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SYNTHESIS OF TETRA- AND OCTAHYDROXANTHENE DERIVATIVES BY THE CONDENSATION OF DIMEDONE WITH AROMATIC ALDEHYDES

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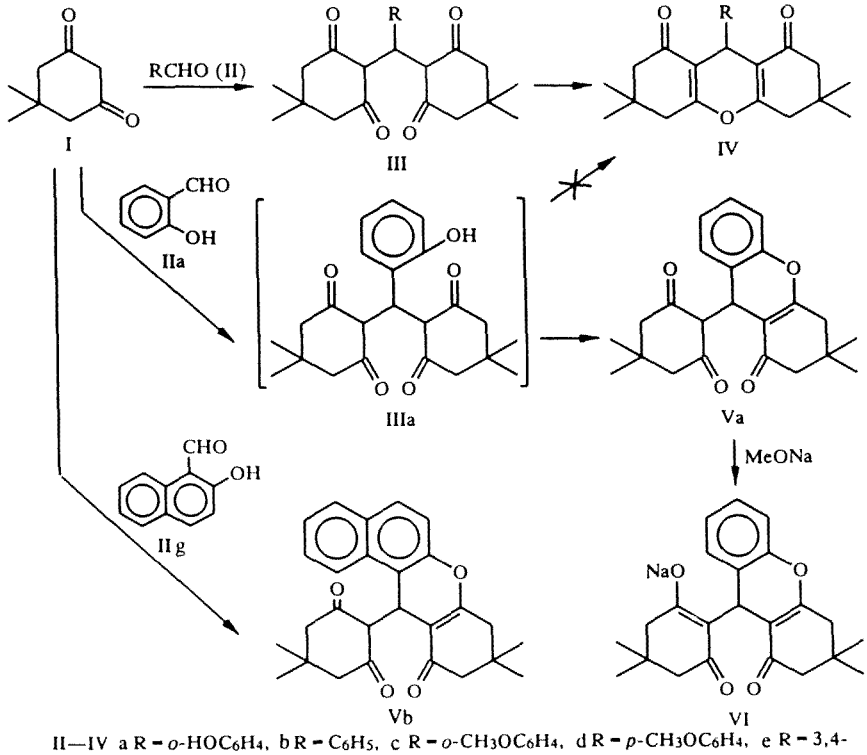
The reaction of dimedone with salicyl and 2-hydroxy-1-naphthoyl aldehydes gave derivatives of tetrahydroxanthene and tetrahydrobenzo[a]xanthene and not aldimedone as occurs in condensations with other aldehydes. Derivatives of decahydroacridine were obtained by reaction of the tetrahydroxanthene derivatives with methyl- and ethylamine. Tetrahydro- and octahydroxanthene derivatives were obtained from the reaction of acetylsalicylaldehyde with dimedone in acetic anhydride. The structures of the ketoenol forms of the products containing a β-ketoenol unit were determined by ^1H and ^{13}C NMR spectroscopy, and the mechanism of their interconversion is discussed.

The condensation of dimedone I with aldehydes II is often used for the identification of aldehydes [1, 2]. One molecule of aldehyde reacts with two molecules of dimedone with the elimination of water to give the tetraketone III (aldimedone). Cyclization to aldimedone anhydride IV requires a special dehydrating medium (H_2SO_4, P_2O_5) [3]. Two routes for water elimination are possible for the condensation product (IIIa) of dimedone with salicylaldehyde (IIa) (Scheme 1). Product IVa is formed by the general reaction for other aldehydes, whereas the tetracycle Va is formed by reaction of the phenolic hydroxyl group to give a pyran ring.

Scheme 1



II—IV a R = *o*-HOC_6H_4, b R = C_6H_5, c R = *o*-$CH_3OC_6H_4$, d R = *p*-$CH_3OC_6H_4$, e R = 3,4-$(CH_3)_2C_6H_3$, f R = *p*-HOC_6H_4, g R = 2-$HOC_{10}H_6$

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Scheme 2

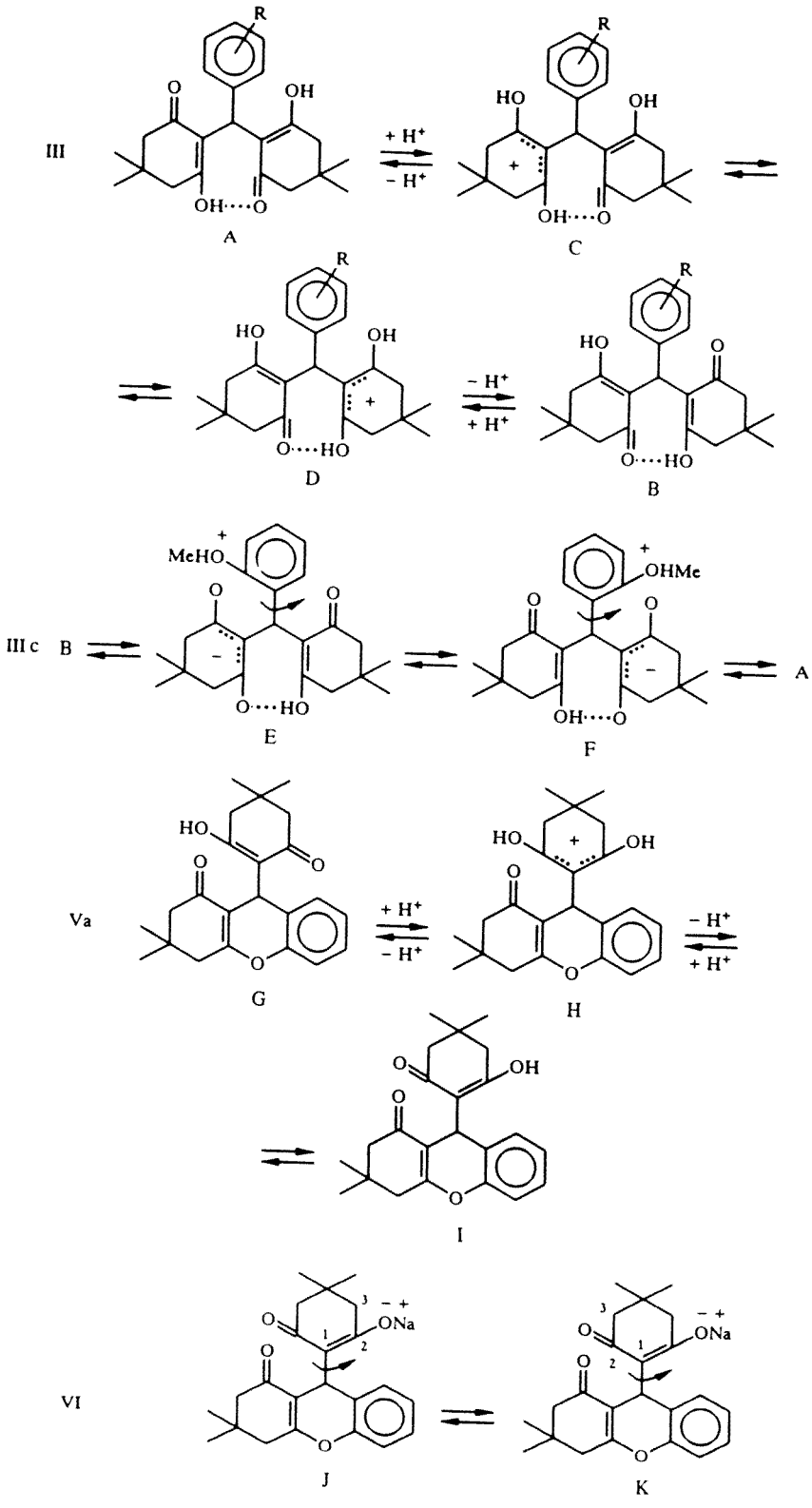


TABLE 1. Characteristics of Compounds IIIb-f, IVb-f, Va and b, VI, IX, XI, and XIIa and b

Compound	Molecular formula	(Found, %) / (Calculated, %)		mp, °C (ethyl acetate) mp, °C	$[M^+]$	IR spectra, ν, cm^{-1}	UV Spectra, λ_{max}, nm (lg ε)	Yield, %
		C	H					
1	2	3	4	5	6	7	8	9
IIIb	$C_{23}H_{28}O_4$	74,88 74,97	7,51 7,66	195...197	368	1375, 1600, 2890, 2975	260 (4,26)	83
IIIc	$C_{24}H_{30}O_5$	72,15 72,33	7,48 7,59	187...188	398	1250, 1380, 1605, 2880, 2965	222 (3,96), 260 (4,19)	87
IIId	$C_{24}H_{30}O_5$	72,18 72,33	7,45 7,59	141...142	398	1250, 1375, 1600, 2880, 2940	228 (4,09), 260 (4,20)	86
IIIe	$C_{25}H_{32}O_6$	69,91 70,07	7,44 7,53	174...175	428	1242, 1258, 1380, 1600, 2960, 2970	233 (4,0), 260 (4,20)	84
IIIf	$C_{23}H_{28}O_5$	71,79 71,85	7,26 7,34	159...160	384	1235, 1265, 1380, 1515, 1600, 2870, 2960, 3280	227 (4,17), 260 (4,34)	81
IVb	$C_{23}H_{26}O_3$	78,79 78,82	7,39 7,48	208...209	350	1202, 1363, 1668, 1680	233 (4,27), 297 (3,78)	80
IVc	$C_{24}H_{28}O_4$	75,71 75,76	7,38 7,42	184...186	380	1203, 1258, 1362, 1602, 1670, 1675	220 (4,15), 235 (4,12), 297 (3,74)	79
IVd	$C_{24}H_{28}O_4$	75,68 75,76	7,37 7,42	244...246	380	1198, 1260, 1360, 1608, 1665, 1670	226 (4,31), 289 (3,78)	83
IVe	$C_{25}H_{30}O_5$	73,07 73,14	7,34 7,37	177...178	410	1198, 1260, 1360, 1608, 1665	230 (4,34), 292 (3,83)	78
IVf	$C_{23}H_{26}O_4$	75,32 75,38	7,12 7,15	247...249	366	1203, 1370, 1622, 1655, 1678, 3250	226 (4,29), 291 (3,77)	84

TABLE 1. (Continued)

Compound	Molecular formula	(Found, %) / (Calculated, %) C	H	mp, °C (ethyl acetate)	$[M']$	IR spectra, ν, cm^{-1}	UV Spectra, λ_{max}, nm (lg ε)	Yield, %
1	2	3	4	5	6	7	8	9
Va	$C_{23}H_{26}O_4$	75.30 75,38	7.31 7,15	206...208	366	1240, 1380, 1585, 1600, 1620, 1645, 3200	224 (4,06), 275 (4,05)	93
Vb	$C_{27}H_{28}O_4$	77.69 77,86	6.71 6,78	234...236	416	1235, 1380, 1600, 1620, 1640, 3200	227 (4,69), 272 (4,34) 279 (4,38), 312 (3,69)	85
VI	$C_{23}H_{25}NaO_4$	70.93 71,12	6.82 6,95	294...298 разл.	–	1240, 1387, 1490, 1582, 1635	224 (4,00), 277 (4,02)	98
IX	$C_{25}H_{28}O_5$	73.46 73,51	6.81 6,91	146...148	408	1208, 1360, 1620, 1660, 1750	231 (4,32), 290 (3,75)	37
X	$C_{25}H_{28}O_5$	73.63 73,51	7.01 6,91	196...197	408	1232, 1380, 1645, 1670, 1765	219 (4,02), 249 (3,84), 288 (3,67)	32
XIIa*	$C_{24}H_{29}NO_3$	75.87 75,96	7.57 7,70	228...229	379	1235, 1373, 1482, 1600, 1640, 3260	225 (4,02), 385 (3,72)	78
XIIb*	$C_{25}H_{31}NO_3$	76.24 76,30	7.82 7,94	209...210	393	1230, 1378, 1600, 1630, 1650, 2960	257 (4,22), 390 (3,93)	76

*Elemental analysis data for nitrogen for compounds XIIa 3.81, 3.69 and XIIb 3.69, 3.56 respectively.

TABLE 2. ^{1}H NMR Spectra of Compounds IIIb-f, IVb-f, Va and b, VI, IX, X, and XIIa and b

Compound	Solvent (conc., moles·liter^{-1})	Chemical shift, δ, ppm (from TMS)				
		gem-$(CH_3)_2$, s	$^4CH_2$	benzyl CH, s, 1H	aromatic CH	other protons
1	2	3	4	5	6	7
IIIb	$CDCl_3$ (0,15)	1,12, 6H; 1,24, 6H	2,30...2,50, m 8H	5,54	7,04...7,34, m 5H	11,92, br.s.1H, enol-OH
	$CDCl_3/CF_3CO_2H$ (0,14)	1,16, 12H	2,44, s, 8H	5,60	7,00...7,40, m 5H	
IIIc	$CDCl_3$ (0,20)	1,08, 12H	2,33, s, 8H	5,60	6,20, m 2H; 6,78, d, 1H, J = 8,0 Hz; 6,88, t, 1H, J = 8,0 Hz;	3,72, s, 3H, OMe; 11,92, br.s, 1H, enol-OH
IIId	$CDCl_3$ (0,20)	1,08, 6H; 1,22, 6H	2,20...2,60, m 8H	5,48	6,78, d, 2H, J = 8,0 Hz; 7,00, d, 2H, J = 8,0 Hz	3,76, s, 3H, OMe; 11,92, br.s,. 1H, enol-OH
	$CDCl_3/CF_3CO_2H$ (0,19)	1,13, 12H	2,46, s, 8H	5,54	6,80, d, 2H, J = 8,0 Hz; 7,00, d, 2H, J = 8,0 Hz	3,80, s, 3H, OMe
IIIe	$CDCl_3$ (0,20)	1,14, 6H; 1,26, 6H	2,38, s, 4H; 2,46, s, 4H	5,54	6,60, m 2H; 6,76, d, 1H, J = 8,0 Hz	3,76, s, 3H, OMe; 3,81, s, 12,01, br.s, enol-OH
	$CDCl_3/CF_3CO_2H$ (0,19)	1,18, 12H	2,46, s, 8H	5,56	6,60, m 2H; 6,82, d, 1H, J = 8,0 Hz;	3,78, s, 3H, OMe; 3,88, s, 3H, OMe
IIIf	$CDCl_3$ (0,20)	1,08, 6H; 1,22, 6H	2,25...2,55, m 8H	5,49	6,65, d, 2H, J = 8,0 Hz; 6,92, d, 2H, J = 8,0 Hz;	11,92, br.s, 1H, enol-OH
	$CDCl_3/CF_3CO_2H$ (0,19)	1,14, 12H	2,42, s, 8H	5,60	6,62, d, 2H, J = 8,0 Hz; 6,94, d, 2H, J = 8,0 Hz	
IVb	$CDCl_3$ (0,15)	0,96, 6H; 1,08, 6H	AB, 4H, δ_A-2,11, δ_B-2,29, J_{AB} = 16,0 Hz; 2,48, s, 4H	4,76	7,03...7,36, m 5H	
IVc	$CDCl_3$ (0,15)	0,96, 6H; 1,08, 6H	AB, 4H, δ_A-2,21, δ_B-2,13, J_{AB} = 16,0 Hz; AB, 4H, δ_A-2,38, δ_B-2,46, J_{AB} = 18 Hz;	4,85'	6,75, d, 1H; 6,87, t, 1H; 7,10, t, 1H; 7,41, d, 1H; $J_1 = J_2 = J_3 = J_4$ = 8,0 Hz	3,80, s, 3H, OMe
IVd	$CDCl_3$ (0,15)	0,98, 6H; 1,10, 6H	AB, 4H, δ_A-2,23, δ_B-2,17, J_{AB} = 16,0 Hz; 2,47, s, 4H	4,.71	6,75, d, 2H; 7,21, d, 2H, $J_1 = J_2$ = 8,0 Hz;	3,74, s, 3H, OMe

TABLE 2. (Continued)

Compound	Solvent (conc., moles·liter^{-1})	Chemical shift, δ, ppm (from TMS)				
		gem-$(CH_3)_2$, s	$^4CH_2$	benzyl CH, s, 1H	aromatic CH	other protons
1	2	3	4	5	6	7
IVe	$CDCl_3$ (0,15)	1,01, 6H; 1,10, 6H	2,22, s, 4H; 2,48, s, 4H	4,71	6,76, m 2H; 6,93, s, 1H	3,81, s, 3H, OMe; 3,86, s, 3H, OMe
IVf	$CDCl_3$ (0,15)	1,01, 6H; 1,10, 6H	2,20, s, 4H; 2,45, s, 4H	4,68	6,56, d, 2H; 7,08, d, 2H, $J_1 = J_2 = 8,0$ Hz	
Va	$CDCl_3$ (0,13)	1,00, 6H; 1,04, 3H; 1,11, 3H	1,96, s, 2H; 2,32, s, 2H; 2,36, s, 2H; AB, 2H, δ_A-2,48, δ_B-2,58, $J_{AB} = 17,0$ Hz	4,70	6,95...7,20, m 4H	10,50, br.s, 1H, enol-OH
Vb	$CDCl_3$ (0,15)	0,70, 3H; 0,94, 3H; 1,06, 3H; 1,15, 3H	AB, 2H, δ_A-1,83, δ_B-1,95, $J_{AB} = 17,0$ Hz; 2,38, s, 4H; AB, 2H, δ_A-2,56, δ_B-2,66, $J_{AB} = 17,0$ Hz	5,25	7,20...7,50, m 3H; 7,60...7,90, m 3H	10,66, br.s, 1H, enol-OH
VI	CD_3OD (0,20)	0,96, 6H; 1,08, 6H	2,08, br.s, 4H; 2,23, s, 2H; AB, 2H, δ_A-2,41, δ_B-2,51, $J_{AB} = 17,0$ Hz	5,15	6,70...7,20, m 4H	
IX	$CDCl_3$ (0,15)	0,99, 6H; 1,08, 6H	2,17, s, 4H; 2,43, s, 4H	4,98	6,96...7,34, m 4H	2,39, s, 3H, COMe
X	$CDCl_3$ (0,15)	1,01, 6H; 1,08, 3H; 1,10, 3H	2,12, s, 2H; 2,32, s, 2H; 2,38, s, 2H; 2,48, s, 2H	5,21	6,90...7,20, m 4H	2,25, s, 3H, COMe
XIIa	$CDCl_3$ (0,15)	1,06, 6H; 1,10, 6H	2,24, s, 4H; AB, 4H, δ_A-2,34, δ_B-2,57, $J_{AB} = 17,0$ Hz	5,22	6,65...7,10, m 4H	9,50, br.s, 1H, OH
XIIb	$CDCl_3$ (0,15)	1,02, 6H; 1,10, 6H	2,26, s, 4H; AB, 4H, δ_A-2,37, δ_B-2,65, $J_{AB} = 17,0$ Hz;	5,18	6,65...7,10, m 4H	1,36, t, 3H; 3,83, q 2H, $J_1 = J_2 = 7,0$ Hz; 9,47, br.s, OH

The condensation of two molecules of dimedone with one molecule of salicylaldehyde with elimination of two molecules of water to give a product with the structure IVa has been reported [4]. However there are references to analogous condensations of salicylaldehyde with other cyclic β-dicarbonyl compounds, in particular 4-oxo-coumarin [5] and 5,6-dihydro-6-methyl-4-oxo-2-pyrone [6], the products of which were ascribed structures corresponding to the alternative cyclization with the phenolic hydroxyl group. The difference in the direction of cyclization reported in the literature led to reinvestigation of the reaction of dimedone with salicyl- and other aromatic aldehydes.

When the reaction was carried out by heating in isopropanol in the presence of piperidine, dilute hydrochloric acid, or without a catalyst, condensation of two molecules of dimedone with one molecule of salicylaldehyde occurred with the elimination of two molecules of water to give a product with the same physicochemical characteristics as those reported previously [4]. The condensation products of dimedone with benzaldehyde and its derivatives were prepared for comparison. However, unlike salicylaldehyde, the condensation reaction occurred with the elimination of just one molecule of water. Spectroscopic data corresponded to the tricyclic structures (IIIb-f) (Table 1). The NMR spectra of the tetraketones IIIb-f, in $CDCl_3$ solution (Tables 2 and 3), corresponded to the completely enolized structures A and B (Scheme 2).

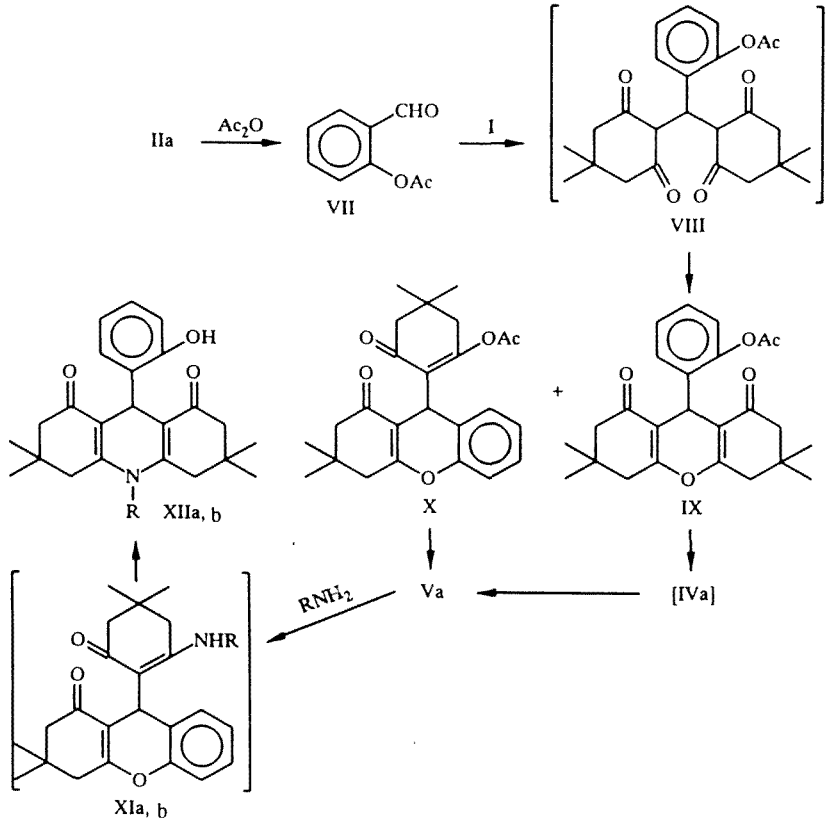
In particular, in the ^1H NMR spectra of compounds IIIb and IIId-f there are two singlet methyl and multiplet methylene signals which indicate the presence of a plane of symmetry in these structures, which includes the plane of the aromatic ring, the benzyl carbon and hydrogen atoms. This conclusion is confirmed by the ^{13}C NMR spectrum of compound IIId in which the signals of the dimedone fragments coincide. The ^1H NMR spectra of compounds IIIb-f contain a signal for an intramolecularly hydrogen bonded enol hydroxyl group, the chemical shift of which (11.92 ppm) is identical for four of them (IIIb-d, f) and only slightly different (12.01 ppm) for the fifth (IIIe). Addition of a few drops of trifluoroacetic acid to the $CDCl_3$ solutions of the tricycles IIIb, IIId-f caused splitting of the methyl and methylene signals into two singlets (Table 2), which indicates acid catalyzed keto-enol tautomerization of the type A ⇄ C ⇄ D ⇄ B via the intermediate formation of the enol cations C and D (Scheme 2) [7]. Evidently the intramolecular process C ⇄ D occurs sufficiently fast that it is fixed on the NMR time scale [8] and the rate-determining step is addition of the proton. Forms A and B are fixed in the spectrum in the absence of acid, but addition of acid leads to an averaged spectrum of all forms in the dynamic equilibrium system. Interestingly the ^1H NMR spectrum of the tricycle IIIc in $CDCl_3$ in the absence of trifluoroacetic acid shows coincidence of the signals of the four methyl and four methylene groups and its ^{13}C NMR spectrum shows coincidence of the four carbonyl groups. This is explained by the catalytic effect of the methoxy substituents, which facilitates intramolecular transfer of the enol to the oxygen of another carbonyl group via formation of the intermediate oxonium ions E and F (Scheme 2). The IR spectra of the tricycles IIIb-f contain very intense ketoenol absorption bands at 1375-1380 (C=C) and 1600-1605 (C=C, C=O) cm^{-1} and an intense UV maximum at 260 nm.

Comparison of the spectroscopic data and the melting points of compounds IIIb-f with the analogous literature data [4, 9] shows that the structure IV previously assigned to the products of the condensation of benzoic aldehydes with dimedone is incorrect. We obtained compounds IVc-f by heating the tricycles IIIb-f in toluene in the presence of *p*-toluenesulfonic acid (Table 1). As expected, the ^1H NMR spectra of compounds IVb-f and the ^{13}C NMR spectra of compounds IVc-e (Tables 2 and 3) show coincidence of the equivalent groups because of the presence of a plane of symmetry which includes the aromatic ring, the benzyl carbon and hydrogen atoms, and the cyclic oxygen atom. A characteristic difference between the ^1H NMR spectra of compounds IVb-f and those of their predecessors, IIIb-f, is the large shift (~ 0.8 ppm) to high field of the signal of the benzyl proton. The IR spectra of compounds IVb-f contain intense absorptions at 1198-1203 (*gem*-CH_3), 1360-1370 (C=C) and 1660-1670 (C=O) cm^{-1}. The UV spectra of these compounds contain two absorption maxima: the more intense at 226-237 nm (lgε 4.12-4.34) and the less intense at 284-292 nm (lg ε 3.74-3.83). As for the condensation product of salicylaldehyde with dimedone, it must be assigned the nonsymmetrical structure Va rather than IVa. The ^1H NMR spectrum of this compound in $CDCl_3$ has three singlets for the four methyl groups and four distinct signals for the methylene groups, two of which are broad singlets (1.96 and 2.36 ppm, Table 2), the widths of which are increased by the addition of a few drops of trifluoroacetic acid. Such a change in the spectrum is explained by the tautomeric interconversion G ⇄ H ⇄ I (Scheme 2) and the broad singlets are the signals of the methylene groups of the dimedone fragment. In the ^1H NMR spectrum of the sodium enolate VI (recorded in CD_3OD solution) prepared by treatment of the ketoenol Va with sodium methoxide, two methylene singlets merge into a broad singlet (2.08 ppm, Table 2) which indicates a greater rate of tautomeric interconversion. This process apparently includes rotation of the fully ionized form of the enolate anion about the single bond between the two rings (J ⇄ K). The observed spectrum is the result of averaging the signals of the two forms in consequence of their identical concentrations. The same conclusion is reached from an analysis of the ^{13}C NMR spectra of compounds Va and VI (Table 3). The $CDCl_3$ solution spectrum of the tetracycle Va (0.12 mole $liter^{-1}$) contains, apart from two methylene (41.56 and 49.95

ppm) and two methyl (27.19 and 27.78 ppm) hydroxanthene units, four broad signals of the methylene (43.21 and 50.61 ppm) and methyl (26.48 and 29.64 ppm) carbons of the dimedone fragment. The signals of the two carbonyl groups are not observed because of their considerable broadening and a seven-fold increase in concentration led to the extinction of the four previously mentioned broad signals. This confirms that autocatalytic tautomeric processes are occurring in solution.

In the ^{13}C NMR spectrum of the sodium enolate VI in CD_3OD solution the broad carbon signals of the dimedone fragment merge pairwise: 2′ and 6′ (192.00 ppm), 3′ and 4′ (51.12 ppm) and the *gem*-$(CH_3)_2$ (28.92 ppm). This agrees with the conclusions drawn from the ^1H NMR spectrum on the speed of the dynamic processes in the salt in comparison with the enol form. The reaction of dimedone with β-oxo-α-naphthoylaldehyde (IIg) is analogous to that with salicylaldehyde. The product is the pentacyclic compound Vb, the structure of which is confirmed from elemental analysis and spectroscopic data. The ^1H NMR spectrum contains signals of four methyl groups (0.70, 0.94, 1.06 and 1.15 ppm) which indicates the absence of symmetry elements in this molecule. In order to extend these conclusions to the acetyl analog, the condensation of acetylsalicylaldehyde VII with dimedone was studied. The reaction was carried out as follows. Salicylaldehyde was mixed with acetic anhydride in the presence of triethylamine and after a day two equivalents of dimedone were added and the mixture was heated. After normal workup of the reaction mixture two products were isolated which were assigned structures IX and X (Scheme 3) on the basis of elemental and spectroscopic analysis.

Scheme 3



XI, XII a R = CH_3, b R = C_2H_5

The reaction evidently proceeds by acylation of the hydroxyaldehyde IIa, condensation of the aldehyde VII with dimedone to give the tricyclic product, dehydration of which gave the symmetric compound IX, while transacylation and dehydration led to the nonsymmetric compound X. The ^1H NMR spectrum of compound X contains three singlets for the four methyl groups (1.01, 1.08, and 1.10 ppm) and four discrete signals for the four methylene groups (2.12, 2.32, 2.38, and 2.48 ppm). The spectrum of the symmetrical isomer IX has two signals for the methyl groups (0.96 and 1.08 ppm) and the methylene groups (2.17 and 2.43 ppm). Similarly the ^{13}C NMR spectra show a smaller number of carbon signals for the symmetrical isomer IX than for the nonsymmetrical compound X.

TABLE 3. ^{13}C NMR Spectra of Compounds IIIc and d, IVc-e, Va, VI, IX, X, and XIIa

Compound	Solvent (conc., moles·liter^{-1})	Chemical shift, δ, ppm (from TMS)							
		CH_3, CH-9	$C(CH_3)_2$	CH_2	OCH_3	aromatic CH	aromatic C	aromatic C–O	C-C, C-O
IIIc	$CDCl_3$ (0,15)	28,16, 29,17	31,17	46,68	55,21	110,07, 119,93, 127,42, 128,45	126,80	157,07	116,41, 189,15
IIId	$CDCl_3$ (0,15)	27,39, 29,63, 32,06	31,39	46,48, 47,09	55,17	113,66, 127,80	129,86	157,63	115,81, 189,32, 190,33
IVc	$CDCl_3$ (0,5)	26,48, 29,42, 29,54	31,95	40,73, 50,60	54,96	110,49, 120,07, 127,63, 132,00	130,25	157,49	113,36, 163,03, 196,51
IVd	$CDCl_3$ (0,5)	27,05, 29,46, 31,02	32,44	40,96, 51,12	55,13	115,78, 129,46	136,54	158,11	113,57, 162,18, 196,69
IVe	$CDCl_3$ (0,5)	27,19, 29,32, 31,22	32,12	40,62, 50,73	55,69, 55,79	110,86, 112,35, 120,08	135,05	147,44, 148,41	115,69, 162,17
Va	$CDCl_3$ (0,13)	26,48, 27,19, 27,78, 29,17, 29,64	30,97, 32,29	41,56, 43,21, 49,95, 50,61		115,72, 124,57, 127,45, 128,03	124,34	151,04	111,07, 118,32, 169,10, 200,65
VI	CD_3OD (0,5)	27,12, 27,88, 28,92, 29,34	32,58, 32,83	42,29, 51,12, 51,91		115,97, 124,58, 126,78, 129,83	129,12	151,69	113,87, 118,30, 167,76, 192,00, 200,36
IX	$CDCl_3$ (0,5)	22,02, 28,08, 29,35, 27,59	32,59	41,32, 51,02		123,38, 125,83, 127,74, 131,42	135,09	148,81	115,09, 162,84, 169,84, 196,76
X	$CDCl_3$ (0,5)	20,68, 26,24, 27,58, 27,87, 27,95, 28,80	32,01, 32,63	41,52, 42,55, 50,62		115,70, 124,77, 127,67, 129,09	123,32	149,26	110,88, 163,57, 164,80, 167,08, 196,69, 197,23
XIIa	$CDCl_3$ (0,5)	25,53, 28,41, 28,70, 33,82	32,66	40,47, 49,52		117,96, 120,04, 127,18, 127,67	132,15	153,18	114,57, 153,57, 196,75

Hydrolysis of compounds IX and X in both acidic and basic conditions gave the tetracycle Va. The diketoalcohol IVa formed by hydrolysis of the ester IX is evidently unstable and readily isomerizes to the diketoenol Va.

The reaction of compound Va with primary amines in acetic acid gave the decahydroacridine derivatives XIIa and b, apparently via the intermediate formation of the enaminoketones XIa and b. The structures of compounds XIIa and b were confirmed by elemental and spectroscopic analysis. In particular the UV spectra of these compounds contain long wavelength absorption maxima (384 and 390 nm) which are characteristic of 3,5-diacyl-1,4-dihydropyridine systems [10].

EXPERIMENTAL

The syntheses and purity of the products were monitored by TLC on Silufol UV-254 strips with 1:2 ethyl acetate–hexane as eluant and detection with UV light or iodine vapor. Melting points were determined with a Boetius block. IR spectra of KBr discs were recorded with a UR-20 spectrometer. UV spectra of ethanol solutions were recorded with a Specord M-400 spectrometer. Mass spectra were recorded with a Varian MAT-311 with direct insertion of the sample and an ionizing energy of 70 eV. ^1H and ^{13}C NMR spectra were obtained with a Bruker AC-200 spectrometer operating at 200 and 50 MHz respectively. The ^{13}C spectra were recorded with proton decoupling.

Characteristics of the compounds synthesized are given in Tables 1 to 3.

9-(2′-Hydroxy-4,4′-dimethyl-6′-oxo-1′cyclohexen-1-yl)-3,3-dimethyl-1,2,3,4-tetrahydro-9H-xanthen-1-one (Va). A. A mixture of dimedone (2.80 g, 20 mmol), salicylaldehyde (1.22 g, 10 mmol) and a few drops of piperidine in isopropanol (10 cm^3) was boiled for 20 min. The precipitate was filtered off after 20 h and washed with ethyl acetate (10 cm^3) to give compound Va (3.41 g). The tetraketones IIIb-f (Table 1) and 12-(2-hydroxy-4,4-dimethyl-6-oxo-1-cyclohexen-1-yl)-9,9-dimethyl-8,9,10,11-tetrahydro-12H-benzo[*a*]xanthen-11-one (Vb) were prepared analogously.

B. A mixture of dimedone (2.80 g, 20 mmol), salicylaldehyde (1.22 g, 10 mmol) and a few drops of 10% hydrochloric acid in isopropanol (15 cm^3) was boiled for 20 min, left for a day, and the precipitate filtered off and washed with ethyl acetate (10 cm^3) to give Va (3.20 g, 87%).

3,3,6,6-Tetramethyl-9-phenyl-1,2,3,4,5,6,7,8-octahydro-9H-xanthen-1,8-dione (IVb). Tetraketone IIIa (250 mg) and *p*-toluenesulfonic acid (3 mg) were boiled in toluene (20 cm^3) for 2 h. The toluene was evaporated and the residue recrystallized from ethyl acetate to give compound IVb (190 mg).

Compounds IVc to IVf were prepared analogously.

Sodium Salt of 9-(2′-Hydroxy-4′,4′-dimethyl-6′-oxo-1′-cyclohexen-1-yl)-3,3-dimethyl-1,2,3,4-tetrahydro-9H-xanthen-1-one (VI). Metallic sodium (0.23 g, 10 mmol) was dissolved in absolute methanol (50 cm^3) and the ketoenol Va (3.66 g, 10 mmol) was then added. After the solid had dissolved the methanol was evaporated in vacuum, the residue was washed with dry ether (30 cm^3) and dried in a vacuum desiccator for one day to give the sodium enolate VI (3.80 g).

9-(2′-Acetoxyphenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydro-9H-xanthen-1,8-dione (IX) and 9-(2′-Acetoxy-4′,4′-dimethyl-6′-oxo-1′-cyclohexen-1′-yl)-3,3-dimethyl-1,2,3,4-tetrahydro-9H-xanthen-1-one (X). A solution of salicylaldehyde (0.6 cm^3, 5 mmol) and triethylamine (3 cm^3) in acetic anhydride (20 cm^3) was maintained at room temperature for 1 day. Dimedone (1.4 g, 10 mmol) was then added and the mixture boiled for 20 min. The mixture was cooled, evaporated to half volume, diluted with water (100 cm^3), neutralized to pH ~6 with KOH, extracted with chloroform and dried over Na_2SO_4. The chloroform was evaporated and the residue recrystallized from 1:2 ethyl acetate–hexane to give compound X (0.45 g, 22%). Separation of the remaining mixture on a silica gel (100/400) column with ethyl acetate–hexane (1:10) as eluant gave compound IX (0.75 g, 37%) and compound X (0.21 g, 10%).

Hydrolysis of Acetate IX. A. Acetate IX (100 mg) was dissolved in methanol (5 cm^3) and sodium carbonate (30 mg, 2 equiv) in water (5 cm^3) was added. The mixture was stirred for 20 h at room temperature, the methanol was removed in vacuum, water (10 cm^3) was added, the mixture was washed with ether (10 cm^3) and neutralized with 5% HCl. The precipitated crystals were filtered off, washed with water and dried in the air to give xanthenone Va (88 mg, 90%).

B. Acetate IX (100 mg) was dissolved in methanol (5 cm^3), water (5 cm^3) and conc. HCl (0.2 cm^3) were added and the mixture was boiled for 3 h. The solvents were removed in vacuum, the residue was dried in a vacuum desiccator over alkali and crystallized from ethyl acetate to give compound Va (72 mg, 72%).

Acetate X was hydrolyzed analogously.

9-(2′-Hydroxyphenyl)-3,3,6,6,10-pentamethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-1,8-dione (XIIa). A mixture of compound Va (3.66 g, 10 mmol), methylammonium chloride (0.657 g, 10 mmol) and fused sodium acetate (0.82 g,

10 mmol) in glacial acetic acid (20 cm^3) was boiled for 1 h. The mixture was cooled, sodium chloride was filtered off, acetic acid evaporated and the residue crystallized from ethyl acetate to give compound XIIa (2.96 g).

9-(2′-Hydroxyphenyl)-3,3,6,6-tetramethyl-10-ethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (XIIb) was prepared similarly.

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