

## Studies of Polarized Ethylenes. IX.\* Electrophilic Addition and Substitution Reactions

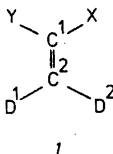
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Strongly push-pull substituted ethylenes are in general unreactive towards electrophilic addition and substitution reagents. 2,2-Bis(dimethylamino)styrene and 2-dimethylamino-2-methylthiostyrene, however, were found to add dimethyl acetylenedicarboxylate to give butadienes, and in the case of the latter styrene an intermediate cyclobutene could be isolated. The structures of the intermediate and final products were ascertained by  $^{13}\text{C}$  NMR spectroscopy.

The two styrenes could also be  $\alpha$ -chlorinated by *N*-chlorosuccinimide, and the bis(dimethylamino)styrene was  $\alpha$ -acetylated by ketene.  $\alpha$ -Nitration by tetranitromethane succeeded only with 2,2-bis(methylthio)styrene. Attempts to add benzyne to the two styrenes by reaction with diazotized anthranilic acid lead to electrophilic substitution in the  $\alpha$ -position by the intermediate diazonium ion.

Push-pull substituted ethylenes, *I*, where  $\text{D}^1$  and  $\text{D}^2$  are good donor groups ( $\text{NR}_2$ , OR, SR) and X and Y are strong acceptors like cyano, acyl, or ester groups, have been the subject of



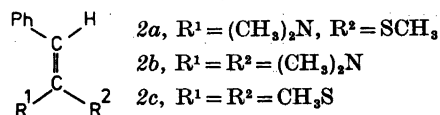
considerable interest from the conformational point of view.<sup>1,2</sup> The electronic structure in several of these compounds has been studied by dipole moment measurements,<sup>3,4</sup> and by ultraviolet photoelectron spectroscopy,<sup>5,6</sup> and the

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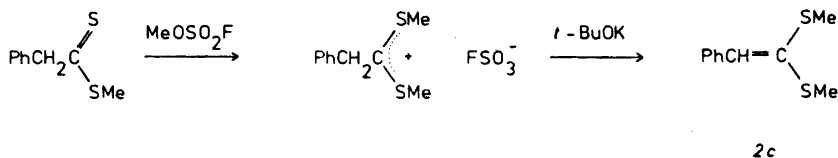
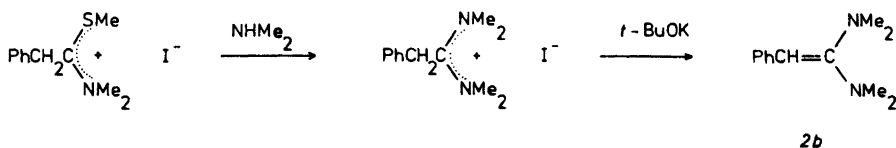
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effect of electron delocalization on bond lengths has been studied by crystallographic methods.<sup>7-9</sup> The strong conjugative interaction between the donor and acceptor parts of the molecules leads to chemically stabilized double bonds, so that compounds of type *I* are resistant to oxidation and reduction and to addition of bromine under normal conditions.<sup>10</sup> Electrophiles attack at C-1<sup>11</sup> and nucleophiles at C-2,<sup>12</sup> but in both cases the reaction leads to substitution rather than to addition. The preferred position of attack is in agreement with the frontier electron densities and also with total charges from CNDO/2 calculations.<sup>4</sup> The reaction with bifunctional nucleophiles, the other part of which is capable of reacting with one of the acceptor groups, has been found a versatile route to several heterocyclic ring systems.<sup>12-16</sup>

The purpose of the present work was to study the electrophilic addition and substitution reactions of push-pull ethylenes. It soon became obvious, however, that substrates with both strong donor and strong acceptor groups were unreactive towards all normal addition reagents, and that only compounds with at most one rather weak acceptor group could undergo additions. We therefore chose to study the reactions of 2-dimethylamino-2-methylthiostyrene (*2a*), 2,2-bis(dimethylamino)styrene (*2b*) and 2,2-bismethylthiostyrene (*2c*).



These compounds were also suitable as substrates for electrophilic substitution reac-



tions, as it is of interest to know if substitution occurs on the electron-rich C-1 atom or in the activated benzene ring. The "ketene *S,N*-acetal" **2a** was prepared by the method of Gompper and Elser,<sup>17</sup> starting from *N,N*-dimethylphenylthioacetamide. The bis(dimethylamino)styrene **2b** was prepared by reaction between the methiodide, which is an intermediate in the preparation of **2a**, and dimethylamine, followed by deprotonation of the amidinium ion.

The ketene mercaptal **2c** was prepared by reaction between methyl phenyldithioacetate and methylfluorosulfonate followed by deprotonation of the bis(methylthio)carbenium ion formed.

## RESULTS AND DISCUSSION

**Addition reactions.** Phenylacetylene, methyl propiolate, dimethyl acetylenedicarboxylate, benzyne and ketene were tried as addition reagents. The first of these reagents gave no reaction, and from the reactions with the second no defined products could be obtained. Dimethyl acetylenedicarboxylate and **2a** reacted smoothly to give a labile, liquid product, which was shown by <sup>13</sup>C NMR spectroscopy to consist of a *ca* 1:2 mixture of two stereoisomeric cyclobutenes (Fig. 1 and Table 1). The structure follows from the chemical shifts. The presence of a dimethyl maleate moiety is indicated by comparison with this model compound, which shows  $\delta$  129.9 (C=C), 167.2 (C=O) and 52.1 (OCH<sub>3</sub>), to be compared with the shifts of carbon atoms *a, b; e, g,* and *f, h* in Fig. 1. An isolated phenyl group is indicated

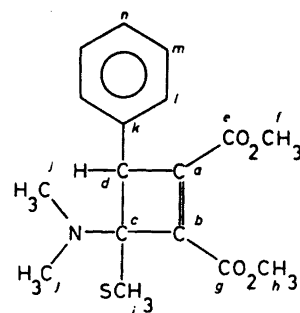


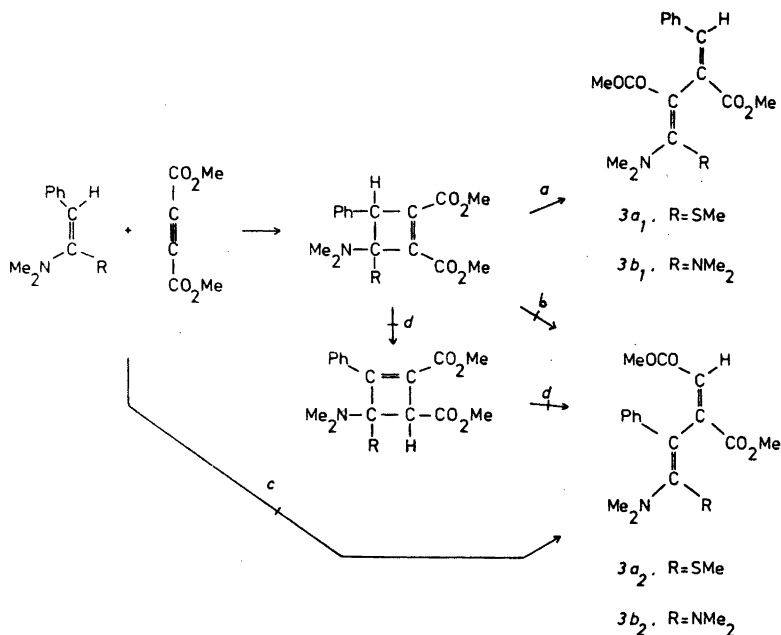
Fig. 1. Assignment of <sup>13</sup>C signals to carbon atoms in the stereoisomeric dimethyl 3-dimethylamino-3-methylthio-4-phenylcyclobutene-1,2-dicarboxylates.

Table 1. <sup>13</sup>C Chemical shifts<sup>a</sup> of the two cyclobutenes (Fig. 1).

Carbon atom	$\delta$ (major)	$\delta$ (minor)
<i>a, b</i>	131.6, 134.5	129.5, 133.0
<i>c</i>	98.9	84.3
<i>d</i>	30.9	39.6
<i>e, g</i>	166.0, 169.7	169.1, 170.4
<i>f, h</i>	50.8, 52.1	51.5, 52.8
<i>i</i>	16.2	17.7
<i>j</i>	42.7	43.7
<i>k</i>	136.4	137.9
<i>l</i>	129.0	129.0
<i>m</i>	128.0	128.0
<i>n</i>	126.5	126.5

<sup>a</sup> In ppm downfield from TMS.

by the similarity of the shifts of carbon atoms *k, l, m,* and *n* with those of C-1 to C-4 in toluene,<sup>18</sup> and the two signals at  $\delta$  30.9 (major)



Scheme 1. Pathways for reaction between dimethyl acetylenedicarboxylate and 2a and 2b.

and 39.6 (minor) are assigned to a proton-bearing  $sp^3$ -hybridized carbon atom by the one bond C-H coupling constant of 127 Hz (carbon atom *d*).

The signals assigned to carbon atom *c* appear unsplit in the coupled spectrum, and their shifts are as expected for rather negatively substituted allylic carbon atoms.

On heating, the cyclobutene is transformed to a crystalline butadiene (3a). The structure of this compound (*vide infra*) is as expected from a normal electrocyclic ring-opening (path *a* in Scheme 1).

In the reaction between 2b and dimethyl acetylenedicarboxylate no cyclobutene could be isolated, but a butadiene was formed directly. Two structures, 3b<sub>1</sub> and 3b<sub>2</sub>, (Scheme 1) have to be taken into account for this product. A direct ring-opening of the cyclobutene according to path *b* seems less likely, but two alternative routes for formation of 3a<sub>2</sub> and 3b<sub>2</sub> have to be considered: *c*, A Michael-type addition of a cyclic phenylketene mercaptal similar to 2c to diethyl azodicarboxylate has been observed,<sup>19</sup> and an analogous reaction here should lead to 3b<sub>2</sub>; *d*, Sarel *et al.*<sup>20</sup> on addition of

dimethyl acetylenedicarboxylate to a 1,1-dicyclopropylethylene obtained a mixture of two isomeric butadienes corresponding to our two alternatives. In this reaction a 1,3-hydrogen shift in the intermediate cyclobutene (not isolated) is assumed to give an isomeric cyclobutene, which on normal electrocyclic ring-opening gives the analogue of 3a<sub>2</sub>/3b<sub>2</sub>. A comparison of the <sup>13</sup>C NMR spectrum of 3b with those of some model compounds (Fig. 2 and Table 2) gives strong support to structure 3b<sub>1</sub>. In 2b the phenyl ring is strongly conjugated with the dimethylamino groups, and the *ortho* and *para* carbon atoms are more shielded than in styrene<sup>21</sup> ( $\Delta\delta_o - 0.6$ ,  $\Delta\delta_p - 6.5$ ). A similar though weaker effect is observed in 2a. Acceptor groups on C<sup>1</sup> have only moderate effects on  $\Delta\delta_p$ . In the 1-cyano compound,  $\Delta\delta_o$  is -1.4 and  $\Delta\delta_p - 5.1$ , and in the 1-acetyl analogue the values are +1.2 and -4.3, respectively.

A similar situation should be likely in 3b<sub>2</sub>. In 3b<sub>1</sub>, on the other hand, the situation of the phenyl group is more like that in methyl cinnamate, where the *ortho* and *para* carbons are less shielded than in styrene,  $\Delta\delta_o$  as well as  $\Delta\delta_p$  being +2.2. In the butadiene 3b,  $\Delta\delta_o$  is

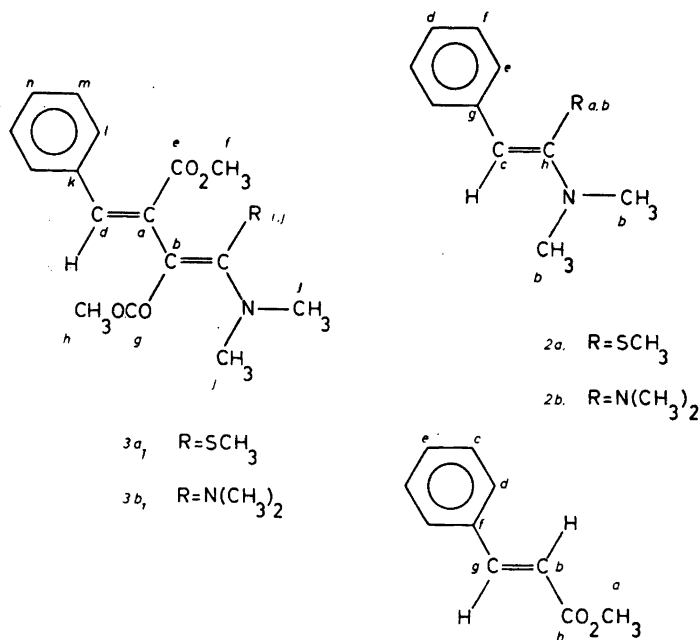


Fig. 2. Assignment of  $^{13}\text{C}$  signals to carbon atoms in  $3a_1$ ,  $3b_1$ ,  $2a$ ,  $2b$  and methyl *trans*-cinnamate.

Table 2.  $^{13}\text{C}$  Chemical shifts of the compounds in Fig. 2.

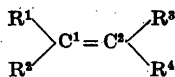
Carbon atom	$3a_1$	$3b_1$	$2a$	$2b$	Methyl cinnamate
a	131.6	— <sup>a</sup>	15.8 (major), 16.2		51.6
b	98.8	81.3	41.4 (major), 42.1	40.1	117.8 (186 <sup>b</sup> )
c	—	166.3	109.4 (154 <sup>b</sup> )	87.7 (152 <sup>b</sup> )	128.1
d	137.7 (161 <sup>b</sup> )	—	124.9	121.7	128.9
e	166.1, 169.8	168.3, 171.6	127.7	126.1	130.3
g			138.1	140.4	144.8 (156 <sup>b</sup> )
f			128.6	127.6	134.4
h	50.9, 52.2	50.3, 51.9		156.3	167.4
i	16.3		147.8		
j	42.8	38.3, 39.0, 39.3, 40.7			
k	136.5	137.0			
l	128.0	127.6			
m	129.0	128.6			
n	128.2	127.6			

<sup>a</sup> Overlap by aromatic signals. <sup>b</sup>  $J(^{13}\text{C}-\text{H})$  Hz.

+0.9 and  $\Delta\delta_p$  is -0.6. This means that the donor and acceptor effects on the phenyl ring are fairly well-balanced, as they should be in

structure  $3b_1$ . The same arguments favour structure  $3a_1$ .

The resonances of C-1 in 2,2-bis(dimethyl-

Table 3.  $^{13}\text{C}$  Chemical shifts <sup>a</sup> of compounds

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	C-1	C-2
Ph	H	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	87.7	156.3
Ph	H	N(CH <sub>3</sub> ) <sub>2</sub>	SCH <sub>3</sub>	109.4	147.8
Ph	H	SCH <sub>3</sub>	SCH <sub>3</sub>	126.8 <sup>c</sup>	136.2
Ph	CN	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	65.8	165.5
Ph	Cl	N(CH <sub>3</sub> ) <sub>2</sub>	SCH <sub>3</sub>	112.2, 115.2 <sup>d</sup>	147.6
Ph	Cl	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	90.3	153.1
H	NO <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	125.0 (189.1 <sup>b</sup> )	164.9
CN	CN	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	38.4	170.6
CH <sub>3</sub> OCO	CH <sub>3</sub> OCO	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	76.9	167.5
H	COCH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	107.4 (164.8)	165.1
Ph	COCH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	101.7	169.4
Ph	H	H	CO <sub>2</sub> CH <sub>3</sub>	144.8	117.8

<sup>a</sup> In ppm downfield from TMS. <sup>b</sup>  $J(^{13}\text{C}-\text{H})$  Hz. <sup>c</sup> The one-bond coupling not visible because of overlap with aromatic carbon signals. <sup>d</sup> *E* and *Z* form.

amino)ethylenes (*1*,  $\text{D}^1 = \text{D}^2 = \text{NMe}_2$ ) appear at quite high field, and the C-2 resonances at low field (Table 3) in agreement with calculated electron densities.<sup>4,\*</sup> In *2a* and *2b* the C-1 resonance is readily identified in the coupled spectrum by its one-bond coupling. The components of the doublet appear as broadened multiplets due to coupling with the aromatic protons. If structure *3a<sub>2</sub>* or *3b<sub>2</sub>* is correct, the C-3 resonance (*b*) should show a similar broadening in the coupled spectrum. This is, however, not the case. Unfortunately, the C-1 resonance (*d*) is not observable in *3b* due to overlap with the aromatic carbon resonances, but in *3a* it appears at somewhat lower field, and the splitting due to the one-bond coupling as well as the broadening due to coupling with the aromatic protons can be observed. The magnitude of this coupling constant, 161 Hz, compared with the olefinic one-bond couplings<sup>4</sup> in methyl cinnamate provides further evidence that this proton is attached to a phenyl-substituted rather than to a methoxycarbonyl-substituted carbon atom.

\*Dr. L. Henriksen from the C. H. Ørsted Institute in Copenhagen has kindly informed us that these data are in agreement with results from several push-pull ethylenes studied by him.<sup>22</sup>

This and the general similarity of the spectra of *3a* and *3b* give further support to structures *3a<sub>1</sub>* and *3b<sub>1</sub>*.

*2a*, *2b*, *3a<sub>1</sub>* and *3b<sub>1</sub>* show temperature-dependent spectra, indicating slow rotation about the C-N and C=C bonds, but this has not yet been studied in any detail. This steric lability makes it impossible to decide whether the cyclobutene ring-opening proceeds in a conrotatory or disrotatory manner.

This reaction is analogous to what has been found in previous additions of dimethyl acetylenedicarboxylate to electron-rich olefins (enamines<sup>23-25</sup> and ketene acetals<sup>26</sup>). In most of these cases no cyclobutenes were isolated but the structures of the butadienes formed were those expected from normal electrocyclic ring-openings of cyclobutene intermediates, amounting to insertion of the acetylenic bond in the electron-rich double bond.

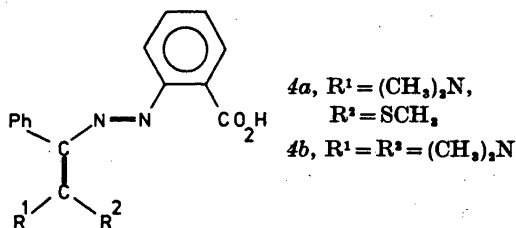
The reactions leading to the cyclobutenes are probably not concerted cycloadditions but proceed with dipolar intermediates.<sup>27,28</sup>

Attempts to add dimethyl acetylenedicarboxylate to the ketene mercaptal *2c* failed.

Attempts to generate benzyne to add to *2a*, *2b* and *2c* were first made by reaction of 1-(2-carboxyphenyl)-3,3-dimethyltriazene with trifluoroacetic acid.<sup>29</sup> These reactions gave, as

the only isolable product from **2a** and **2b**, *N,N*-dimethylphenylacetamide, which was later found to be the major product in all reactions in acid medium. The same reaction with **2c** gave no identifiable products.

When **2b** reacted with benzenediazonium-*o*-carboxylate<sup>22</sup> in tetrahydrofuran, an azo compound formed by electrophilic substitution of the diazonium ion at C-1 (**4b**) was the only isolable product. Evidently this substitution is faster than the decomposition of the diazonium ion. The analogous reaction with **2a** seemed to proceed in a similar manner, but no reasonable spectroscopic or analytical data corresponding to **4a** could be obtained for the product. This compound as well as **4b** showed liquid crystal behaviour above the melting point.



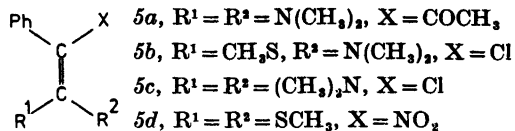
Under the same conditions no reaction was obtained with **2c**, which is surprising, since diazo coupling has been observed with a very similar ketene mercaptal<sup>19</sup> though with the more reactive *p*-nitrobenzenediazonium ion.

Several reactions between ketenes and electron-rich olefins have been described,<sup>21-25</sup> and the products are in general cyclobutanones. In the reaction between **2b** and ketene, however, acetylation on C-1 occurred instead of cycloaddition, giving 1-acetyl-2,2-bis(dimethylamino)styrene (**5a**).<sup>26</sup> Reaction of **2a** and **2c** with ketene gave no defined products.

**Substitution reactions.** Gompper and Elser<sup>27</sup> have studied the reactions of simple analogues of **2a** with acyl chlorides and with activated vinylic chlorides and have observed substitution at C-1.

Electrophilic substitution of **2a**, **2b** and **2c** was attempted with *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), bromine and tetraniromethane. Of these, only NCS gave substitution products, the unstable 1-chlorostyrenes **5b** and **5c**. Nitration could only be performed with **2c**, giving the unstable 1-nitrostyrene **5d**.

The reactions of **2a** and **2b** with bromine gave no isolable product.



Reaction of a cyclic analogue of **2c** with among other reagents bromine, NCS and NBS have been reported to lead to substitution products in good yield.<sup>19</sup> Evidently the inclusion of the sulfur atoms in a ring greatly enhances the stability of the unsaturated system.

## EXPERIMENTAL

<sup>13</sup>C Spectra were recorded at ambient temperature in CDCl<sub>3</sub> solution on a JEOL Model FX-60 NMR spectrometer operating at 15.03 MHz, with TMS as internal reference, and <sup>1</sup>H NMR spectra on a JEOL Model MH-100 NMR spectrometer.

The elemental analyses give poor agreement with calculated values for some of the compounds. This is due to instability or to some of the products being high-boiling liquids, difficult to purify by fractional distillation. The proposed structures are in all cases verified by NMR and mass spectra.

**2-Dimethylamino-2-methylthiostyrene (2a).** To *N,N*-dimethylphenylthioacetamide<sup>28</sup> (0.04 mol) in dry acetone was added methyl iodide (0.044 mol). A quantitative yield of the *S*-methiodide gave pale yellow prisms, m.p. 170–173 °C. Anal. C<sub>11</sub>H<sub>16</sub>INS: C, H, I, N. This salt (0.135 mol) was suspended in dry ether, and potassium *tert*-butoxide (0.202 mol) was added. The reaction mixture was refluxed with stirring for 24 h and stirred at room temperature for another 48 h. The ether solution was filtered and evaporated, and the residue was distilled under reduced pressure to give a 60% yield of a pale yellow liquid, b.p. 110–112 °C/0.08–0.09 kPa, *n*<sub>D</sub><sup>25</sup> 1.6025. (Found: C 68.3; H 7.81; N 7.35; S 14.4, 14.5. Calc. for C<sub>11</sub>H<sub>16</sub>NS: C 68.3; H 7.83; N 7.25; S 16.6).

**2,2-Bis(dimethylamino)styrene (2b).** A solution of dimethylamine (0.042 mol) in benzene was added to a solution of the methiodide obtained in the previous reaction sequence (0.038 mol) in dry chloroform. The solution was left at room temperature for 12 h and then evaporated. The resulting *N,N,N',N'*-tetramethylphenylacetamidinium iodide was purified by precipitation with dry ether from a chloroform solution, colourless prisms, d. 145–154 °C, in 94% yield. Found: C 42.9; H 5.98; I 42.3; N 8.78. Calc. for C<sub>13</sub>H<sub>19</sub>IN<sub>2</sub>: C 45.3; H 6.02; I 39.9; N 8.80. On treatment of this iodide with

potassium *tert*-butoxide and work-up as in the preparation of **2a**, an 84 % yield of **2b** resulted as a yellow liquid, b.p. 80–84°C/0.13 kPa,  $n_D^{20}$  1.5909 (lit. b.p. 80°C/0.13 kPa,<sup>39</sup> 118–122°C/1.9 kPa,<sup>40</sup>  $n_D^{25}$  1.5905<sup>39</sup>). Anal. C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>: C, H, N.

**2,2-Bis(methylthio)styrene (2c).** Methyl fluorosulfonate (0.023 mol) was added dropwise with stirring to a solution of methyl phenyl-dithioacetate<sup>41,42</sup> (0.023 mol) in dry ether during 10 min. The stirring was continued under reflux for 24 h and at room temperature for 48 h. 1,1-Bis(methylthio)-2-phenylethyl fluorosulfonate had separated as a brown oil. It was not isolated but treated directly with potassium *tert*-butoxide as in the previous experiments to give a 42 % yield of **2c** as a pale yellow liquid, b.p. 98–100°C/0.05 kPa,  $n_D^{20}$  1.6411 (lit. b.p. 105–107°C/0.007 kPa,<sup>43</sup> 94–96°C/0.03 kPa<sup>44</sup>). (Found: C 61.7; H 6.15; S 30.1. Calc. for C<sub>10</sub>H<sub>12</sub>S<sub>2</sub>: C 61.2; H 6.16; S 32.7).

**Dimethyl 3-dimethylamino-3-methylthio-4-phenylcyclobutene-1,2-dicarboxylate.** Dimethyl acetylenedicarboxylate and **2a** reacted in toluene at room temperature during 24 h to give a nearly quantitative yield of the above product (stereoisomer mixture) as a reddish viscous liquid. Attempts to separate the stereoisomers by column chromatography on alumina were without success. The <sup>13</sup>C NMR spectrum showed no significant impurity peaks. The MS was identical with that of **3a**, (*vide infra*) probably because of rearrangement prior to ionization.

**Dimethyl 1-phenyl-4-dimethylamino-4-methylthiobutadiene-2,3-dicarboxylate (3a<sub>1</sub>).** The above cyclobutene was distilled at 169–170°C and 7 Pa, and the resulting brownish viscous liquid on dissolution in ethanol and cooling to –20°C deposited an 80 % yield of yellow prisms, m.p. 96–98°C. Anal. C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>S: C, H, N, S. MS [IP 70 eV; *m/e* (% rel. int.)]: 335 (75, M), 320 (100, M–CH<sub>3</sub>), 304 (11, M–CH<sub>3</sub>O), 288 (23, M–CH<sub>3</sub>), 276 (18, M–CH<sub>2</sub>OCO); *m\** 335→320, obs. 306, calc. 306.

**Dimethyl 1-phenyl-4,4-bis(dimethylamino)-butadiene-2,3-dicarboxylate (3b<sub>1</sub>).** On reaction between **2b** and dimethyl acetylenedicarboxylate in benzene as above, a brown, viscous liquid was obtained after evaporation. It crystallized after standing at +5°C for some days, and three recrystallizations from light petroleum (b.p. 80–100°C) gave a 64 % yield of yellow prisms, m.p. 110–111.5°C. Anal. C<sub>18</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>: C, H, N, O. MS [IP 70 eV; *m/e* (% rel. int.)]: 332 (100, M), 273 (83, M–CH<sub>2</sub>OCO), 214 (23, M–2CH<sub>2</sub>OCO).

**1-o-Carboxybenzenazo-2,2-bis(dimethylamino)-styrene (4b).** A slurry of benzenediazonium-carboxylate in tetrahydrofuran was added in portions to a boiling solution of **2b** in dry tetrahydrofuran. The reaction mixture turned dark and some gas was evolved at each addition. When the addition was finished, the

solution was evaporated, and the residue was subjected to column chromatography on alumina. The only definable product (64 % yield) was eluted by a 1:1 (v/v) mixture of acetone and ethanol and was obtained as yellow crystals, which showed the following transition

points: Solid  $\xrightarrow{135^\circ\text{C}}$  smectic phase  $\xrightarrow{141^\circ\text{C}}$  nematic phase  $\xrightarrow{197^\circ\text{C}}$  isotropic liquid. [Found: C 66.1; H 7.04; N 16.1; O 10.6 (after drying *in vacuo* at 105°C). Calc. for C<sub>16</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>: C 67.4; H 6.55; N 16.6; O 9.46]. MS [IP 70 eV, *m/e* (% rel. int.)]: 338 (41, M), 189 (22, M–CO<sub>2</sub>–C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>).

**1-Acetyl-2,2-bis(dimethylamino)styrene. (5a).** Ketene was bubbled at a rate of 0.3 mol/h through a solution of **2b** (0.008 mol) in dry ether at 30°C during 10 min. Evaporation of the dark solution gave a viscous residue, which was dissolved in ethyl acetate. Upon addition of light petroleum (b.p. 80–100°C) and cooling to –78°C a dark brown oil separated, and the pale yellow liquid phase on evaporation gave a crystalline residue. By integration of the NMR spectrum of the crude product the yield was found to be >50%. After recrystallization of a small amount of the crystals from ethyl acetate–light petroleum it was identified as **5a** (m.p. 102–103°C) by comparison of the IR and NMR spectra with those of an authentic specimen (lit. m.p. 103–104°C<sup>46</sup>).

**1-Chloro-2-dimethylamino-2-methylthiostyrene (5b).** A warm solution of NCS (0.0165 mol) in chloroform was added dropwise with stirring and cooling to 10–14°C during 42 min to a solution of **2a** (0.015 mol) in chloroform. The stirring was continued for 70 min at 7–9°C, when TLC showed all **2a** to be consumed. The solution was evaporated, and the residue was extracted with carbon tetrachloride and filtered from undissolved succinimide. The solution was evaporated, and the remaining liquid was distilled *in vacuo* to give a 42 % yield of a yellow liquid, b.p. 93–100°C/0.03 kPa,  $n_D^{25,2}$  1.5958. (Found: C 59.8; H 6.18; Cl 13.3; N 6.23; S 11.5. Calc. for C<sub>11</sub>H<sub>11</sub>ClNS: C 58.0; H 6.20; Cl 15.6; N 6.15; S 14.1). MS [IP 70 eV; *m/e* (% rel. int.)]: 229, 227 (100, M), 192 (60, M–Cl), 182, 180 (55, M–SCH<sub>3</sub>), 177 (69, M–Cl–CH<sub>3</sub>), 167, 165 (62, M–SCH<sub>3</sub>–CH<sub>3</sub>), 152, 150 (50).

**1-Chloro-2,2-bis(dimethylamino)styrene (5c).** Under the same condition as in the previous experiment, **2c** gave a 50 % yield of a yellow liquid, b.p. 82–89°C/0.03 kPa,  $n_D^{25,2}$  1.5893. (Found: C 64.7; H 7.58; Cl 13.3; N 11.6. Calc. for C<sub>12</sub>H<sub>17</sub>ClN<sub>2</sub>: C 64.1; H 7.63; Cl 15.8; N 12.5). MS [IP 70 eV; *m/e* (% rel. int.)]: 226, 224 (53, M), 211, 209 (5, M–CH<sub>3</sub>), 189 (24, M–Cl), 182, 180 [9, M–N(CH<sub>3</sub>)<sub>2</sub>], 167, 165 [11, M–N(CH<sub>3</sub>)<sub>2</sub>–CH<sub>3</sub>], 152, 150 (21), 146 (100, M–Cl–CH<sub>2</sub>–N–CH<sub>3</sub>), 131 (38, M–Cl–CH<sub>2</sub>NCH<sub>3</sub>–CH<sub>3</sub>).

**1-Nitro-2,2-bis(dimethylamino)styrene (5d).**

Tetranitromethane (0.0084 mol) in dichloromethane was added dropwise with stirring and cooling to  $-60^{\circ}\text{C}$  to a solution of *2c* (0.0076 mol) in dichloromethane. The dark mixture was allowed to reach room temperature, and the solvent was evaporated. The remaining yellow-red liquid was purified by column chromatography on activated silica. A liquid which appeared uniform on TLC was obtained by elution with chloroform.  $^1\text{H NMR}$  (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.18 (3 H, s), 2.47 (3 H, s), 7.42 (5 H, s). MS [IP 70 eV;  $m/e$  (% rel. int.)]: 241 (46, M), 195 (7, M- $\text{NO}_2$ ), 180 (37, M- $\text{NO}_2$ - $\text{CH}_3$ ).

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## REFERENCES

- Kalinowski, H.-O. and Kessler, H. *Top. Stereochem.* 7 (1973) 295.
- Sandström, J. and Sjöstrand, U. *Tetrahedron. In press*, and earlier works in this series.
- Gompper, R., Schmidt, R. R. and Kutter, E. *Justus Liebigs Ann. Chem.* 684 (1965) 37.
- Ericsson, E., Marnung, T., Sandström, J. and Wennerbeck, I. *J. Mol. Struct.* 24 (1975) 373.
- Betteridge, D., Henriksen, L., Sandström, J., Wennerbeck, I. and Williams, M. A. *Acta Chem. Scand. A* 31 (1977) 14.
- Colonna, F. P., Distefano, G., Sandström, J. and Sjöstrand, U. *J. Chem. Soc. Perkin Trans. 2. In press*.
- Shmueli, U., Shanan-Atidi, H., Horwitz, H. and Shvo, Y. *J. Chem. Soc. Perkin Trans. 2* (1973) 657.
- Abrahamsson, S., Rehnberg, G., Liljefors, T. and Sandström, J. *Acta Chem. Scand. B* 28 (1974) 1109.
- Ammon, H. L. *Acta Crystallogr. B* 30 (1974) 1731.
- Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* 22 (1968) 1107.
- Henriksen, L. and Autrup, H. *Acta Chem. Scand.* 24 (1970) 2629.
- Gompper, R. and Töpfl, W. *Chem. Ber.* 95 (1962) 2871.
- Gompper, R. and Töpfl, W. *Chem. Ber.* 95 (1962) 2881.
- Gompper, R., Kutter, E. and Töpfl, W. *Justus Liebigs Ann. Chem.* 659 (1962) 90.
- Liljefors, T. and Sandström, J. *Acta Chem. Scand.* 24 (1970) 3109.
- Chauhan, S. M. S. and Junjappa, H. *Synthesis* (1975) 798.
- Gompper, R. and Elser, W. *Tetrahedron Lett.* (1964) 1971.
- Woolfenden, W. R. and Grant, D. M. *J. Am. Chem. Soc.* 88 (1966) 1496.
- Carey, F. A. and Neergaard, J. R. *J. Org. Chem.* 36 (1971) 2731.
- Sarel, S., Felzenstein, A. and Yovell, J. *Chem. Commun.* (1973) 859.
- Stothers, J. B. *Carbon-13 NMR Spectroscopy*, Academic, New York 1972, p. 197.
- Henriksen, L. *To be published*.
- Brannock, K. C., Burpitt, R. D., Goodlett, V. W. and Thweatt, J. G. *J. Org. Chem.* 28 (1963) 818.
- Berchtold, G. A. and Uhlig, G. F. *J. Org. Chem.* 28 (1963) 1459.
- Huebner, C. F. and Donoghue, E. *J. Org. Chem.* 28 (1963) 1732.
- Brannock, K. C., Burpitt, R. D. and Thweatt, J. G. *J. Org. Chem.* 28 (1963) 1697.
- Gompper, R. *Angew. Chem.* 81 (1969) 348.
- Huisgen, R., Schug, R. and Steiner, G. *Bull. Soc. Chim. Fr.* (1976) 1813.
- Nakayama, J., Simamura, O. and Yoshida, M. *Chem. Commun.* (1970) 1222.
- Org. Synth.* 48 (1968) 12.
- Binsch, G., Feiler, L. A. and Huisgen, R. *Tetrahedron Lett.* (1968) 4497.
- Hasek, R. H. and Martin, J. C. *J. Org. Chem.* 28 (1963) 1468.
- Martin, J. C., Gott, P. G. and Hostettler, H. U. *J. Org. Chem.* 32 (1967) 1654.
- Huisgen, R. and Otto, P. *Tetrahedron Lett.* (1968) 4491.
- Ghosez, L., Montaigne, R., Vanlierde, H. and Dumay, F. *Angew. Chem.* 80 (1968) 630.
- Ericsson, E., Sandström, J. and Wennerbeck, I. *Acta Chem. Scand.* 24 (1970) 3102.
- Gompper, R. and Elser, W. *Justus Liebigs Ann. Chem.* 725 (1969) 73.
- Kindler, K. *Justus Liebigs Ann. Chem.* 431 (1923) 187.
- Weingarten, H. and White, W. A. *J. Org. Chem.* 31 (1966) 2874.
- Bredereck, H., Simchen, G. and Kapaun, G. *Chem. Ber.* 104 (1971) 792.
- Houben, J. and Schultze, K. M. L. *Ber. Dtsch. Chem. Ges.* 43 (1910) 2481.
- Corse, J. W., Jones, R. G., Soper, Q. F., Whitehead, C. W. and Behrens, O. K. *J. Am. Chem. Soc.* 70 (1948) 2837.
- Bestmann, H. J., Engler, R. and Hartung, H. *Angew. Chem.* 78 (1966) 1100.
- Russel, G. A. and Ochrymowycz, L. A. *J. Org. Chem.* 35 (1970) 764.

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