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Formation of *1H*-Aziridines from Chalcones and Hydroxylamine

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Highly substituted chalcones **1** do not react with two molecules of hydroxylamine affording dioximes **2** or hydroxyamino-oximes **3** as expected according to *von Auwers*' procedure[1]: only one molecule of hydroxylamine is consumed leading to *trans*-configurated 2-benzoyl-3-phenyl-1*H*-aziridines **4**.

1*H*-Aziridine aus Chalkonen und Hydroxylamin

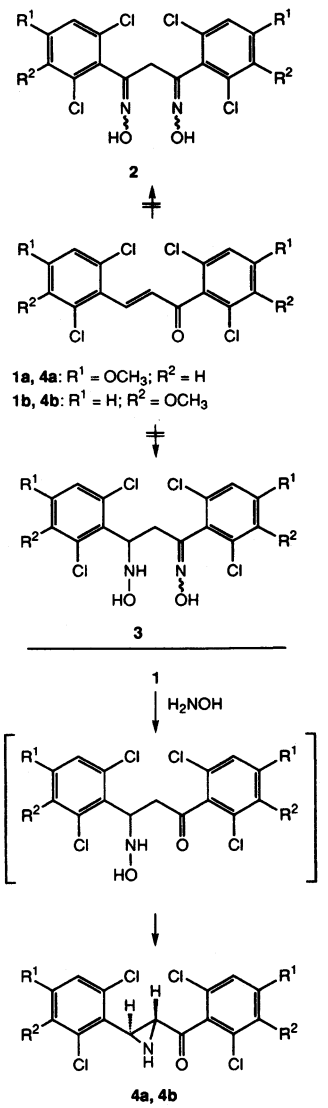
Aus den hochsubstituierten Chalkonen **1** entstehen nicht die nach *von Auwers*[1] zu erwartenden Dioxime **2** oder Hydroxyamino-oxime **3** unter Verbrauch von zwei Mol Hydroxylamin. Statt dessen wird nur ein Mol Hydroxylamin verbraucht, und es entstehen *trans*-konfigurierte 2-Benzoyl-3-phenyl-1*H*-aziridine **4**.

Schönenberger et al.[2)3)] have reported on cytostatic Pt-complexes of the 1,2-diamino-1,2-diphenylethane type. Especially *meso*-1,2-bis-(2,6-dichloro-4-hydroxyphenyl)ethylenediamine-dichloro-Pt(II) (**5**) is of interest as it shows low affinity to the estrogen receptor when compared with the Pt-free ligand, it has, however, an enhanced endocrinological activity.

In our first paper in this field[4)] we have touched on the conformational flexibility of Pt-complexes of 1,2-diamino-ethanes in comparison with that of 1,3-diaminopropane-Pt-complexes, prepared according to *von Auwers*[1)] by reacting chalcones with two molecules of hydroxylamine followed by reduction (Scheme 2 in lit.[4)]). Here we describe an anomality of *von Auwers*' procedure:

When 0.1 mol of the chalcones **1** - prepared from 2,6-dichloro-x-methoxybenzaldehydes **6** and 2,6-dichloror-x-methoxyacetophenones **7** (which in turn could not be prepared by *Friedel-Crafts* acylation but were obtained from **6a**, **6b** with H_3CMgI and subsequent oxidation) - were treated in a slightly modified *von Auwers*-procedure[1)] as described[4)] with 0.263 mol $H_2NOH{\cdot}HCl$ in water/KOH (Experim. Part and Lit.[4)]) we obtained ketones which contain one N-atom only. ^{1}H-NMR spectra revealed that *trans*-configurated aziridines were formed: according to *Brois*[5)] $^3J_{HCCH}$ in *cis*-aziridines is always greater than that in *trans*-aziridines. For *cis*-aziridines J-values of 5.0 - 8.5 Hz are reported, whilst *trans*-isomers show 2.0 - 6.3 Hz. These data are corroborated by *Weber* and *Liepert*[6)]. In our cases J = 3.0 Hz indicates *trans*-substitution. Under EI-conditions the mass spectra reveal prominent signals for (Ar-CH(NH)-CH)$^+$, Ar-CO$^+$, and Ar-CH$_2^+$ ions.

von Auwers and *Müller*[1)] have assumed that the reaction of chalcones with hydroxylamine proceeds *via* a hydroxyamino-ketone which subsequently reacts with a second molecule of hydroxylamine (the authors could not trap the intermediate hydroxyamino-ketone under various conditions. We did not performe pertinent experiments). - The formation of our aziridines with a highly hindered benzoyl group (Cl-substituents in both *o*-positions) favours *von*



Scheme 1

[+] Respectfully dedicated to Prof. *Zymalkowski*, Bonn, at the occasion of his 80th birthday.

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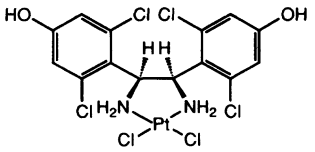
Auwers'[1] hypothesis. Moreover, 2,6-dichloro-4-methoxybenzaldehyde (**6a**) and 2-chloro-4-methoxyacetophenone are smoothly converted to the pertinent oximes; 2,6-dichloro-4-methoxyacetophenone (**7a**) and 2,6-dichloro-3-methoxyacetophenone (**7b**) did not react with hydroxylamine under various conditions on a prep. scale (boiling with hydroxylamine in pyridine for 110 h afforded about 12% of the corresponding oxime (^{1}H-NMR) in accordance with *Laird*[7]).



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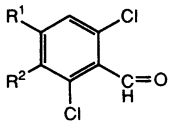
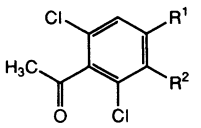


6a: $R^1 = OCH_3$; $R^2 = H$
6b: $R^1 = H$; $R^2 = OCH_3$



7a: $R^1 = OCH_3$; $R^2 = H$
7b: $R^1 = H$; $R^2 = OCH_3$

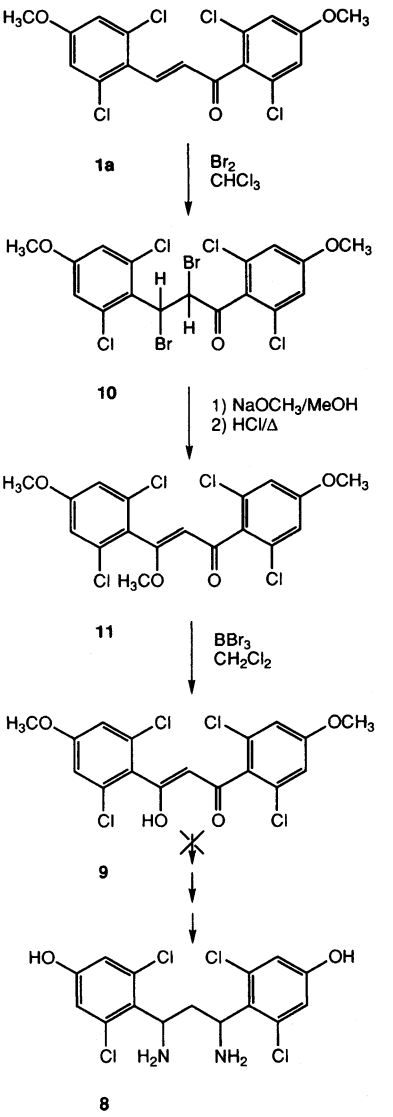
Scheme 2

We tried to prepare 1,3-bis-(2,6-dichloro-4-hydroxyphenyl)-1,3-diaminopropane (**8**), the CH_2-homologue of *Schönenberger's* ligand[2,3] of complex **5**, by converting chalcone **1a** into the 1,3-dicarbonyl compound **9** (Scheme 3) by addition of Br_2 [**10**], substitution with $^-OCH_3$, HBr-elimination [**11**], and enolate cleavage, but **9** so obtained is completely enolized and does not react with hydroxylamine.

It is well known that in most cases 1,3-diketones yield isoxazoles when treated with hydroxylamine, but „in some instances the isolation of dioximes in the reaction of hydroxylamine with β-diketones has been reported"[8].

Chalcone aziridines are known already for a long time. They can be prepared by the reaction of chalcone dibromides with NH_3[9], by reaction of chalcones with *prim.* amines in the presence of I_2[10], and by 1,3-elimination of MeOH from 1,3-diaryl-3-methoxyamino-1-propanones[11].

In 1904 *Wieland*[9] obtained a chalcone aziridine from 2,3-dibromo-1-phenyl-3-(4-nitrophenyl)-1-propanone and NH_3, but he assumed that a piperazine derivative had been formed by ring closure of two molecules of dibromo-ketone and two molecules of NH_3. - Analogously, *Ruhemann* and *Watson* [12] prepared 2-benzoyl-3-phenylaziridine. They excluded a piperazine structure on account of the determination of the molecular mass and



Scheme 3

discussed a 2-amino-1,3-diphenyl-1-propen-3-one structure. So did *Blatt* [11] who obtained chalcone aziridines by the 1,3-elimination of MeOH (*vide supra*). *Cromwell* et al. [13] ascertained the aziridine character of the compounds obtained according to *Wieland* [9], *Ruhemann* [12], and *Blatt* [11] by their chemical and spectroscopic properties, and established *trans*-configuration of the compounds obtained by *Blatt* [11]. *Cromwell's* results [14] were corroborated by experiments concerning the mechanism of aziridine formation and spectroscopic measurements performed by *Weber* et al. [6].

The amino-propenone structure emerged again in 1974 when *Reichel* [15] regarded some of *Blatt's* chalcone aziridines [11] as amino-chalcones.

According to *Cromwell* [14] chalcone aziridines are formed by 1,4-addition of *O*-methyl-hydroxylamine to the chalcone, followed by deprotonation at C-2 to a resonance-stabilized carbanion and intramolecular nucleophilic attack at the N-atom with $^-OCH_3$ as a leaving group. - According to our view this is an intramolecular electrophilic amination [16] (*O*-methyl-hydroxylamine is a reagent for (intermolecular) electrophilic aminations).

Having these data in mind, a base catalyzed formation of our 1*H*-aziridines from 3-hydroxyamino-1,3-diphenylpropan-1-ones by the attack of C-2-carbanion at the N-atom with HO^- as the leaving group is conceivable.

To the best of our knowledge this is the first case of aziridine formation with the intermediacy of 1,3-diaryl-3-hydroxyamino-1-propanones and with OH^- as a leaving group in the ring closure.

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Experimental Part

General remarks: Lit.[4].

1-(2,6-Dichloro-4-methoxyphenyl)ethan-1-ol

To a *Grignard* reagent from 4.26 g (30 mmole) CH_3I and 0.73 g (30 mmole) Mg in 15 ml of absol. Et_2O are added dropwise 2.05 g (10 mmole) 2,6-dichloro-4-methoxybenzaldehyde (**6a**) [2] in 20 ml of absol. Et_2O and 20 ml of absol. THF at -5°C. After stirring for 1 h at room temp., 30 ml of satd. NH_4Cl-solution are slowly added with ice bath cooling. The org. solvents are evaporated *in vacuo*, the water phase is diluted with 30 ml of water and extracted with CH_2Cl_2 (3 x 50 ml). The org. phase is washed with satd. NaCl solution and evaporated *in vacuo*: The remaining oil is distilled at 126 - 127°C/0.6 Torr; 94% yield. - $C_9H_{10}Cl_2O_2$ (221.2) Calcd. C 48.9 H 4.56 Found C 49.2 H 4.56. - FT-IR (film): $\tilde{\nu}$ = 3287 cm^{-1} (br., OH); 3085 (CH aromat.); 2977, 2936 (CH aliph.); 2832 (OCH_3); 1605 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.82 (s; 2H aromat.), 5.48 (dq; $^3J_{HCOH}$ = 10.5 Hz, $^3J_{HCCH}$ = 7.5 Hz, 1H, CH; H/D exch.: q), 3.75 (s; 3H, OCH_3), 2.87 (d; $^3J_{HCOH}$ = 10.5 Hz, 1H, OH, exch.), 1.59 (d; ^3J = 7.5 Hz, 3H, CH_3).

2,6-Dichloro-4-methoxyacetophenone (**7a**)

The solution of 2.21 g (10 mmole) 1-(2,6-dichloro-4-methoxyphenyl)ethan-1-ol in 40 ml of benzene is heated for 15 h with freshly precipitated, active MnO_2. After cooling to room temp. MnO_2 is filtered off using Celite^R and washed with benzene. Benzene is evaporated *in vacuo*, the residue is purified (SiO_2; Et_2O/hexane 1/4; v/v) and distilled at 125 - 128°C/0.6 Torr; 87% yield. - $C_9H_8Cl_2O_2$ (219.1) Calcd. C 49.3 H 3.68 Found C 49.4 H 3.61. - FT-IR (film): $\tilde{\nu}$ = 3100, 3020 cm^{-1} (CH aromat.); 2980, 2944 (CH aliph.); 2840 (OCH_3); 1717 (C=O); 1599 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.85 (s; 2H aromat.), 3.79 (s; 3H, OCH_3), 2.53 (s, 3H, CH_3).

1-(2,6-Dichloro-3-methoxyphenyl)ethan-1-ol

Prepared as described for the 4-methoxy-isomer from 2,6-dichloro-3-methoxybenzaldehyde (**6b**)[17]: colourless, viscous oil, b.p. 150 - 152°/2.5 Torr; 95% yield. - $C_9H_{10}Cl_2O_2$ (221.1) Calcd. C 48.9 H 4.56 Found C 49.2 H 4.73. - CW-IR (film): $\tilde{\nu}$ = 3400 cm^{-1} (OH); 3095 (CH aromat); 2980; 2945 (CH aliph.); 2845 (OCH_3); 1575 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.24 (d; ^3J = 9.0 Hz, 1H aromat), 6.79 (d; ^3J = 9.0 Hz, 1H aromat.), 5.60 (dq; $^3J_{HCOH}$ = 10.5 Hz, $^3J_{HCCH}$ = 7.5 Hz, 1H, CH; H/D-exch.: q), 3.89 (s; 3H, OCH_3), 3.10 (d; $^3J_{HCOH}$ = 10.5 Hz, 1H, OH; exch.), 1.60 (d; ^3J = 7.5 Hz, 3H, CH_3).

2,6-Dichloro-3-methoxyacetophenone (**7b**)

Prepared from 1-(2,6-dichloro-3-methoxyphenyl)ethan-1-ol as described for the 4-methoxy isomer: colourless, viscous oil, b.p. 121 - 122°C/0.5 Torr; 74% yield; m.p. 38 - 40°C. - $C_9H_8Cl_2O_2$ (219.1) Calcd. C 49.3 H 3.68 Found C 49.5 H 3.73. - CW-IR (Film): $\tilde{\nu}$ = 3090, 3010 cm^{-1} (CH aromat.); 2980, 2950 (CH aliph.); 2850 (OCH_3); 1720 (C=O); 1570 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.26 (d; ^3J = 9.0 Hz, 1H aromat.), 6.87 (d; ^3J = 9.0 Hz, 1H aromat.), 3.90 (s; 3H, OCH_3), 2.55 (s; 3H, CH_3).

trans-1,3-Bis-(2,6-dichloro-x-methoxyphenyl)-2-propen-1-ones (**1a, 1b**), *General procedure*

Under vigorous stirring the solution of 5.07 g NaOH (0.126 mole) in 45 ml of water and 29 ml of EtOH (96%) is mixed simultaneously with 0.1 mole each of the pertinent benzaldehyde **6** and the corresponding acetophenone **7** at room temp. Stirring is continued for 12 h. Then the org. phase is separated, diluted with 200 ml of CH_2Cl_2, washed with water and satd. NaCl-solution, dried (Na_2SO_4) and evaporated *in vacuo*.

trans-1,3-Bis-(2,6-dichloro-4-methoxyphenyl)-2-propen-1-one (**1a**)

Yield 94%, m.p. 122 - 123°C (absol. EtOH). - $C_{17}H_{12}Cl_4O_3$ (406.1) Calcd. C 50.3 H 2.98 Found C 50.4 H 3.01. - CW-IR (KBr): $\tilde{\nu}$ = 3090, 3010 cm^{-1} (CH aromat.); 2980, 2940, 2890 (CH aliph.); 2845 (OCH_3); 1660 (C=O); 1635, 1595 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.46 (d; ^3J = 16.5 Hz, 1H, =CH), 7.08 (d; ^3J = 16.5 Hz, 1H, =CH), 6.92 (s; 4H, aromat.), 3.83, 3.80 (2s; 6H, OCH_3).

trans-1,3-Bis-(2,6-dichloro-3-methoxyphenyl)-2-propen-1-one (**1b**)

Yield 95%, m.p. 122 - 124°C (absol. EtOH). - $C_{17}H_{12}Cl_4O_3$ (406.1) Calcd. C 50.3 H 2.98 Found C 50.3 H 3.12. - CW-IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1} (CH aromat.); 2980; 2940 (CH aliph.); 2840 (OCH_3); 1660 (C=O); 1630, 1565 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.41 (d; ^3J = 16.5 Hz, 1H, =CH), 7.35 - 6.84 (m; 4H aromat.), 6.88 (d; ^3J = 16.5 Hz, 1H, =CH), 3.92, 3.89 (2s; 6H, OCH_3).

2-Benzoyl-3-phenyl-1H-aziridines (**4a, 4b**)

At 50°C 18.3 g (0.263 mole) of hydroxylamine-HCl in 40 ml of water are added drop by drop to a solution of 0.1 mole **1** in 240 ml of EtOH, followed by dropwise addition of 24 g (0.428 mole) KOH in 40 ml of water. After boiling for 20 min, the mixture is evaporated to dryness *in vacuo*. After addition of 1.5 L of water stirring is continued for 1 h. The precipitate is filtered off, dried over night *in vacuo* and purified by CC (SiO_2): impurities are removed by CH_2Cl_2, the aziridines are eluated by EtOAc and crystallized from 96% EtOH: faint yellow crystals.

trans-2-(2,6-Dichloro-4-methoxybenzoyl)-3-(2,6-dichloro-4-methoxyphenyl)-1H-aziridine (**4a**)

From **1a**; yield 51%; m.p. 111 - 112°C. - $C_{17}H_{13}Cl_4NO_3$ (421.1) Calcd. C 48.5 H 3.11 N 3.3 Found C 48.5 H 3.31 N 3.0. - FT-IR (KBr): $\tilde{\nu}$ = 3291, 3258 cm^{-1} (NH); 3087, 3010 (CH aromat.); 2975, 2948 (CH aliph.); 2842 (OCH_3); 1697 (C=O); 1597 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.90 (s; 2H aromat.) 6.83 (s; 2H aromat.), 3.83 (s; OCH_3), 3.77 (s; 3H, OCH_3), 3.48 (dd; $^3J_{HCCH}$ = 3.0 Hz, $^3J_{HCNH}$ = 9.0 Hz, 1H, CH; H/D exch.: d; ^3J = 3.0 Hz), 3.28 (dd; $^3J_{HCCH}$ = 3.0 Hz, $^3J_{HCNH}$ = 9.0 Hz, 1H, CH; H/D exch: d; ^3J = 3.0 Hz), 2.62 (t; $^3J_{HCNH}$ = 9.0 Hz, 1H, NH; exch.). - ^{13}C-NMR ($CDCl_3$): δ (ppm/62.5 MHz) = 199.2 (C-1), 160.9 (C-4' aromat.), 159.5 (C-4'' aromat.), 136.8 (C-Cl), 132.3 (C-Cl), 130.4 (C-Cl), 125.1 (C-Cl), 114.4 (C-H aromat.), 114.3 (C-H aromat.), 55.9 (OCH_3), 55.7 (OCH_3), 46.3 (C-2), 41.1 (C-3). These data are in accordance with those published by *Cromwell* [18] for benzoyl-phenyl-aziridines. - EI-MS: m/z (%) = 419 (9; ^{35}Cl-$M^{+\cdot}$); 384 (43; (M - $^{\cdot}$Cl)$^+$), *ortho*-effect); 356 (7; (384 - CO)$^+$); 348 (8; 384 - HCl)$^+$; 216 (25; (Ar-CH(NH)CH)$^+$); 203 (100; (Ar-CO)$^+$); 189 (44; (Ar-CH_2)$^+$). The formation of Ar-CH_2^+ in phenylaziridines by rearrangement is discussed by *Searles* [19] and *Weber* [20].

trans-2-(2,6-Dichloro-3-methoxybenzoyl)-3-(2,6-dichloro-3-methoxyphenyl)-aziridine (**4b**)

From **1b**, yield 55%; m.p. 117 - 118°C. - $C_{17}H_{13}Cl_4NO_3$ (421.1) Calcd. C 48.5 H 3.11 N 3.3 Found C 48.6 H 3.09 N 3.3. - FT-IR (KBr): $\tilde{\nu}$ = 3291, 3258 cm^{-1} (NH); 3087, 3010 (CH aromat.); 2975, 2948 (CH aliph.); 2842 (OCH_3); 1697 (C=O); 1597 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.33 (d; ^{3}J = 9.0 Hz, 1H aromat.), 7.21 (d; ^{3}J = 9.0 Hz, 1H aromat.), 6.94 (d; ^{3}J = 9.0 Hz, 1H aromat.), 6.82 (d; ^{3}J = 9.0 Hz, 1H aromat.), 3.93 (s; 3H, OCH_3), 3.86 (s; 3H, OCH_3), 3.51 (dd; $^3J_{HCCH}$ = 3.0 Hz, $^3J_{HCNH}$ = 9.0 Hz, 1H, CH; exch.: d; ^{3}J = 3.0 Hz), 3.37 (dd; $^3J_{HCCH}$ = 3.0 Hz, $^3J_{HCNH}$ = 9.0 Hz, 1H, CH; H/D exch.: d; ^{3}J = 3.0 Hz), 2.72 (t; $^3J_{HCNH}$ = 9.0 Hz, 1H, NH, exch.). - ^{13}C-NMR ($CDCl_3$): δ (ppm/62.5 MHz) = 198.9 (C-1), 154.4 (C-4' aromat., C-4'' aromat.), 139.1 (C-Cl), 133.3 (C-Cl), 129.1 (C-H aromat.), 128.1 (C-H aromat.), 125.5 (C-Cl), 121.9 (C-Cl), 114.1 (C-H aromat.), 112.7 (C-H aromat.), 57.1 (OCH_3), 55.2 (OCH_3), 46.2 (C-2), 41.6 (C-3). - EI-MS: m/z (%) = 419 (7; ^{35}Cl-$M^{+\cdot}$); 384 (44; (M - $^{\cdot}$Cl)$^+$, *ortho*-effect); 356 (9; (M - $^{\cdot}$Cl - CO)$^+$); 348 (8; M - $^{\cdot}$Cl - HCl)$^+$); 216 (32; (Ar-CH(NH)CH)$^+$); 203 (93; (Ar-CO)$^+$); 189 (100; (Ar-CH_2)$^+$).

1,3-Bis-(2,6-dichloro-4-methoxyphenyl)-2,3-dibromopropan-1-one (**10**)

At room temp. 0.32 g (2 mmole) of Br_2 in 2 ml of $CHCl_3$ are added dropwise to a solution of 0.812 (2 mmole) of **1a** in 10 ml of $CHCl_3$. After stirring for 2 h 10 ml of aqueous satd. $NaHSO_3$ solution are added slowly and the org. phase is separated. After washing with 10 ml of water and satd. NaCl solution each, the solvent is evaporated *in vacuo* and the residue is crystallized from 96% EtOH: white crystalls; yield 97%, m.p. 155 - 156°C. - $C_{17}H_{12}Br_2Cl_4O_3$ (565.9) Calcd. C 36.1 H 2.14. Found C 36.2 H 2.12. - FT-IR (KBr): $\tilde{\nu}$ = 3093, 3052, 3015 cm^{-1} (CH aromat.); 2979, 2944 (CH aliph.); 2840 (OCH_3); 1699 (C=O); 1589 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.93 (s; 2H aromat.), 6.92 (s; 2H aromat.), 6.69 (d; ^{3}J = 10.8 Hz, 1H, CHBr), 6.51 (d; ^{3}J = 10.8 Hz, 1H, CHBr), 3.84 (s; 3H, OCH_3), 3.81 (s; 3H, OCH_3).

1,3-Bis-(2,6-dichloro-4-methoxyphenyl)-3-methoxy-2-propen-1-one (**11**)

Freshly prepared $NaOCH_3$ solution (0.14 g Na in 3 ml MeOH) is added drop by drop to 1.58 g (2.8 mmole) of **10** dissolved in 10 ml of absol. MeOH. The solution is refluxed for 1 h with stirring, cooled to 0°C, mixed with 10 ml of water and 1 ml of conc. HCl, and stirred for 1 h. The precipitate is washed with water and dried *in vacuo* (40°C, 5 Torr): white crystals; yield 90%; m.p. 148 - 150°C (70% EtOH). - $C_{18}H_{14}Cl_4O_4$ (436.1) Calcd. C 49.2 H 3.22 Found C 49.5 H 3.29. - CW-IR (KBr): $\tilde{\nu}$ = 3090, 3020 cm^{-1} (CH aromat.); 2990, 2950 (CH aliph.); 2850 (OCH_3); 1690 (C=O); 1600, 1585 (C=C). - ^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.89 (s; 2H aromat.), 6.80 (s; 2H aromat.) 5.98 (s; 1H, =CH), 3.83 (s; 3H, OCH_3), 3.77 (s; 3H, OCH_3), 3.74 (s; 3H, OCH_3).

1,3-Bis-(2,6-dichloro-4-methoxyphenyl)-3-hydroxy-2-propen-1-one (**9**)

To the solution of 1.31 g (3 mmole) **11** in 90 ml of absol. CH_2Cl_2 are added at 0 - 5°C 3.8 g (15 mmole) BBr_3 under N_2 during 10 min with stirring. Stirring is continued for 10 min with ice/NaCl cooling, then 90 ml of water are added drop by drop. The org. phase is separated, the aqueous phase is extracted twice with 50 ml of CH_2Cl_2 each. The combined org. phase is washed with satd. NaCl solution, dried (Na_2SO_4) and evaporated to dryness: white crystals; yield 79%. - m.p. 117 - 118°C (96% EtOH). - $C_{17}H_{12}Cl_4O_4$ (422.1) Calcd. C 48.4 H 2.87 Found C 48.7 H 3.01. - FT-IR (KBr): $\tilde{\nu}$ = 3089, 3021 (CH aromat.); 2967, 2938 (CH aliph.), 2840 (OCH_3); 1597 (C=O···HO and C=C). - ^{1}H-NMR ($CDCD_3$): δ (ppm) = 14.60 (br. s; 1H, OH, exch.), 5.90 (s; 4H aromat.), 6.90 (s; 1H, =CH), 3.80 (s; 6H, OCH_3).

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