Monatshefte für Chemie 125, 95–105 (1994)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Reactions of Cyclic 1,3-Dicarbonyl Compounds with 1,2(1,4)-Dihydro-1-methyl-2(4)-methylene-N-heterocycles. A New Access to 6,12-Methano-dibenz[d,g]-[1,3]oxazocinones

Hans-Georg Henning[1,*], **Le Hoang Thanh**[1], **Jörg Laue**[1], **Barbara Urban**[1], and **Günter Reck**[2]

[1] Institut für Organische Chemie, Humboldt-Universität Berlin, D-10115 Berlin, Bundesrepublik Deutschland
[2] Bundesanstalt für Materialforschung und -prüfung, D-12489 Berlin, Bundesrepublik Deutschland

Summary. The enamine-type methylene-N-heterocycles **1–5** react with cyclic 2-ethoxymethylene-1,3-dicarbonyl compounds **6** to give 2-[2-(hetarylidene)ethylidene]-1,3-dicarbonyl compounds **7–14**. The result of the reactions between 1,2-dihydro-1-methyl-2-methylene-quinoline (**1a**) and cyclic 1,3-dicarbonyl compounds depends on the nature of the dihydro intermediates **A**/**B**. Dehydrogenation of keton intermediates **A** results in 2-(1,2-dimethyl-4(1*H*)-quinolylidene)-1,3-dicarbonyl compounds **17–21**. Enol intermediates **B** with 6-membered dicarbonyl ring form 6,12-methano-dibenz-[d,g][1,3]oxazocinones **22–25**. ^{1}H NMR spectra and X-ray structure analysis prove the structure of **23**.

Keywords. 2-[2-(Hetarylidene)ethylidene]-1,3-dicarbonyl compounds; 2-(1,2-Dimethyl-4(1*H*)quinolylidene)-1,3-dicarbonyl compounds; 6,12-Methano-dibenz[d,g][1,3]oxazocinones; X-ray analysis.

Reaktionen cyclischer 1,3-Dicarbonylverbindungen mit 1,2(1,4)-Dihydro-1-methyl-2(4)-methylen-N-heterocyclen. Ein neuer Zugang zu 6,12-Methano- dibenz[d,g][1,3]oxazocinonen

Zusammenfassung. Aufgrund ihres Enamincharakters reagieren die Methylen-N-heterocyclen **1–5** mit cyclischen 2-Ethoxymethylen-1,3-dicarbonylverbindungen **6** zu den 2-[2-(Hetaryliden)ethyliden]-1,3-dicarbonylverbindungen **7–14**. Das Ergebnis der Reaktionen zwischen 1,2-Dihydro-1-methyl-2-methylen-chinolin (**1a**) und cyclischen 1,3-Dicarbonylverbindungen hängt von der Natur der zwischenzeitlich entstehenden Dihydroverbindungen **A**/**B** ab. Die Intermediat-Ketone **A** gehen durch Dehydrierung während der Reaktion in die 2-(1,2-Dimethyl-4(1*H*)chinolyliden)-1,3-dicarbonylverbindungen **17–21** über. Die Intermediat-Enole **B** mit sechsgliedrigem Dicarbonylring bilden in intramolekularer Reaktion die 6,12-Methano-dibenz[d,g][1,3]oxazocinone **22–25**, deren Struktur am Beispiel der Verbindung **23** durch ^{1}H-NMR sowie durch Röntgenkristallstrukturanalyse bewiesen wird.

Introduction

Previously, we have found that N-alkyloxycarbonylpyridinium cations react directly with Meldrum's acid [1]. By this method we were able to extend former general observations with methylene ketones [2] to a practical application for the synthesis of 4-pyridylacetic acid derivatives. It is well known that N-alkyl quinolinium cations also react with methylene ketones to give new C–C-bonded products [3]. In constrast to the electrophilic pyridinium and quinolinium cations the methylene bases **1–5** of heterocycles are enamines and therefore nucleophilic in character. Now we were interested to connect **1–5** with Meldrum's acid and other cyclic 1,3-dicarbonyl compounds to new synthons for the construction of heterocycles. Because of the nucleophilic nature of the methylene bases and the dicarbonyl compounds as well we used triethyl orthoformate as source for an electrophilic C_1-bridge either by its partial reaction with the dicarbonyl compound or as a component in a three-particle reation.

Results and Discussion

As expected the enamine-type methylene bases **1–5** reacted with 2,2-dimethyl-5-ethoxymethylene-1,3-dioxan-4,6-dione (**6a**) (X-Y-Z = O–CMe_2–O) [4] to give the 5-substituted 1,3-dioxan-4,6-diones **7**, **9**, **10**, **12**, **13**. Accordingly the reactions with 5,5-dimethyl-2-ethoxymethylene-1,3-cyclohexanedione (**6b**) (X-Y-Z = CH_2–CMe_2–CH_2) and 1,3-dimethyl-5-ethoxymethylene-2,4,6-pyrimidinetrione (**6c**) (X-Y-Z = NMe–CO–NMe) [5] gave the compounds **11**, and **8**, **14**, respectively (Scheme 1).

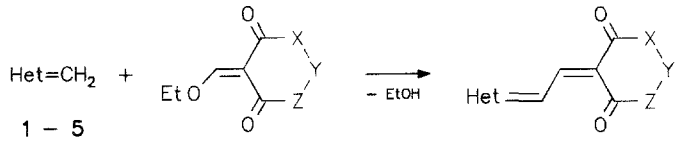
Products **7–14** are merocyanine-type compounds. Therefore, they absorb at relatively long wavelengths. The fluorescence bands show very small bathochromic shifts. Absorption and emission are only slightly influenced by the polarity of the solvent. The lifetime of the excited S_1 state of **10** in ethanol at room temperature was determined from the fluorescence decay to 130 ps. The quantum yield of fluorescence $\phi_f = 0.0055$ proves that the deactivation is predominantly a radiationless process.

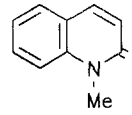
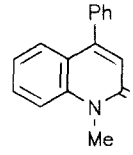
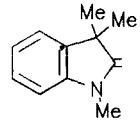
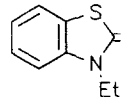
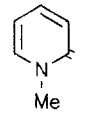
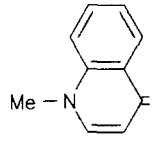
Heating of **10** with aniline in *o*-dichlorobenzene yielded the anilide (**15**) of 4-(3-ethyl-2(3*H*)-benzothiazolylidene)-2-butenoic acid besides acetone and carbon dioxide (Scheme 2).

Applying the same conditions (toluene, 2 h, 60–80 °C) as in the reaction of **1a** and **6a**, the 2-methylene-quinoline **1a** reacted completely differently with a mixture of triethyl orthoformate and Meldrum's acid (**16a**). In the 5-(1,2-dimethyl-4(1*H*)-quinolyliden)-2,2-dimethyl-1,3-dioxan-4,6-dione (**17**) the C_1-bridge originated by the orthoformate is missed. In a separate experiment without the orthoformate **17** was also formed.

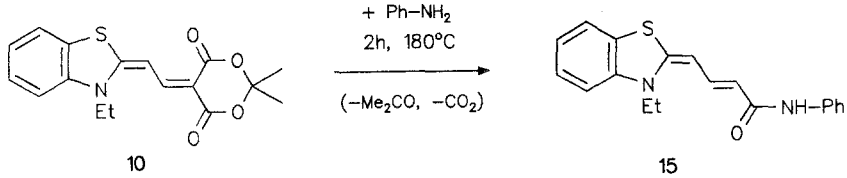
Obviously in the first step of the reaction **1a** is protonated by **16a**. The generated quinolinium cation is then attacked by the dioxandione anion in 4-position. In the same manner, **1a** is converted to **18**, **19**, **20** and **21** by treatment with N,N'-dimethylbarbituric acid (**16b**), 1,5,5-trimethyl-2,4-pyrrolidindione (**16c**), 5,5-dimethyl-2,3,4,5-tetrahydro-2,4-furandione (**16d**), and 1,3-indanedione (**16e**), respectively.

17–21 are not primary products of the reaction (Scheme 3). They result from the dehydrogenation of intermediates **A** by oxygen or by the quinolinium cation. Due to the extent of their π-systems the yellow-red crystalline **17–21** absorb at relatively long wavelengths.

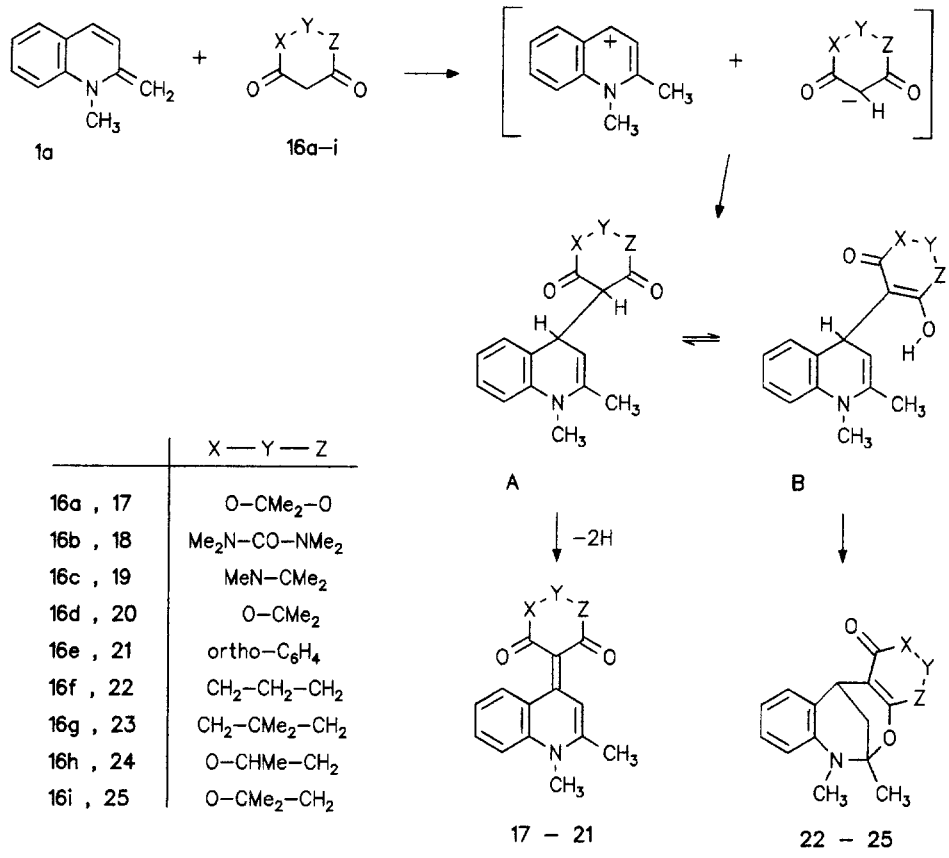


	Het	X	Y	Z
1a		–	–	–
7a		O	CMe_2	O
8		NMe	CO	NMe
1b		–	–	–
7b		O	CMe_2	O
2		–	–	–
9		O	CMe_2	O
3		–	–	–
10		O	CMe_2	O
11		CH_2	CMe_2	CH_2
4		–	–	–
12		O	CMe_2	O
5		–	–	–
13		O	CMe_2	O
14		NMe	CO	NMe

Scheme 1



Scheme 2



	X—Y—Z
16a , 17	O–CMe_2–O
16b , 18	Me_2N–CO–NMe_2
16c , 19	MeN–CMe_2
16d , 20	O–CMe_2
16e , 21	ortho–C_6H_4
16f , 22	CH_2–CH_2–CH_2
16g , 23	CH_2–CMe_2–CH_2
16h , 24	O–CHMe–CH_2
16i , 25	O–CMe_2–CH_2

Scheme 3

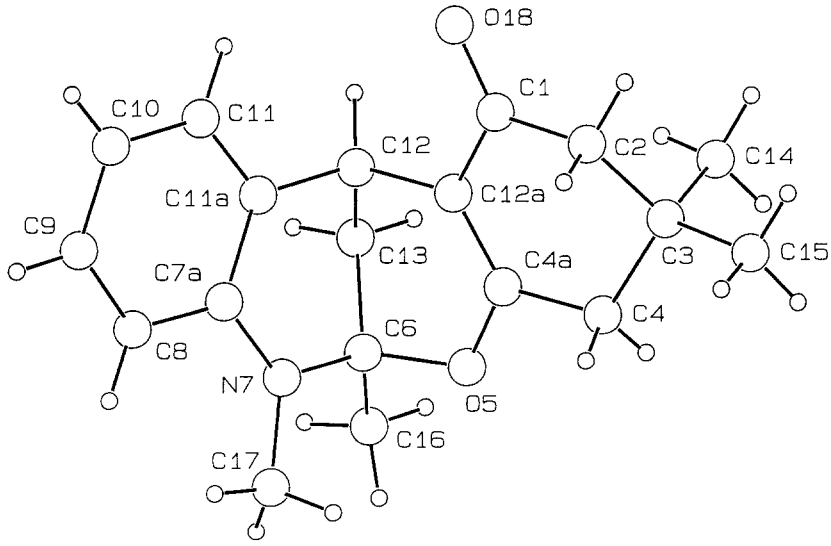
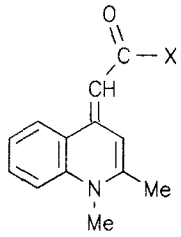


Fig. 1. X-ray structure of compound **23**



26: X = OH
27a: X = OMe
27b: X = OEt
28: X = NH–Ph

Scheme 4

Table 1. Analytical data of the reaction products

Cpd.	Yield (%)	m.p. (°C)	Elemental analysis			C	H	N	S
7a	92	265–266	$C_{18}H_{17}NO_4$	311.3	Calcd.	69.44	5.50	4.50	–
					Found	69.74	5.64	4.29	–
7b	34	270 (dec)	$C_{24}H_{21}NO_4$	387.4	Calcd.	74.40	5.46	3.62	–
					Found	74.05	5.47	4.11	–
9	98	232–235	$C_{19}H_{21}NO_4$	327.4	Calcd.	69.70	6.47	4.28	–
					Found	70.01	6.51	4.16	–
10	72	218–219	$C_{17}H_{17}NO_4S$	331.4	Calcd.	61.61	5.17	4.23	9.67
					Found	61.41	5.15	4.11	9.41
12	5	255–257 (dec)	$C_{14}H_{15}NO_4$	261.3	Calcd.	64.36	5.79	5.36	–
					Found	64.05	5.82	5.71	–
13	55	236–238 (dec)	$C_{18}H_{17}NO_4$	311.3	Calcd.	69.44	5.50	4.50	–
					Found	69.42	5.63	4.17	–
17	45	242 (dec)	$C_{17}H_{17}NO_4$	299.3	Calcd.	68.21	5.73	4.68	–
					Found	68.64	5.92	4.37	–
18	28	330 (dec)	$C_{17}H_{17}N_3O_3$	311.3	Calcd.	65.58	5.50	13.50	–
					Found	65.43	5.76	13.78	–
19	39	201–202	$C_{18}H_{20}N_2O_2 \cdot H_2O$	314.4	Calcd.	68.77	7.05	8.91	–
					Found	68.96	7.25	8.79	–
21	51	288 (dec)	$C_{20}H_{15}NO_2$	301.3	Calcd.	79.71	5.02	4.65	–
					Found	79.32	5.25	4.52	–
22	44	126 (dec)	$C_{17}H_{19}NO_2$	269.3	Calcd.	75.81	7.11	5.20	–
					Found	76.07	7.13	5.15	–
23	72	128 (dec)	$C_{19}H_{23}NO_2$	297.4	Calcd.	76.73	7.80	4.71	–
					Found	76.52	7.84	4.72	–
24	2	124–127	$C_{17}H_{19}NO_3$	285.3	Calcd.	71.56	6.71	4.91	–
					Found	71.69	6.83	4.92	–
25	26	121 (dec)	$C_{18}H_{21}NO_3$	299.4	Calcd.	72.22	7.07	4.68	–
					Found	72.60	7.05	4.68	–

Table 2. Spectral data of the reaction products

Cpd.	^{1}H NMR ($CDCl_3$)	IR (KBr) [cm^{-1}]	MS [m/z] (% rel. int.)
7a	1.71 (s, 6H, CMe_2), 3.95 (s, 3H, NMe), 7.45–7.80 (m, 7H, arom + CH), 8.50 (d, 1H, CH)	3000 1535 1665 1420 1625	311 (35) 208 (78)
7b	1.69 (s, 6H, CMe_2), 4.01 (s, 3H, NMe), 7.38–7.73 (m, 11H, arom + CH), 8.50 (d, 1H, CH)	2997 1530 1680 1370	387 (9) 284 (12)
9	1.71 (s, 6H, CMe_2), 1.73 (s, 6H, CMe_2), 3.53 (s, 3H, NMe), 7.09–7.41 (m, 4H, arom), 7.30 (d, 1H, CH; J = 14.4 Hz), 8,65 (d, 1H, CH; J = 14.4 Hz)	2990 1560 1698 1535	327 (52) 224 (49)
10	1.48 (t, 3H, CH_2CH_3; J = 7.3 Hz), 1.69 (s, 6H, CMe_2), 4.24 (q, 2H, CH_2CH_3; J = 7.3 Hz), 7.36–7.72 (m, 4H, arom), 7.42 (d, 1H, CH; J = 13.7 Hz), 8.29 (d, 1H, CH; J = 13.7 Hz)	2995 1560 1680 1540	331 (21) 230 (34)
12	1.69 (s, 6H, CMe_2), 3.87 (s, 3H, NMe), 6.77–8.39 (m, 6H, arom + CH)	2997 1640 1660 1530	261 (7) 158 (76)
13	1.72 (s, 6H, CMe_2), 3.94 (s, 3H, NMe), 7.19–8.55 (m, 8H, arom + CH)	2997 1466 1658 1433	311 (33) 209 (15)
17	1.85 (s, 6H, CMe_2), 2.74 (s, 3H, CMe), 4.03 (s, 3H, NMe), 7.30–8.29 (m, 5H, arom)	3080 1636 2993 1583 1686 1519	299 (2) 43 (100)
18	2.75 (s, 3H, CMe), 3.39 (s, 6H, NMe), 4.08 (s, 3H, NMe), 7.29–8.30 (m, 5H, arom)	3080 1615 2990 1510 1690 1460	311 (98) 310 (100)
19	1.34 (s, 6H, CMe_2), 1.82 (b, 2H, H_2O), 2.60 (s, 3H, CMe), 2.97 (s, 3H, NMe), 3.85 (s, 3H, NMe), 7.42–7.70 (m, 3H, arom), 8.39 (s, 1H, arom), 8.72 (d, 1H, –CH=)	3464 1639 3402 1600 3220 1568 2970 1552	296 (19) 281 (19) 197 (100)
20	1.51 (s, 6H, CMe_2), 2.73 (s, 3H, CMe), 4.03 (s, 3H, NMe), 7.57–8.74 (m, 4H, arom), 8.28 (s, 1H, –CH=)	3070 1624 2870 1598 1713 1581	283 (4) 268 (0.2) 197 (100)
21	2.72 (s, 3H, CMe), 3.99 (s, 3H, NMe), 7.38–8.75 (m, 9H, arom)	3080 1651 2926 1622 1707 1579	301 (100)
22	1.77 (s, 3H, CMe), 1.80 (s, 2H, CH_2), 1.93–1.98 (m, 2H, CH_2; AB), 2.19–2.33 (m, 4H, CH_2), 3.04 (s, 3H, NMe), 4.02 (m, 1H, CH; X), 6.57–7.37 (m, 4H, arom)	2946 1495 1644 1382	269 (17) 158 (100)
23	0.93 (s, 3H, CMe), 1.02 (s, 3H, CMe), 1.76 (s, 3H, CMe), 1.89–2.03 (m, 2H, CH_2; AB), 2.19 (d, 4H, CH_2), 3.03 (s, 3H, NMe), 4.02 (m, 1H, CH; X), 6.57–7.37 (m, 4H, arom)	2955 1500 1660 1395 1630	297 (10) 158 (100)
24	1.31/1.38 (dd, 3H, O–CMe), 1.78 (s, 3H, CMe), 1.97–2.09 (m, 2H, CH_2), 2.25–2.35 (m, 2H, CH_2), 3.05 (ss, 3H, NMe), 3.74–5.89 (m, 2H, 2CH), 6.60–7.45 (m, 4H, arom)	3000 1700 2900 1628	285 (10) 267 (10)
25	1.23 (s, 3H, CMe), 1.42 (s, 3H, CMe), 1.78 (s, 3H, CMe), 2.06 (d, 2H, CH_2), 2.39–2.42 (m, 2H, CH_2; AB), 3.04 (s, 3H, NMe), 3.89 (m, 1H, CH; X), 6.59–7.40 (m, 4H, arom)	2987 1691 2945 1644	299 (7) 43 (100)

Table 3. Atomic coordinates and isotropic equivalent temperature factors of **23** (**a** and **b**). $B_{eq.}$-values were calculated as (4/3) $[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\alpha)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

Atom	x/a	y/b	z/c	$B_{eq.}$ (A^2)
		23a		
O5	0.70621(8)	0.8299(4)	0.5656(2)	4.07(7)
O18	0.59489(9)	0.7833(4)	0.6820(2)	4.92(8)
N7	0.6725(1)	0.7968(5)	0.4551(2)	4.6(1)
C1	0.6274(1)	0.7571(5)	0.6776(2)	3.4(1)
C2	0.6470(1)	0.6620(5)	0.7298(2)	3.8(1)
C3	0.6873(1)	0.7017(5)	0.7459(2)	3.7(1)
C4	0.7061(1)	0.7085(5)	0.6744(3)	4.0(1)
C4a	0.6846(1)	0.7874(5)	0.6185(2)	3.23(9)
C6	0.6878(1)	0.8995(6)	0.5029(3)	4.1(1)
C7a	0.6351(1)	0.7661(5)	0.4508(2)	3.8(1)
C8	0.6199(2)	0.6849(6)	0.3951(3)	5.1(1)
C9	0.5831(2)	0.6535(6)	0.3931(3)	5.9(1)
C10	0.5606(2)	0.6994(6)	0.4446(3)	5.7(1)
C11	0.5755(1)	0.7801(5)	0.4999(3)	4.5(1)
C11a	0.6121(1)	0.8145(5)	0.5035(2)	3.43(9)
C12	0.6295(1)	0.9015(5)	0.5623(3)	3.6(1)
C12a	0.6485(1)	0.8134(5)	0.6196(2)	3.25(9)
C13	0.6583(1)	0.9920(5)	0.5298(3)	4.2(1)
C14	0.6897(2)	0.8424(6)	0.7834(3)	5.2(1)
C15	0.7056(2)	0.5931(6)	0.7946(3)	5.4(1)
C16	0.7186(2)	0.9817(7)	0.4716(3)	6.1(1)
C17	0.6971(2)	0.7087(8)	0.4171(3)	6.8(2)
		23b		
O5	0.54060(8)	0.2530(4)	0.5777(2)	3.89(7)
O18	0.6319(1)	0.3154(4)	0.4115(2)	5.45(9)
N7	0.5901(1)	0.2547(4)	0.6649(2)	3.76(8)
C1	0.6031(1)	0.2638(5)	0.4286(2)	3.7(1)
C2	0.5830(2)	0.1589(6)	0.3808(3)	4.4(1)
C3	0.5418(1)	0.1561(5)	0.3881(3)	4.0(1)
C4	0.5345(1)	0.1378(5)	0.4673(3)	3.9(1)
C4a	0.5564(1)	0.2348(5)	0.5143(2)	3.28(9)
C6	0.5614(1)	0.3377(5)	0.6320(2)	3.7(1)
C7a	0.6269(1)	0.2739(5)	0.6517(2)	3.33(9)
C8	0.6545(1)	0.2200(5)	0.6975(3)	4.3(1)
C9	0.6907(2)	0.2388(6)	0.6825(3)	5.4(1)
C10	0.7005(1)	0.3105(6)	0.6229(3)	5.4(1)
C11	0.6731(1)	0.3656(6)	0.5777(3)	4.5(1)
C11a	0.6365(1)	0.3481(5)	0.5910(2)	3.4(1)
C12	0.6057(1)	0.4065(5)	0.5443(2)	3.5(1)
C12a	0.5874(1)	0.2982(5)	0.4963(2)	3.15(9)
C13	0.5772(1)	0.4601(5)	0.5935(3)	3.9(1)
C14	0.5249(2)	0.0348(6)	0.3458(3)	5.8(1)
C15	0.5245(2)	0.2901(6)	0.3597(3)	5.8(1)
C16	0.5325(2)	0.3786(6)	0.6829(3)	5.3(1)
C17	0.5796(2)	0.1422(6)	0.7117(3)	4.8(1)

In contrast, colorless crystalline products **22**–**25** are obtained in the reaction of **1a** with 1,3-cyclohexanedione (**16f**), 5,5-dimethyl-1,3-cyclohexanedione (**16g**), 6-methyl-5,6-dihydro-2,4-pyrandione (**16h**), and 6,6-dimethyl-5,6-dihydro-2,4-pyrandione (**16i**), respectively. The mass spectra indicate that these products contain two additional hydrogen atoms compared with a structure according to **17**–**21**. It is remarkable that **22**–**25** are not dehydrogenated even by strong oxidants like tetrachloroquinone or potassium permanganate. (Comparable results were reported by Kröhnke et al. [6].) The ^{1}H-NMR spectra contain ABX systems. This excludes a structure like that of the dihydro intermediates **A**/**B** (Scheme 3).

Computer modelling showed that the enol-intermediates **B** may undergo an intramolecular transfer of the enol proton to the electron-rich C(3)-atom of the quinoline moiety. In the resulting betain the attack of the enolate oxygen on C(2) is electronically and sterically favored. Probably, these two reactions occur very rapidly in competition with the intermolecular reactions with oxidants. The result is the strainless structure of 6,12-methano-dibenz[d,g][1,3]-oxazocinones **22**–**25** (Scheme 3), proved by X-ray analysis (Fig. 1, Table 3). Previously, Svetlik et al. synthesized a similar compound with comparable ABX ^{1}H NMR data [7].

Among the compounds listed in Scheme 3 only **17** has the dioxandione moiety. Consequently, heating of **17** with hydrochloric acid gave 2-(1,2-dimethyl-4(1*H*)quinolylidene)acetic acid (**26**) in nearly quantitative yield (Scheme 4). With alcohols in the presence of catalytical amounts of hydrochloric acid **17** was converted of the esters of **26** (methyl ester **27a**, 62% yield; ethyl ester **27b**, 81% yield). Refluxing of **17** in aniline afforded the anilide **28** (38% yield).

Experimental Part

Melting points: Boetius Heiztisch-Mikroskop (Küster Nachf., Dresden), uncorrected values. IR spectra: Carl-Zeiss-Jena-Specord IR-71 and Perkin-Elmer 580-B. ^{1}H NMR spectra: Tesla BS 487-C and Bruker AM-300. MS spectra: Hewlett-Packart GCMS-5995-A.

General Procedure for the Synthesis of 2-[2-(Hetarylidene)ethyliden]-1,3-dicarbonyl Compounds **7**–**14**

a) Preparation of the Methylene Bases **1**–**5**

15 mmol of the onium salts prepared from 2-methyl-N-heterocycles and methyl iodide was dissolved in 40 ml of water. After addition of 40 ml of toluene a solution of 1 g potassium hydroxide in 20 ml of water was slowly added with intensive shaking until a precipitate had formed. The toluene phase became yellow, later red-brown. The phases were separated, and the toluene phase was dried with sodium sufate. This toluene solution must be immediately used for further reactions.

b) 2-[2-(Hetarylidene)ethyliden]-1,3-dicarbonyl Compounds **7**–**14**

The dried solution of the methylene base was added to solutions of 5-ethoxymethylene-2,2-dimethyl-1,3-dioxan-4,6-dione (**6a**: X-Y-Z = O–CMe_2–O), 5,5-dimethyl-2-ethoxymethylene-1,3-cyclohexanedione (**6b**: X-Y-Z = CH_2–CMe_2–CH_2), or 1,3-dimethyl-5-ethoxymethylene-2,4,6-pyrimidinetrione (**6c**: X-Y-Z = NMe–CO–NMe), respectively, in toluene. The mixtures were heated to 60 °C for 20 min. After standing for another 2 h at room temp. the precipitated crystals were collected by filtration and recrystallized from ethanol. (For analytical data see Tables 1 and 2.)

2-[2-(3-Ethyl-2(3H)benzothiazolylidene)ethylidene]-5,5-dimethyl-cyclohexane-1,3-dione (**11**)

According to the general procedure 5 g of 3-ethyl-2-methyl-benzothiazolium tosylate was converted to 1.8 g of 2,3-dihydro-3-ethyl-2-methylene-benzothiazole (**3**) (70% yield; m.p. 126–128 °C after recrystallization from petroleum ether 80/100). To a solution of this methylene base in toluene 6 ml of trimethyl orthoformate and 1.4 g dimedone (**16g**) were added. The mixture was then refluxed for 30 min. The solid product was recrystallized from ethanol to give 2.5 g (76%) of **11** (m.p. 211–213 °C). IR (KBr): ν = 2965, 2945, 2930, 2880 (CH), 1650 (C=O), 1600 (C=C) cm^{-1}. UV: Absorption maxima: ethanol 479 nm (lg 4.87), chloroform 487 nm (lg 4.86); fluorescence maxima: ethanol 494 nm, chloroform 503 nm. MS (70 eV): m/z(%) = 327 (11) [M^+], 312 (4) [M – 15], 149 (100).

5-[2-(1-Methyl-2(1H)pyridyliden)ethyliden]-2,2-dimethyl-1,3-dioxan-4,6-dione (**12**)

The methylene base is generated by treatment of 1.3 g (5.5 mmol) of 1,2-dimethyl-pyridinium iodide with conc. KOH. After addition of lg (5 mmol) of **6a** and standing for 2 weeks at room temp. 59 mg (5%) of **12** (m.p. 255–257 °C) was obtained. (For analytical data see Tables 1 and 2.) By the same method were prepared:

5-[2-(1-Methyl-2(1H)quinolyliden)ethyliden]-1,3-dimethyl-2,4,6(1H,3H,5H)-pyrimidintrione (**8**)

Yield 71%, orange-red crystals. Sublimation point 350 °C. IR (KBr): ν = 2955, 1698, 1632, 1615, 1549, 1439 cm^{-1}. ^{1}H NMR (*TFA/TMS*): δ = 8.75–9.90 (M, 8H, Ph), 5.45 (s, 3H, N–Me), 4.30 (s, 6H, N–Me). MS (70 eV): m/z(%) = 323 (35) [M^+], 308 (14) [M – 15].

5-[2-(1-Methyl-4(1H)quinolyliden)ethyliden]-1,3-dimethyl-2,4,6(1H,3H,5H)-pyrimidintrione (**14**)

Yield 34%, violet crystals. Sublimation point 350 °C. IR (KBr): ν = 2944, 1628, 1614, 1522, 1431 cm^{-1}. ^{1}H NMR (*TFA/TMS*): δ = 8.84–9.84 (m, 8H, Ph), 5.49 (s, 3H, N–Me), 4.27 (s, 6H, N–Me). MS (70 eV): m/z (%) = 323 (3) [M^+], 308 (10) [M – 15].

4-(3-Ethyl-2(3H)benzothiazolylidene)-2-butenanilide (**15**)

A solution of 0.4 g (1.2 mmol) of **10** and 0.5 g (5.4 mmol) of aniline in 10 ml of *o*-dichlorobenzene was refluxed for 3h. After workup of the reaction mixture the crude product was recrystallized from ethanol. Yield: 0.1 g (26%) of **15** as yellow crystals (m.p. 248–250 °C). IR (KBr): ν = 3260, 3238, 2995, 1642, 1610, 1598, 1560, 1532, 1503, 1492, 1473, 1460, 1442 cm^{-1}. ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 7.06–8.13 (m, 11H, Ph, NH, CH), 5.53–5.93 (m, 2H, CH), 3.89 (q, 2H, CH_2), 1.27 (t, 3H, Me). MS (70 eV): m/z (%) = 322 (14.3) [M^+], 230 (100) [M–PhNH], 202 (40.3) [230–28], 173 (52) [202–Et].

General Procedure for the Synthesis of 5-(1,2-Dimethyl-4(1H)quinolyliden)-1,3-dicarbonyl compounds **17**–**21** *and 6,12-Methano-dibenz[d,g][1,3]oxazocinones* **22**–**25**

According to the general procedure used for the preparation of methylene bases 15 mmol of 1,2-dimethylquinolinium iodide was converted to 1,2-dihydro-1-methyl-2-methylene-quinoline (**1a**). A solution of **1a** in toluene was added to a suspension of 14 mmol of the 1,3-dicarbonyl compound **16** in dry toluene. After shaking for 1 min and standing at 60–80 °C for 2h the formed oil crystallized. Recrystallization from ethanol or acetone gave the pure products. (For analytical data see Tables 1 and 2.)

2-(1,2-Dimethyl-4(1H)quinolyliden)-acetic acid (**26**)

1 g (33.4 mmol) of 5-(1,2-dimethyl-4(1*H*)quinolyliden)-2,2-dimethyl-1,3-dioxan-4,6-dione (**17**) was cooled to 0 °C. After addition of 25–30 drops of conc. HCl the resulting mixture was heated to 45 °C for

30–40 min without solvent until gas was no longer generated and the color of the mixture changed from yellow to gray. After trituration with acetone the solid product was dried on a porous plate. Yield: 0.71 g (99%) of **26**·HCl as colorless needles. Decarboxylation at 170–180 °C furnished a product with m.p. 278–280 °C. **26**·HCl also underwent decarboxylation in *DMSO* during recording of the ^{1}H NMR spectrum. IR (KBr): ν = 3020, 2913, 2840, 2546, 1707, 1613, 1424 cm^{-1}. MS (70 eV): m/z (%) = 171 (100) [M – 44], 156 (30) [171–15].

Reaction of **17** *with Alcohols (General Procedure)*

A solution of 0.2 g (0.67 mmol) of **17** in 5 ml of the alcohol was mixed with 3 drops of conc. HCl and refluxed for 1 h. After evaporation of the excess alcohol the residue was dissolved in water and the solution was mixed with ether. After addition of a saturated solution of sodium carbonate the solid ester **27** precipitated. Workup of the etheral phase afforded an additional amount of ester.

Methyl 2-(1,2-dimethyl-4(1H)quinolyliden)-acetate (**27a**)

Yield: 95 mg (62%), yellow crystals, m.p. 142–143 °C (dec.). IR (KBr): ν = 2930, 1670, 1557, 1530, 1500 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.17–8.0 (m, 5H, arom), 5.61 (s, 1H, CH), 3.70 (s, 3H, OMe), 3.55 (s, 3H, NMe), 2.36 (s, 3H, CMe). MS (70 eV): m/z (%) = 229 (45) [M^+], 198 (88) [M–OMe], 171 (100) [M – 44–14].

Ethyl 2-(1,2-dimethyl-4(1H)quinolyliden)-acetate (**27b**)

Yield: 132 mg (81%), yellow crystals, m.p. 116–117 °C (dec.). IR (KBr): ν = 2960, 1655, 1596, 1533, 1505 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.16–8.01 (m, 5H, arom), 5.60 (s, 1H, CH), 4.17 (s, 3H, OMe), 3.54 (s, 3H, NMe), 2.35 (s, 3H, CMe), 1.30 (t, 2H, Me). MS (70 eV): m/z (%) = 243 (15) [M^+], 198 (37) [M–Et], 171 (100) [M – 44–28].

2-(1,2-Dimethyl-4(1H)quinolyliden)-acetanilide (**28**)

A mixture of 330 mg (1.1 mmol) of **17**, 103 mg (1.1 mmol) of aniline and 4 drops of conc. HCl was heated to 60 °C until no longer gas was generated. The residue was dissolved in water and the solution was mixed with a saturated solution of sodium carbonate. The formed precipitate was separated and washed with water. Yield: 120 mg (38%) of **27**, yellow–brown crystals, m.p. 180–182 °C (dec.). IR (KBr): ν = 3298, 3050, 2910, 1640, 1598, 1535 cm^{-1}. ^{1}H NMR (*DMSO-d$_6$/TMS*): δ = 9.34 (s, 1H, NH), 6.68–7.97 (m, 10H, arom), 5.82 (s, 1H, CH), 3.52 (s, 3H, NMe), 2.33 (s, 3H, CMe). MS (70 eV): m/z (%) = 290 (5) [M^+], 198 (92) [M–PhNH], 171 (43) [M–PhNCO].

X-Ray Crystal Structure Determination of **23**

In the crystal are two undependent molecules A and B with slight difference in the conformation. Colorless transparent crystal (1.400 × 0.300 × 0.150); monoclinic, space group C2/c (no. 15); a = 36.517 (6), b = 9.654 (3), c = 18.752 (4) Å, β = 92.66(2)°; V = 6603.6 Å^3; Z = 16; D_{cal} = 1.196 gcm^{-3}; μ(MoK$_\alpha$) = 0.718 cm^{-1}; F(000) = 2560; Enraf-Nonius CAD-4 diffractometer; graphite monochromator; Mo-K$_\alpha$; T = 293 K; 2θ-Ω scan; 5155 reflections were measured up to $2\theta_{max}$ = 48°, with 3932 independent observed with $I > 1\sigma(I)$; number of variables 398; no correction of absorption; solution of the structure by direct methods and anisotropic refinement of all non-hydrogen atoms by full matrix least-squares calculations; all hydrogen atoms calculated; R = 0.072, R_W = 0.080. All calculations were made with the Enraf-Nonius SDP-program system. (Additional details to the structure determination can be ordered from Fachinformationszentrum Karlsruhe Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, referring to the deposition no. CDS-57849, the names of the authors and citation of the paper.)

Acknowledgements

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged. We are also very grateful to Dozent Dr. J. Bendig for recording and interpreting of some absorption and fluorescence spectra.

References

[1] Henning H.-G., Stemplinger G., Rothe K. (1992) Liebigs Ann. Chem.: 813
[2] (a) Claisen L., Haase E. (1903) Ber. Dtsch. Chem. Ges. **36**: 3674; (b) v.E. Doering W., McEwen W. E. (1951) J. Am. Chem. Soc. **73**: 2104; (c) Kröhnke F., Ellegast K., Bertram E. (1956) Liebigs Ann. Chem. **600**: 176
[3] Kröhnke F., Vogt I. (1956) Liebigs Ann. Chem. **600**: 211
[4] Bihlmayer G. A., Derflinger G., Derkosch J., Polansky O. E. (1967) Monatsh. Chem. **98**: 564
[5] Clark-Lewis J. W., Thompson M. J. (1959) J. Chem. Soc.: 2401
[6] (a) Kröhnke F., Honig H. L. (1959) Liebigs Ann. Chem. **624**: 97; (b) Ahlbrecht H., Kröhnke F. (1968) Liebigs Ann. Chem. **717**: 96
[7] Svetlik J., Turacek F., Hanus V. (1988) J. Chem. Soc. Perkin Trans. 1: 2053

Received March 18, 1993. Accepted April 1, 1993

Verleger: Springer-Verlag KG, Sachsenplatz 4–6, A-1201 Wien. – Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, A-1010 Wien, und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. – Redaktion: Währinger Straße 38, A-1090 Wien. – Satz und Umbruch: Thomson Press Ltd., New Delhi, India. – Reproduktion und Offsetdruck: Eugen Ketterl Gesellschaft m.b.H., Schopenhauerstraße 45, A-1180 Wien. – Verlagsort: Wien. – Herstellungsort: Wien. – Printed in Austria.

Offenlegung gem. § 25 Abs. 1 bis 3 Mediengesetz: Unternehmensgegenstand: Verlag von wissenschaftlichen Büchern und Zeitschriften. An der Springer-Verlag KG ist beteiligt: Dr. Konrad F. Springer, Sachsenplatz 4–6, A-1201 Wien, als Kommanditist zu 52,38%. Geschäftsführer: Dr. Konrad F. Springer, Prof. Dr. Dietrich Götze, Ing. Wolfram F. Joos, Dipl.-Kfm Claus Michaletz und Rudolf Siegle, alle Sachsenplatz 4–6, A-1201 Wien.