Synthesis of 1*H*,7*H*,12b*H*-Pyrano[3′,4′:5,6]pyrano[3,4-*c*][1]benzopyran-1-one *via* Domino *Knoevenagel*/Hetero-*Diels–Alder* Reaction with Theoretical Investigations

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Dedicated to Prof. *Lutz F. Tietze* on the occasion of his 70th birthday

The CuI-catalyzed intramolecular oxa-*Diels–Alder* reaction of 2-(prop-2-yn-1-yloxy)benzaldehydes as unactivated terminal alkynes with 4-hydroxy-6-methyl-2*H*-pyran-2-one is described. The reaction proceeds with remarkable chemoselectivity to yield pyranones **3** (*Scheme 1*). A theoretical investigation of the reaction in terms of HOMO–LUMO interactions in the gas phase is also reported. The reaction could be regarded as an inverse-electron-demand *Diels–Alder* cycloaddition. The theoretical results are in high agreement with the experimental evidences.

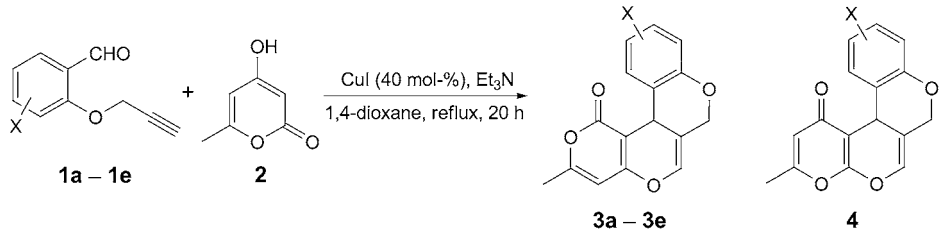
Introduction. – The hetero-*Diels–Alder* reaction is of great importance for industrial chemistry. This reaction represents one of the most powerful ways to construct heterocyclic systems, especially in cases of natural products, biologically active compounds, and drugs [1]. The oxa-*Diels–Alder* reaction has been shown to be a useful way to prepare pyran rings, which are structural components in a wide variety of natural products [2][1e]. The oxa-*Diels–Alder* reaction with alkenes as dienophiles has been widely investigated from the theoretical and experimental point of view [3][2a]. However, the related process with unactivated terminal alkynes has been far less studied, due to the lower reactivity of unactivated alkynes in hetero-*Diels–Alder* reactions.

Recently, copper(I) salts have emerged as efficient *Lewis* acid activators in various C–C and C–X bond-formation reactions [4]. Specifically, the utility of this catalyst has been well documented for the activation of alkynes in organic reactions [5]. The intramolecular oxa-*Diels–Alder* reaction with unactivated terminal alkynes in the presence of the *Lewis* acid CuI has been recently studied in our laboratory [6], and *Moghaddam's* and *Majumdar's* research groups reported novel domino *Knoevenagel*/hetero-*Diels–Alder* reactions for the construction of tetracyclic skeletons in the presence of different *Lewis* acids [7].

Compared to the extensively studied *Diels–Alder* reaction [8], very few theoretical calculations on *Lewis* acid-catalyzed hetero-*Diels–Alder* reactions have been reported.

Therefore, with the aim of gaining detailed insight into the oxa-*Diels–Alder* reaction and the role of CuI as *Lewis* acid, we performed a computational study on the intramolecular oxa-*Diels–Alder* reaction with unactivated terminal alkynes. We now report the domino *Knoevenagel*/hetero-*Diels–Alder* reaction of 2-(prop-2-yn-1-yloxy)benzaldehydes **1a** – **1e** with 4-hydroxy-6-methyl-2*H*-pyran-2-one (**2**) in the presence of CuI to construct pyranones **3a** – **3e** (*Scheme 1*). The calculated HOMO–LUMO interaction involved in the reaction confirmed the experimental results.

Scheme 1



1a – **1e** **2** **3a** – **3e** **4**

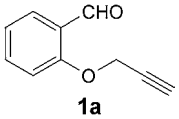
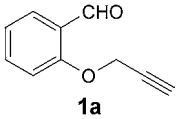
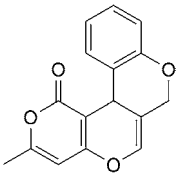
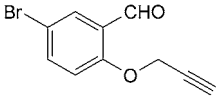
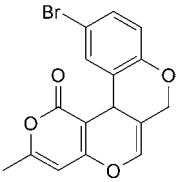
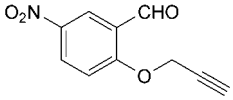
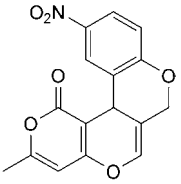
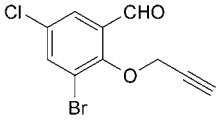
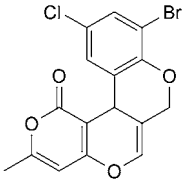
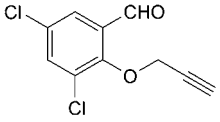
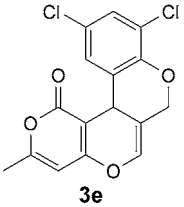
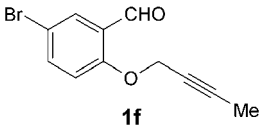
Results and Discussion. – First, the 2-(prop-2-yn-1-yloxy)benzaldehydes **1a** – **1e** were prepared from the corresponding substituted salicylaldehydes (= 2-hydroxybenzaldehydes) with good to excellent yields by our recently published method [6a]. The domino *Knoevenagel*/hetero-*Diels–Alder* reaction of **1a** – **1e** with 4-hydroxy-6-methyl-2*H*-pyran-2-one (**2**) was performed in the presence of CuI as *Lewis* acid; the best results were obtained in refluxing 1,4-dioxane in the presence of 40 mol-% of CuI, and Et_3N as base (*Scheme 1* and *Table 1*). The reaction showed a remarkable regioselectivity since only one of the two possible products, *i.e.*, **3**, was formed.

The structures of the products were established on the basis of their spectroscopic data. The characteristic signal for **3a** – **3e** in the ^{1}H-NMR spectra are an *AB* pattern for CH_2(7)–O at δ(H) 4.65 – 4.83 and 4.77 – 4.91 and a *s* for H–C(12b) at δ 4.25 – 4.75. The corresponding signals for C(12b) and C(7) of **3a** appear in the ^{13}C-NMR spectrum at δ (C) 28.3 and 66.1, respectively.

A probable mechanism for the domino *Knoevenagel*/hetero-*Diels–Alder* reaction is depicted in *Scheme 2*. The first step is the *Knoevenagel* condensation between 4-hydroxy-6-methyl-2*H*-pyran-2-one (**2**) and the benzaldehyde **1** to give an alkenylidene intermediate which was not isolated. This intermediate provides two different heterodiene fragments which can undergo the corresponding hetero-*Diels–Alder* reaction, leading *via Path A* to product **3** and *via Path B* to product **4**. As only product **3** was isolated, the reaction proceeded most likely *via Path A* involving the keto C=O as heterodiene. High polarizability makes the HOMO–LUMO energy gap smaller when the lactone group acts as heterodiene instead of the keto C=O group, thus favoring *Path A*, *i.e.*, in all cases, the major product **3** probably arised from the hetero-*Diels–Alder* reaction of the keto C=O group. Our results involving 4-hydroxycoumarin (= 4-hydroxy-2*H*-1-benzopyran-2-one) instead of **2** in the reaction with **1** could confirm this pathway [6b].

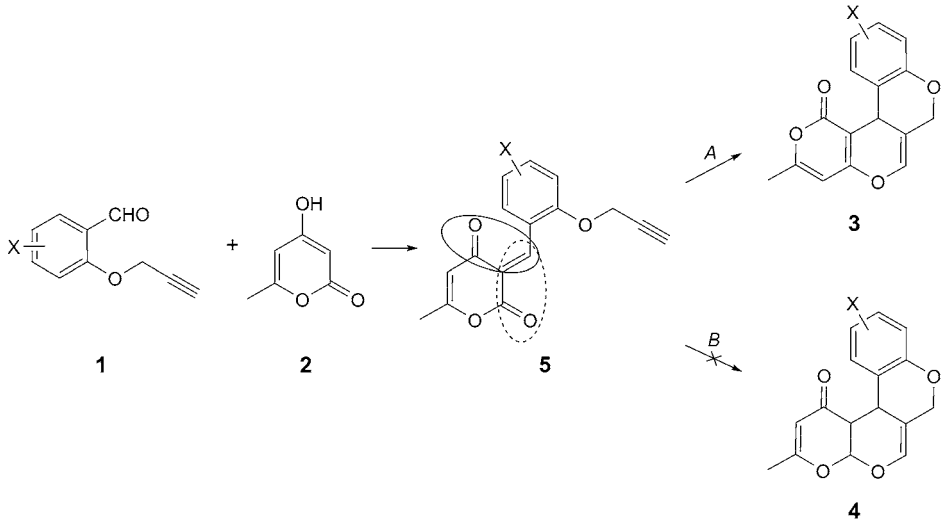
In the reaction reported above, our attention was focused on the intramolecular oxa-*Diels–Alder* reaction of different heterodienes containing unactivated terminal

Table 1. *CuI-Catalyzed Domino* Knoevenagel/*Oxa*-Diels–Alder *Reaction of* **1a**–**1f** *with* **2**

Entry	Aldehyde	Product	Yield [%][a])
1	 **1a**	–	–[b])
2	 **1a**	 **3a**	72
3	 **1b**	 **3b**	82
4	 **1c**	 **3c**	85
5	 **1d**	 **3d**	85
6	 **1e**	 **3e**	80
7	 **1f**	–	–

a) Yield of isolated product. b) Attempted reaction without CuI.

Scheme 2. *Proposed Mechanism for the Formation of 1*H,7H,*12b*H-*Pyrano[3′,4′:5,6]pyrano[3,4-c][1]benzopyran-1-one* via *Domino* Knoevenagel/*Hetero*-Diels–Alder *Reaction*



acetylenes in the presence of CuI as *Lewis* acid. CuI could play two different roles in the reaction; *i.e.*, being the *Lewis* acid or reacting to give the copper acetylide. To established the major contribution of CuI, 2-(but-2-yn-1-yloxy)benzaldehyde (**1f**) was synthesized from salicylaldehyde and 1-bromobut-2-yne and treated with **2** in the presence of CuI under the same conditions as before (*Table 1*, *Entry 7*). But, the desired 1*H*,7*H*,12b*H*-pyrano[3′,4′:5,6]pyrano[3,4-*c*][1]benzopyran-1-one was not formed, thus confirming that the reaction of **1** and **2** proceeds *via* the formation acetylide intermediates.

With the aim to get a detailed insight into the described domino reaction and to clarify the role of CuI, we performed a computational study. All structures were computed by the density-functional theory (B3LYP) with the 6–31G basis set in Gaussian 98, and all calculations were performed for the gas phase, and the effect of solvent was not taken into account. In the absence of CuI, the activation barrier for the concerted reaction was 26.5 kcal/mol. It seems that this barrier is too high to allow the oxa-*Diels–Alder* reaction. Experimental results also support this prediction (*Table 1*, *Entry 1*). The optimized transition-state structure is shown in *Fig. 1*. Our studies show that the metal-catalyzed hetero-*Diels–Alder* reaction follows the stepwise mechanism.

In analogy to the CuI-catalyzed 1,3-dipolar cycloaddition of azides and terminal alkynes [9] and *Diels–Alder* reactions of terminal alkynes [10], where theoretical and experimental studies have shown that a copper acetylide must be generated for the reactions, a similar mechanism for the here described hetero-*Diels–Alder* reaction is suggested (*Scheme 3*).

The formation of an intermediate copper acetylide is consistent with the observation that only unactivated terminal acetylenes participate in the reaction, and end-capped substrates do not undergo the cycloaddition (*Table 1*, *Entry 7*).

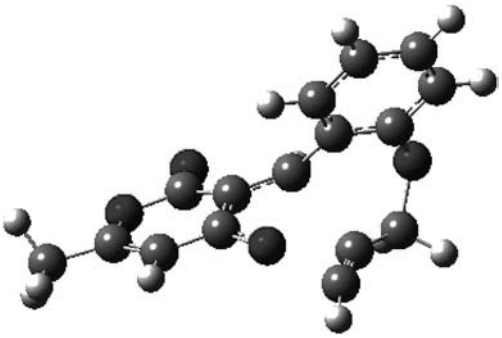
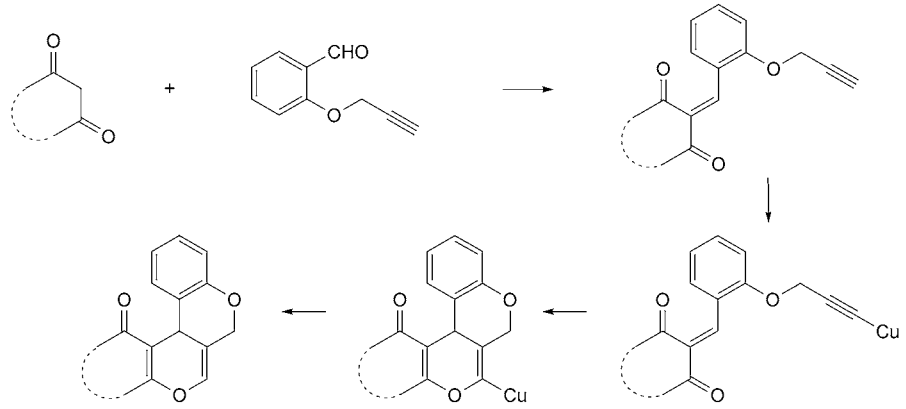


Fig. 1. *Optimized transition-state structure of the concerted cycloaddition in the absence of CuI*

Scheme 3. *Proposed Mechanism for the Synthesis of Tetracyclic Compounds* via *Domino* Knoevenagel/*Hetero*-Diels–Alder *Reaction of Unactivated Alkynes*



The role of CuI as the *Lewis* acid and the chemoselectivity observed in the reaction were rationalized by the quantum-mechanics calculations (see above). The energy difference between the HOMO and LUMO plays a major role for the rate of a *Diels–Alder* reaction. To simplify the computations and to determine the energies of the HOMO and LUMO, the heterodiene and dienophile fragments were considered distinct and independent, and the computations were performed for both uncatalyzed and catalyzed reactions. Thus, formation of a copper acetylide increases the energy of the HOMO and decreases the level of the LUMO (*Fig. 2*). The energy data also show that the HOMO–LUMO gaps of the heterodiene and the copper acetylide are smaller than the HOMO–LUMO gaps of the heterodiene and acetylene (as the dienophile). Therefore, the formation of the copper acetylide allows a more favorable pathway, and the reaction can proceed better in the presence of the *Lewis* acid CuI. The experimental results support this hypothesis no product being formed in the absence of CuI.

According to the energy data, the $HOMO_{dienophile}$–$LUMO_{diene}$ energy gap is smaller, leading to a better interaction between the LUMO of the diene and the HOMO of the

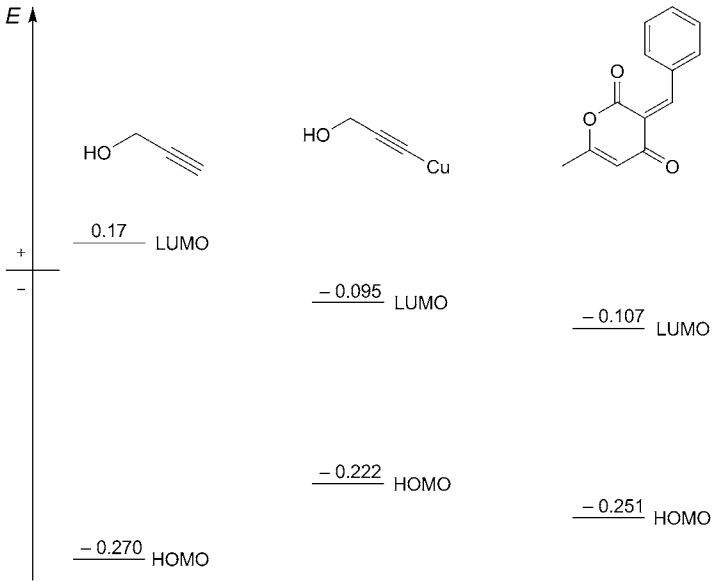
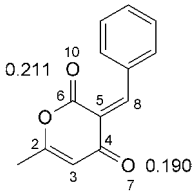


Fig. 2. *Energy-level diagram for molecular orbitals of heterodiene and dienophile*

dienophile. *Table 2* shows the calculated energies for the frontier orbital of some diene fragments.

In a next step, the influence of the substituents on the heterodiene was investigated. The presence of electron-withdrawing substituents (such as nitro) in the structure of the diene can accelerate the reaction, whereas electron-donating substituents (such as Br) can slow down the *Diels–Alder* reaction. The reason for this observation can be easily explained by the FMO theory. Introducing an electron-withdrawing group in the oxa-diene system lowers the LUMO energy level, which can more easily overlap with the HOMO of the dienophile, leading to an increase of the reaction rate. Hence, the CuI-catalyzed oxa-*Diels–Alder* reaction with unactivated terminal alkynes can be considered as an inverse-electron-demand cycloaddition.

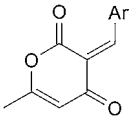
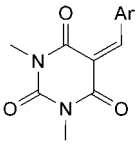
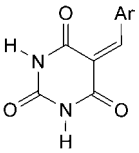
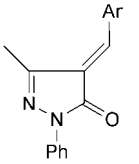
Finally, to explain the chemoselectivity observed in this reaction, the coefficients of the LUMO of the diene must be taken into account, *i.e.*, the LUMO coefficient values at the two C=O O-atoms. From the data presented in *Fig. 3*, it is clear that the preferred reaction path should be controlled by overlap of the keto C=O with the dienophile, in



LUMO

Fig. 3. *Coefficients of the LUMO of the diene*

Table 2. *Energy of the HOMO and LUMO of Some Dienes*

	Ar = Ph		Ar = 3-$NO_2C_6H_4$		Ar = 3-BrC_6H_4	
	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}
	– 0.251	– 0.107	– 0.268	– 0.127	– 0.256	– 0.115
	– 0.252	– 0.103	– 0.272	– 0.121	– 0.256	– 0.111
	– 0.258	– 0.109	– 0.281	– 0.128	– 0.260	– 0.117
	– 0.207	– 0.096	– 0.226	– 0.122	– 0.211	– 0.103

full agreement with the experimental results, *i.e.*, with the chemoselective formation of adducts **3**.

In conclusion, we have developed an efficient way for the synthesis of pyrano[3′,4′:5,6]pyrano[3,4-*c*][1]benzopyran-1-ones **3** *via* a domino *Knoevenagel*/hetero-*Diels–Alder* reaction of unactivated alkynes. Good to high yields, high bond-forming efficiency (BFE), and high chemoselectivity are advantages of this reaction. Moreover, theoretical investigations suggest the intermediate formation of a reactive copper acetylide and also the presence of an inverse hetero-*Diels–Alder* reaction pathway, confirming the observed chemoselectivity of the product.

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Experimental Part

General. Commercially available materials were used without further purification. M.p.: *Electrothermal-9100* apparatus; uncorrected. IR Spectra (KBr): *ABB-FT-IR-FTLA-2000* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-DRX-500 Avance* spectrometer; at 500 (^1H) and 125 MHz (^{13}C); in (D_6)DMSO; δ in ppm, *J* in Hz. HR-EI-MS: *Jeol-JMS-700* mass spectrometer; in *m*/*z*.

Domino Knoevenagel*/Hetero*-Diels–Alder *Reaction: General Procedure.* A mixture of 2-(prop-2-yn-1-yloxy)benzaldehyde **1a**–**1f** (1 mmol), 4-hydroxy-2*H*-pyran-2-one **2** (1.2 mmol), Et_3N (0.6 ml,

1mmol), and CuI (76 mg, 0.04 mmol) in dioxan (25 ml) was heated to reflux for 20–24 h (TLC (hexane/AcOEt 3:1) monitoring). Then the mixture was diluted with H_2O, the org. phase washed with brine and dried (Na_2SO_4), the solvent distilled off, and the crude product crystallized from AcOEt.

*3-Methyl-1*H,*7*H,*12b*H-*pyrano[3′,4′:5,6]pyrano[3,4-c][1]benzopyran-1-one* (**3a**): Yield 193 mg (72%). M.p. 201–202°. IR: 1714, 1664. ^{1}H-NMR: 2.26 (*s*, Me–C(3); 4.25 (*s*, H–C(12b)); 4.66, 4.79 (*AB*, J_{AB} = 11.6, CH_2(7)); 6.22 (*s*, H–C(4)); 6.75 (*t*, *J* = 7.4, 1 arom. H); 6.80 (*d*, *J* = 7.4, 1 arom. H), 6.98 (*d*, *J* = 7.4, 1 arom. H); 7.00 (*s*, H–C(6)); 7.09 (*t*, *J* = 7.4, 1 arom. H). ^{13}C-NMR: 19.0; 28.3; 66.1; 96.3; 98.3; 111.7; 116.4; 119.9; 125.6; 126.4; 127.5; 134.6; 153.1; 160.9; 162.4; 163.8. HR-EI-MS: 268.0745 (M^+, $C_{16}H_{12}O_4^+$; calc. 268.0736).

*11-Bromo-3-methyl-1*H,*7*H,*12b*H-*pyrano[3′,4′:5,6]pyrano[3,4-c][1]benzopyran-1-one* (**3b**). Yield 325 mg (82%). M.p. 220–220.5°. IR: 1720, 1653. ^{1}H-NMR: 2.25 (*s*, Me–C(3)); 4.59 (*s*, H–C(12b)); 4.66, 4.77 (*AB*, *J* = 11.7, CH_2(7)); 6.21 (*s*, H–C(4)); 6.71 (*d*, *J* = 7.91, 1 arom. H); 7.01 (*s*, H–C(6)); 7.12 (*s*, 1 arom. H); 7.24 (*d*, *J* = 7.9, 1 arom. H). ^{13}C-NMR: 17.6; 26.9; 64.8; 94.4; 96.9; 109.2; 109.6; 117.4; 126.7; 127.1; 128.9; 133.8; 151.1; 159.7; 161.4; 162.5. HR-EI-MS: 345.9833 (M^+, $C_{16}H_{11}{}^{79}BrO_4^+$; calc. 345.9841), 347.9824 ($[M+2]^+$, $C_{16}H_{11}{}^{81}BrO_4^+$; calc. 347.9820).

*3-Methyl-11-nitro-1*H,*7*H,*12b*H-*pyrano[3′,4′:5,6]pyrano[3,4-c][1]benzopyran-1-one* (**3c**). Yield 266 mg (85%). M.p. 245–246°. IR: 1717, 1652, 1590. ^{1}H-NMR: 2.28 (*s*, Me–C(3)); 4.75 (*s*, H–C(12b)); 4.83, 4.93 (*AB*, *J* = 11.5, CH_2(7)); 6.26 (*s*, H–C(4)); 6.96 (*d*, *J* = 8.8, 1 arom. H); 7.12 (*s*, H–C(6)); 7.99 (*s*, 1 arom. H); 8.01 (*d*, *J* = 8.8, 1 arom. H). ^{13}C-NMR: 19.1; 28.4; 67.2; 95.7; 98.5; 109.5; 117.6; 122.5; 123.9; 126.6; 136.1; 140.1; 159.2; 161.4; 163.2; 164.0. HR-EI-MS: 313.0559, (M^+, $C_{16}H_{11}NO_6^+$; calc. 313.0586).

*9-Bromo-11-chloro-3-methyl-1*H,*7*H,*12b*H-*pyrano[3′,4′:5,6]pyrano[3,4-c][1]benzopyran-1-one* (**3d**). Yield 325 mg (85%). M.p. 229–230°. IR: 1709, 1692, 1579. ^{1}H-NMR: 2.27 (*s*, Me–C(3)); 4.65 (*s*, H–C(12b)); 4.83, 4.91 (*AB*, br. *s*, CH_2(7)); 6.26 (*s*, H–C(4)); 7.02 (*s*, H–C(6)); 7.08 (*s*, 1 arom. H); 7.44 (*s*, 1 arom. H). ^{13}C-NMR: 19.2; 28.9; 66.2; 95.7; 98.5; 110.7; 112.7; 123.9; 125.2; 129.4; 130.3; 135.9; 149.0; 161.5; 163.2; 164.1. HR-EI-MS: 379.9429 (M^+, $C_{16}H_{11}{}^{79}Br{}^{35}ClO_4^+$; calc. 379.9451), 381.9411 ($[M+2]^+$, $C_{16}H_{11}{}^{79}Br{}^{37}ClO_4^+$; calc. 381.9400), 383.9391 ($[M+4]^+$, $C_{16}H_{11}{}^{81}Br{}^{37}ClO_4^+$; calc. 383.9381).

*9,11-Dichloro-3-methyl-1*H,*7*H,*12b*H-*pyrano[3′,4′:5,6]pyrano[3,4-c][1]benzopyran-1-one* (**3e**). Yield 270 mg (80%). M.p. 218–219°. IR: 1710, 1665, 1580. ^{1}H-NMR: 2.26 (*s*, Me–C(3)); 4.64 (*s*, H–C(12b)); 4.82, 4.90 (*AB*, *J* = 11.7, CH_2(7)); 6.25 (*s*, H–C(4)); 6.98 (*s*, H–C(6)); 7.07 (*s*, 1 arom. H); 7.41 (*s*, 1 arom. H). ^{13}C-NMR: 18.7; 28.3; 66.8; 95.2; 98.0; 109.5; 120.9; 123.0; 124.1; 127.1; 139.0; 135.4; 147.6; 161.0; 162.7; 163.6. HR-EI-MS: 335.9937 (M^+, $C_{16}H_{10}{}^{35}Cl_2O_4^+$; calc. 335.9956), 337.9945 ($[M+2]^+$, $C_{16}H_{10}{}^{37}Cl{}^{35}ClO_4^+$; calc. 337.9927), 339.9952 ($[M+4]^+$, $C_{16}H_{10}{}^{37}Cl_2O_4^+$; calc. 339.9897).

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