CDCl_3$) δ 1.05 (3 H, s), 1.13 (3 H, s), 1.91 (2 H, m), 2.30 (3 H, s), 2.86 (2 H, m), 3.06 (2 H, tr), 3.57 (3 H, s), 3.65 (3 H, s), 3.81 (3 H, s), 3.93 (3 H, s), 4.04 (1 H, d, J = 13.4 Hz), 4.14 (1 H, d, J = 13.4 Hz), 4.32 (2 H, s), 4.71 (1 H, s), 5.61 (1 H, d, J = 1.6 Hz), 5.63 (1 H, d, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.9 (q), 20.5 (q), 20.6 (q), 25.5 (t), 29.2 (q), 29.3 (q), 40.5 (s), 48.3 (t), 49.9 (q), 50.3 (q), 52.3 (q), 52.5 (q), 53.6 (t), 58.6 (t), 84.8 (d), 123.9 (s), 126.2 (s), 126.6 (s), 135.4 (d), 135.7 (s), 137.7 (s), 139.8 (d), 154.4 (s), 162.3 (s), 162.5 (s), 167.0 (s), 167.9 (s); MS [CI-NH_3] 733 (100, M^+ + 1), 689 (15), 645 (15), 427 (20), 397 (25), 307 (16), 288 (38), 250 (30), 164 (60), 146 (30).

The analogue **12d** was obtained as a red solid, mp 55–57 °C, in 40% yield: ^{1}H NMR ($CDCl_3$) δ 1.02 (3 H, s), 1.11 (3 H, s), 1.15 (6 H, d, J = 6.6 Hz), 1.89 (2 H, m), 2.87 (4 H, m), 3.54 (1 H, sept, J = 6.6 Hz), 3.60 (3 H, s), 3.61 (3 H, s), 3.77 (3 H, s), 3.90 (3 H, s), 4.05 (1 H, d, J = 13.4 Hz), 4.13 (1 H, d, J 669.2308, 13.4 Hz), 5.54 (1 H, d, J = 1.6 Hz), 5.57 (1 H, d, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.9 (q), 20.5 (q), 20.6 (q), 25.9 (t), 29.2 (q), 29.3 (q), 40.0 (s), 41.9 (t), 50.1 (t), 50.5 (q), 52.4 (q), 52.60 (q), 52.65 (q), 58.6 (q), 83.0 (d), 123.6 (s), 126.2 (s), 126.5 (s), 128.0 (s), 135.6 (d), 136.0 (s), 137.6 (s), 139.4 (d), 153.9 (s), 162.3 (s), 166.1 (s), 167.2 (s), 168.3 (s); MS [CI-NH_3] 685 (100, M^+ + 1), 627 (12), 595 (12), 349 (32), 259 (12), 216 (16); high-resolution MS (M^+ – 15) found 669.2308, calcd for $C_{34}H_{41}N_2O_8S_2$ 669.2304.

Hydrolysis/Methanolysis of the Spiro Compound 7a. A solution of **7a** (0.114 g) in concentrated HCl (0.05 mL) diluted with methanol (30 mL) was refluxed for 10 min, rapidly cooled with ice, and quenched with an excess of solid sodium acetate. Most of the methanol was evaporated, and the residue was dissolved in water and extracted several times with methylene chloride. After drying with magnesium sulfate the organic phase was subjected to flash chromatography on silica gel with a hexane–ethyl acetate mixture with gradually increased ethyl acetate concentration as eluent. The following products were isolated (% yield): Unreacted **7a** (18), **8** (51), **9** (9), **10** (9), **11a** (13).

Dimethyl 5-(methylthio)-7,7-dimethyl-4-oxo-7,8-dihydrobenzo[*b*]thiopyran-2,3-dicarboxylate (8) was obtained as orange prisms, mp 138–139 °C, after recrystallization from toluene–heptane: ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 6 H, 7-(CH_3)$_2$), 2.23 (s, 3 H, CH_3S), 2.56 (s, 2 H, H-8), 3.92, 3.93 (2 s, 6 H, CO_2CH_3), 5.43 (s, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 16.6 (CH_3S), 26.7 (7-(CH_3)$_2$), 32.5 (C-7), 44.3 (C-8), 53.0, 54.0 (CO_2CH_3), 128.1 (C-6), 131.7 (C-3), 132.0 (C-4a), 132.3 (C-2), 140.4 (C-5), 148.8 (C-8a), 161.2, 165.1 (CO_2CH_3), 175.2 (C-4); MS [70 eV] 354 (63, M^+), 339 (93), 321 (22), 307 (78), 235 (37), 135 (21), 121 (22), 105 (20), 77 (45), 59 (100), 45 (66), 39 (40); high-resolution MS (M^+) found 354.0605, calcd for $C_{16}H_{18}O_5S_2$ 354.0596; UV (EtOH) 350 sh (4000), 326 (4250), 294 (6000), 252 (20700).

Dimethyl 4-methoxy-5-(methylthio)-7*H*-7,7-dimethylbenzo[*b*]thiopyran-2,3-dicarboxylate (9) was obtained as a reddish, semisolid mass: ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 6 H, 7-

($CH_3)_2$), 2.26 (s, 3 H, CH_3S), 3.67 (s, 3 H, 4-CH_3O), 3.79, 3.85 (2 s, 6 H, CO_2CH_3), 5.46, 5.55 (2 d, 2 H, J = 1.6 Hz, H-6, H-8); ^{13}C NMR ($CDCl_3$) δ 16.3 (CH_3S), 30.0 (7-($CH_3)_2$), 40.4 (C-7), 52.9, 53.0 (CO_2CH_3), 63.5 (4-CH_3O), 123.1 (C-4a), 126.5 (C-3), 127.8 (C-2), 128.7 (C-5), 129.3 (C-8a), 132.5, 134.5 (C-6, C-8), 134.3 (C-4), 161.7, 166.2 (CO_2CH_3); MS [CI-NH_3] 386 (100, M^+ + 18), 369 (50, M^+ + 1); UV (EtOH) 458 (650), 358 (700), 269 (4300), end absorption at 200 (8000).

Dimethyl 5,6,7,8-tetrahydro-7,7-dimethyl-4,5-dioxobenzo[*b*]thiopyran-2,3-dicarboxylate (10) was obtained as pale yellow needles, mp 149–151 °C, after recrystallization from toluene–heptane: ^1H NMR ($CDCl_3$) δ 1.08 (s, 6 H, 7-($CH_3)_2$), 2.47 (s, 2 H, H-6), 2.77 (s, 2 H, H-8), 3.87, 3.90 (2 s, 6 H, CO_2CH_3); ^{13}C NMR ($CDCl_3$) δ 27.8 (7-($CH_3)_2$), 34.0 (C-7), 45.3 (C-6), 53.1 (C-8), 53.4, 54.3 (CO_2CH_3), 129.7 (C-3), 134.7 (C-4a), 141.9 (C-2), 161.0 (C-8a), 163.8, 164.6 (CO_2CH_3), 174.8 (C-4), 191.1 (C-5); MS [70 eV] 324 (26, M^+), 309 (37), 277 (49), 268 (42), 208 (64), 82 (20), 77 (42), 69 (25), 66 (75), 59 (100), 55 (38), 41 (45), 39 (60); high-resolution MS (M^+) found 324.0660, calcd for $C_{15}H_{16}O_6S$ 324.0668; UV (EtOH) 338 sh (3100), 326 sh (5200), 302 (9700), 295 sh (9300), 252 sh (7700), 223 (13 700).

Hydrolysis of 11a. First, 0.2 N HCl (5 mL) was added to a boiling solution of **11a** (0.0144 g) in methanol (20 mL). After being refluxed for 20 min the mixture was cooled, $NaHCO_3$ (0.1 g) was added, and after being stirred the mixture was filtered and worked up as described above. Column chromatography of the methylene chloride extract gave unreacted **11a** (0.0056 g) and **8** (0.0053 g, nearly quantitative yield based on reacted material), identified by its ^1H NMR spectrum.

All solvents were carefully dried and distilled before use, and the reactions were performed under argon or nitrogen atmosphere.

NMR spectra were recorded with a Varian Model XL-300 NMR spectrometer. Resonances of protonated carbons were assigned by use of the DEPT pulse sequence and in some cases by 2D ^1H–^{13}C chemical shift correlation,[19] and those of quaternary carbons by use of coupled spectra and by predicted chemical shifts.[20]

The temperature-dependent ^1H NMR spectra of **11a** and **11c** were recorded in toluene-d_8 solution in the temperature range 50–85 °C, and the rate constants were evaluated by complete bandshape analysis.[21] The major source of error is the temperature regulation, which was found by calibration with a standardized sample of ethylene glycol to be precise to within ±2 °C. This corresponds to error limits of ±0.1 kcal/mol in the free energies of activation.

Mass spectra were recorded with a Finnigan Model 4021 and a JEOL Model SX-102 (for high resolution) mass spectrometer, ultraviolet–visible spectra with a Cary Model 2290 spectrometer, and the CD spectrum with a JASCO Model J-500A spectropolarimeter. The elemental analyses are precise within ±0.4%.

The enantiomer resolution of **7b** was performed with the equipment described by Isaksson and Roschester[22] with ethanol as the mobile phase. The eluted fractions were used directly to record the CD spectra, and their concentrations were monitored by UV spectroscopy after suitable dilution.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of 1-benzyl-3-isopropyl-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)imidazolidine, 1,3-dibenzyl-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hexahydropyrimidine, **3b**, **3e**, **4a–c**, **5a**, **5b**, **7a**, **7b**, **8–10**, **11a–d**, **11d$_2$**, **12a**, **12c**, **12d**; assigned chemical shifts (^1H and ^{13}C) (Tables I–IV and Scheme IV), and UV spectra (Table V) (67 pages). Ordering information is given on any current masthead page.

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Novel Photoreactions of Benzhydrylidenequadricyclane and Quadricyclanone: A New Route to Trimethylenemethane and Oxyallyl Derivatives

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The irradiation of 3-benzhydrylidenequadricyclane (**1**) generated a trimethylenemethane (TMM) derivative, 3-benzhydrylidenebicyclo[3.2.0]hept-6-ene-2,4-diyl (**3**), which dimerized and could be chemically captured by molecular oxygen and acrylonitrile, but not by furan, methanol, or ethyl vinyl ether. The triplet nature of **3** was confirmed by EPR, emission, and absorption spectra. By contrast, the irradiation of quadricyclanone (**2**) generated the singlet oxyallyl (OA), 3-oxobicyclo[3.2.0]hept-6-ene-2,4-diyl (**4**), which could be captured by furan, methanol, and ethyl vinyl ether, but not by molecular oxygen or acrylonitrile, indicating the zwitterionic and electron-accepting nature of **4**.

Trimethylenemethane (TMM) and its hetero analogue oxyallyl (OA) are intriguing 1,3-diradical species which have been widely discussed not only experimentally[1,2] but also theoretically.[3,4] Among a variety of precursor for

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