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SYNTHESIS AND STRUCTURE OF NOVEL ALKYLIDENEMALONALDEHYDES: 2-(DIFORMYLMETHYLENE)-1,3-DITHIANE AND -1,3-DITHIOLANE AS WELL AS (2,3-DIPHENYLCYCLOPROPEN-1-YLIDENE)MALONALDEHYDE [1]

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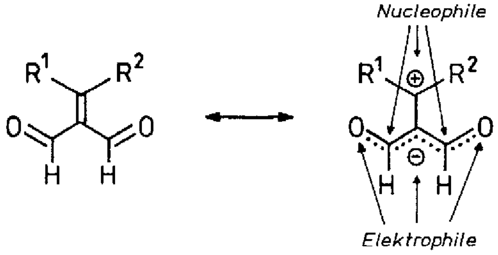
Summary: The alkylidenemalonaldehydes 4,4-diformyl-1,2-diphenyltriafulvene (4), 2-(diformylmethylene)-1,3-dithiane (7), and -1,3-dithiolane (8) have been synthesized by various methods, isolated as crystalline substances and studied by X-ray analysis.

Monosubstituted malonaldehydes are valuable C_3-synthons which are completely enolized; their reactivity corresponds to that of vinylogous carboxylic acids. [3] Non-enolized alkylidene-malonaldehydes and 2,2-disubstituted malonaldehydes, however, are genuine aliphatic dialdehydes with an enhanced chemical reactivity. As cross-conjugated π-systems, alkylidenemalonaldehydes 1 are particularly interesting because of their potential ambifunctional reactivity towards electrophiles and nucleophiles.



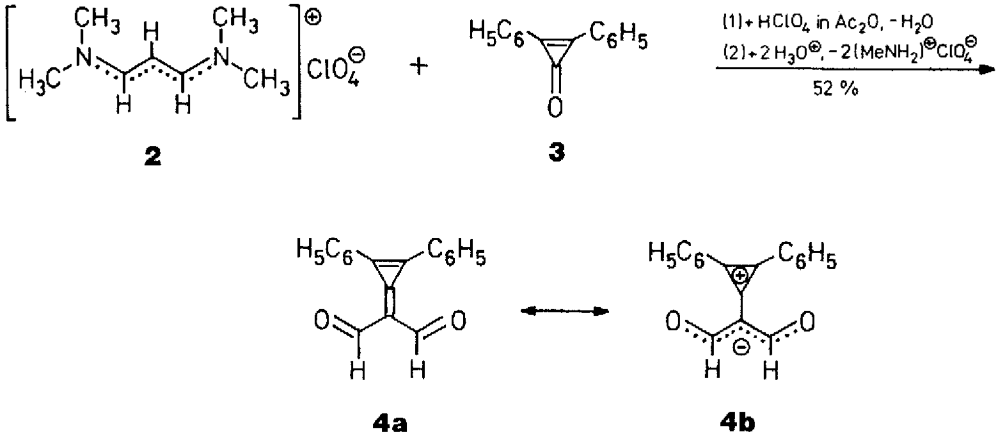
1a **1b**

The first alkylidenemalonaldehydes (1: R^1 = H; R^2 = CO_2R) have been prepared in situ by Woodward et al. [4] and used as intermediates in his cephalosporine C synthesis. [5] Alkylidenemalonaldehyde-bis(dimethylacetals) have been synthesized by Reichardt et al., [6] followed by the first syntheses of isolable alkylidenemalonaldehydes by Reichardt et al. [7,8] (benzylidene- [7] and cycloheptatrienylidene-malonaldehyde [8] and by Arnold et al. [9,10] (aryl- and diarylalkylidenemalonaldehydes); see reference [1] for a survey of older literature, and references [11,12] for recent reviews on the chemistry of alkylidenemalonaldehydes.

In continuation of our work on aliphatic dialdehydes, [1] we now report on the syntheses of further substituted alkylidenemalonaldehydes which are stable enough to be isolated as crystals and studied by X-ray analysis. A recent publication of Gompper et al. [13] gives rise to this preliminary communication of our results.

The idea that delocalization of the positive charge in the dipolar mesomeric structure 1b into an aromatic ring [14] should stabilize the corresponding alkylidenemalonaldehyde, led to the synthesis of stable (2,4,6-cycloheptatrien-

1-ylidene)malonaldehyde. [8] An analogous charge delocalization into a three-membered aromatic ring should also give a resonancestabilized alkylidenemalonaldehyde. Indeed, acid-catalyzed condensation of 2,3-diphenylcyclopropenone 3 with the trimethinium salt 2 in $Ac_2O/HClO_4$ (70 %) at room temperature and subsequent hydrolysis with 1N HCl at 65 °C gives - according to Arnold's method [9] - (2,3-diphenylcyclopropen-1-ylidene)malonaldehyde 4 with 52% yield as brownish-yellow crystals with m.p. 183 - 184 °C (from cyclohexane).



The structure of 4 was proven by elemental analysis, IR, ^1H, and ^{13}C NMR, mass spectrum, and X-ray analysis (cf. Fig. 1). The C-1/C-4 bond length of 4 (Fig. 1) is with 137 pm slightly longer as expected for a normal C(sp^2)=C(sp^2) double bond (ca. 134 pm), indicating a small contribution of the dipolar

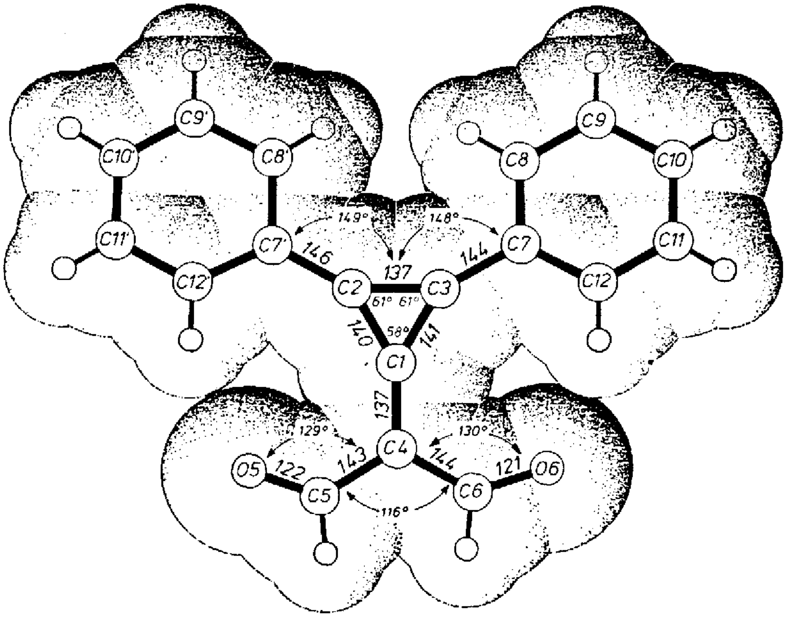
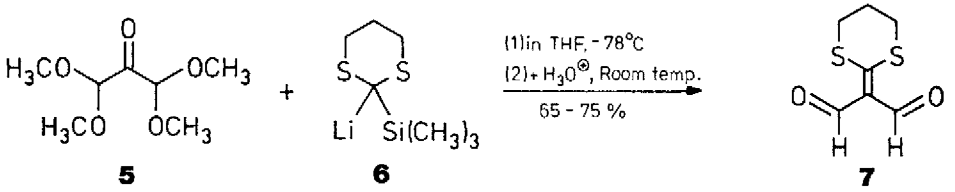


Fig. 1. Crystal structure of 4 (space group Pc; Z = 2; wR = 0.056 for 1825 reflections). [15]

form 4b. The plane of the cyclopropene ring is slightly twisted by 3.5° relative to the malonaldehyde moiety.

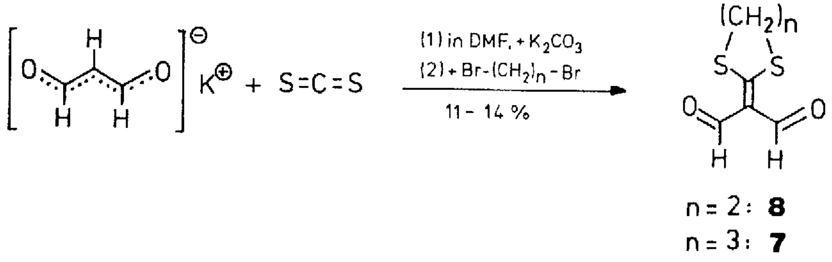
(2-Diformylmethylene)-1,3-dithiane (7) has been obtained by addition of lithiated 2-trimethylsilyl-1,3-dithiane (6) to mesoxalaldehyde-1,3-bis(dimethylacetal) (5) [16] in tetrahydrofuran at -70 °C, subsequent hydrolysis and extraction with dichloromethane as follows:



After removal of the solvent, the partially crystalline product was several times washed with diethyl ether, to give 7 as fine, yellowish crystals (73%) with m.p. 90 - 92 °C.

Corresponding 6,6-diformyl-1,3-dithiafulvenes have been obtained by Gompper et al., [13] however, starting with "umpoled" reaction partners such as the sodium salt of malonaldehyde and 2-methylthio-1,3-dithiolium salts.

There is even a simpler way to get these alkylidenemalonaldehydes, analogous to Pak et al.: [17] direct nucleophilic attack of carbon disulfide by the malonaldehyde anion, followed by a two-fold alkylation reaction of the intermediate anion with 1,n-dibromoalkanes leads to 7 (n = 3) and 8 (n = 2), however, in rather low yields. [18]



The C-2/C-7 bond length of 7 (Fig. 2) is with 139 pm again larger as expected for a normal $C(sp^2)=C(sp^2)$ double bond (ca. 134 pm), indicating a significant contribution of the dipolar form 1b. The SCHAKAL drawing of 7 (Fig. 2) indicates steric interactions between the sulfur and oxygen atoms, thus leading to a slightly twisted conformation of 7. The angle between the best planes (C-2/C-7/C-8/O-8/C-9/O-9) and (S-1/C-2/S-3/C-7) is 3.8(2)°. Disorder of the ring atoms C-4, C-5, and C-6 may falsify the geometry of this region.

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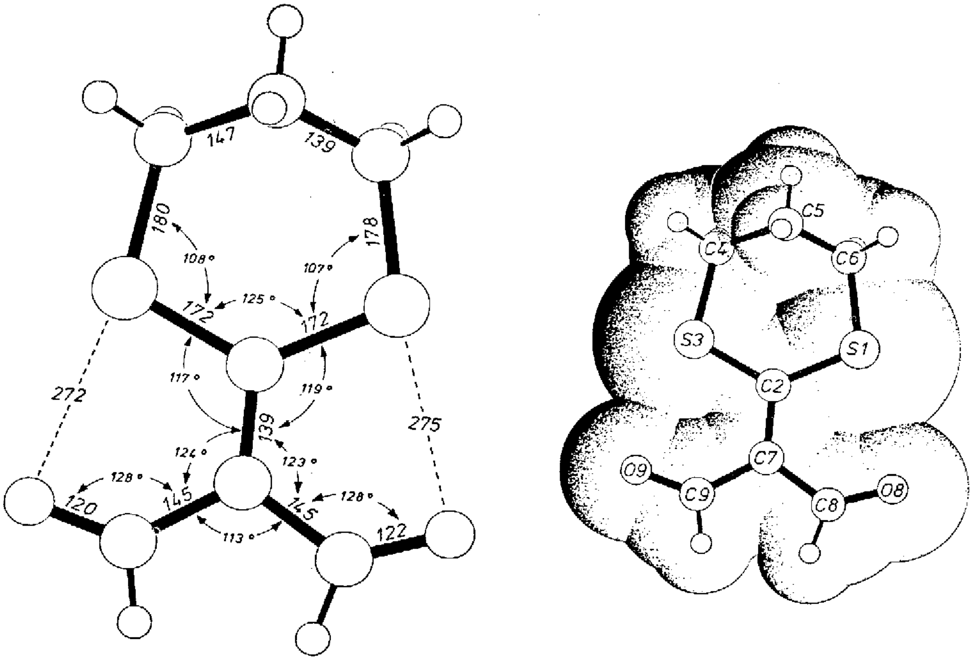

Fig. 2. Crystal structure of 7 (space group C2/c; Z = 8; wR = 0.037 for 921 reflections).[15]

References and Notes

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18 For example, to a suspension of 6.0 g (60 mmol) malonaldehyde-potassium salt and 21 g K_2CO_3 in 30 ml dry DMF and 5.7 g (75 mmol) carbon disulfide, 12.2 g (65 mmol) of 1,2-dibromoethane have been added at 0 °C and the mixture was stirred overnight. The yellow solution was added to 75 ml ice-cold water, the precipitate was filtered off, and recrystallized from ethanol to give 1.2 g (14%) of 8 as yellow crystals with m.p. 130-132 °C (Lit.[13] 132-133 °C).-The dialdehyde 7 can be analogously synthesized with 11% yield. These yields are not optimized yet.

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