SYNTHESIS OF POLYNUCLEAR HETEROCYCLIC QUINONE IMINES — DERIVATIVES OF 4a,9-DIAZAHYDROFLUOREN-6-ONES

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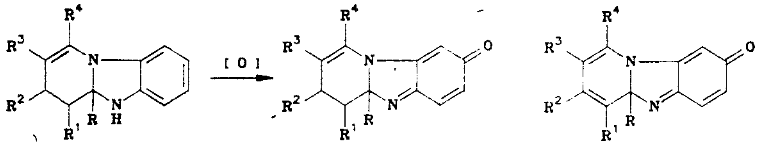
When derivatives of 4a-9-diaza-1,2,4a,9a-tetrahydrofluorene are oxidized by treatment with MnO_2, the corresponding derivatives of 4a,9-diaza-1,2,4a,9a-tetrahydrofluoren-6-one are obtained. In a number of cases the reaction is accompanied by dehydrogenation of the side chains as well as the diazahydrofluorene fragment.

Derivatives of 4a,9-diaza-1,2,4a,9a-tetrahydrofluorene are readily formed by the reaction of a wide range of 1,5-diketones with o-phenylenediamine [1-3] and exhibit pronounced antioxidant properties [4]. In this connection a study of their oxidative changes is of interest. It is also related to the possibility of synthesizing polycyclic compounds containing conjugated enamine and quinoid structures, such compounds having received little study.

Compounds Ia-g were used as starting materials; compound Ib, which had not previously been reported, we obtained from 1,3,5-triphenylpentane-1,5-dione and o-phenylenediamine. We have established that compound I is readily oxidized by manganese dioxide in benzene, ether, or methylene chloride to give polycyclic quinone imines. The yields of the products are at preparative levels in most cases, and in several instances are almost quantitative. Examples are known where MnO_2 has been used to synthesize quinoid compounds by oxidation of hydroquinones [5], p-toluidine [6], and benzimidazolines to 2H-benzimidazoles [7]. The preparation of quinone monimines from secondary amines using the present method has not been reported.



Ia-g IIa-k IIIa-c

I, II a $R=R^4=C_6H_5$, $R^1=R^2=R^3=H$; b $R=R^2=R^4=C_6H_5$, $R^1=R^3=H$; c $R+R^1=(CH_2)_4$, $R^2=R^4=C_6H_5$, $R^3=H$; d $R+R^1=R^3+R^4=(CH_2)_4$, $R^2=H$; e $R+R^1=R^3+R^4=(CH_2)_4$, $R^2==C_6H_5$; f $R+R^1=(CH_2)_4$, $R^2=C_6H_5$, $R^4+R^3=$1′,2′-(3′,4′dihydronaphtho); g $R+R^1==R^4+R^3=$1′,2′-(3′,4′dihydronaphtho), $=H$; II h $R+R^1=(CH_2)_4$, $R^2=H$, $R^3+R^4=$ benzo i $R+R^1=(CH_2)_4$, $R^2=C_6H_5$, $R^3+R^4=$ benzo; j $R+R^1=(CH_2)_4$, $R^2=C_5H_5$, $R^4+R^3==$1′,2′naphtho; k $R+R^1=$1′,2′-(3′,4′dihydronaphtho), $^2=H$, $R^4+R^3=$1′,2′naphtho; II a $R+R^1=(CH_2)_4$, $R^2=H$, $R^3+R^4=$ benzo; b $R+R^1=R^4+R^3=$1′,2′-(3′,4′dihydronaphtho), $R^2=H$; c $R+R^1=$1′,2′-(3′,4′dihydronaphtho), $=R^2=H$, $R^4+R^3=$1′,2′-naphtho

The rates and results of oxidation depend on the form of MnO_2 used. Oxidation occurs the most rapidly when y-MnO_2 (A), prepared according to [8], is used. The reaction proceeds much more slowly when form (B), prepared according to [5], and unactivated dioxide (C) are used. When forms B and C are used, oxidation occurs only at the 6-position and the corresponding derivatives of 4a,9-diaza-1,2,4a,9a-tetrahydrofluoren-6-one are formed — enaminoquinone imines IIa-g. When form A is used, oxidation of compounds Ia-c also gives only the corresponding enaminoquinone imines IIa-c; however, when compounds Id,e and particularly If,g are oxidized, aromatization products of condensed (R^3 + R^4) cyclohexene (Id, e) and dihydronaphthalene (If,g) fragments — compounds IIh-k — are formed together with enaminoquinone imines IId-g. When the temperature of oxidation is increased dehydrogenation products predominate, with products from the dehydrogenation of the diazatetrahydrofluorene structure — 4a,9-diaza-4a,9a-dihydrofluoren-6-one derivatives (IIIa-c) — also being formed under these conditions. In particular, oxidation of compound Ie at 20°C gives mainly compound IIe, while at 80°C the dehydrogenation prod-

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uct IIi is formed. Compound If at 20°C forms a mixture of quinone imines IIf and IIj (1:10), while at 80°C only aromatization product IIj is formed. Oxidation of compound Ig using γ-MnO_2 proceeds with very little selectivity; mixtures of compounds IIg, k (3:2) and IIIb, c (4:1) were isolated with low yields.

According to our data, the best results for the preparation of enaminoquinone imines IIa-c are obtained with form A, for preparation of compounds IIe-g form B gives the best results, and for preparation of compound IId form C gives the best results.

Formation of quinone imines IIa-g has been identified when compounds Ia-g are oxidized by PbO_2 in benzene, $KMnO_4$ in acetone, an alkaline solution of $K_3Fe(CN)_6$, and atmospheric oxygen in the presence of Fe^{2+} ions. However, these reactions proceed considerably less selectively than oxidation using MnO_2; complex and difficult to separate product mixtures are formed together with compounds II.

The electronic spectra of all compounds II as well as IIIa (Table 1) contain three maxima appearing in the regions 210-230 nm, 260-285 nm, and in the visible region at 460-495 nm, which is characteristic of quinoid [9] and, in particular, quinone imine [10, 11] structures. A hypsochromic shift of the absorption in the visible region is recorded when the enamine fragment is replaced by an aromatic fragment (IId-IIh, IIe-IIi, IIf-IIj); on changing from IIh to IIIa this band undergoes a bathochromic shift. The slight hypsochromic shift of the absorption band in the visible region for compounds IIa,c relative to compounds IIf,g is probably due to the distinct lack of coplanarity of the benzene ring (R^4) with the enamine C=C bond in compounds IIa,c.

In the IR spectra of compounds II and III (Table 1) there are four absorption bands from the quinoid fragment in the region 1550-1645 cm^{-1}, while for enaminoquinone imines IIa-g there is also an absorption band from the enamine C=C bond with approximately the same frequency as for the initial compounds I [1, 2]. In the spectrum of compounds IIh-j and III this band is absent.

The PMR spectral data of compounds II and III (Table 2) are fully consistent with the proposed structures. For the nonquinoid part of these compounds there are distinctive signals from the 2-H protons, that is, "benzyl" protons for the 2-phenyl-substituted compounds IIb, c, e, f, i, j or vinyl protons for compounds IIIa-c. A considerable downfield shift of the signal from the 2-H proton is recorded when changing from IIe to IIi and from IIf to IIj, which is confirmation of aromatization of the condensed structures in compounds IIi, j. This aromatization is also confirmed by the appearance of signals from aromatic protons when changing from IId to IIh and IIIa, and also by the pattern of signals typical of naphthalene derivatives in the region 7.4-8.0 ppm in the spectra of compounds IIj, k and IIIc. In the spectra of compounds IIa-c the signals from the 3-H vinyl protons are also distinctive. The nature of the signals from the 5-H, 7-H, and 8-H quinoid protons and also the chemical shifts of the 7-H and 8-H protons are fully consistent with the results for quinone monimines [12]. The signal from the 5-H proton in the spectra of compounds IIa-c, f, g, j, k and IIIb, c is shifted upfield relative to the values for quinoid compounds [9a, 12]. This is due to the shielding effect of the aromatic ring attached to the 4-position (R^4). A similar shielding effect was recorded previously for compounds Ia, c, f, g [2, 3]; it also occurs for compound Ib obtained by us, in which the signal from the 5-H proton (d, J = 7 Hz) occurs at 5.82 ppm. In the spectra of compounds IIa-c this upfield shift is more significant than in the spectra of compounds IIf, g, j, k; this is probably due to the lack of coplanarity as mentioned above of the shielding R^4 ring with the enamine structure in compounds IIa-c. Inspection of models shows that in this case the 5-H proton falls within the cone of the shielding ring to a greater extent than in compounds IIf, g, j, k, where the shielding ring and the enamine C=C bond must be coplanar because of the rigidity of the structure. In the spectra of compounds IId, e, h, i and IIIa, which do not have a shielding aromatic ring, the signal from the 5-H proton does not display an upfield shift. Aromatization of the side rings causes a slight downfield shift of the signal from the 5-H proton relative to the spectra of the corresponding enaminoquinone imines (IId-IIh, IIIa, IIe-IIi, IIf-IIj, IIg-IIk, IIIc); this is probably due to the disappearance of the donor enamine group.

In the ^{13}C NMR spectra (Table 3), recorded using off-resonance, the position of the signals from the quinoid carbon atoms is generally characteristic of quinoid compounds containing donor substituents [9b]. The occurrence of the $C_{(5)}$ signal at high field is worthy of note. For quinoid compounds with donor groups, the signal from the C atom at a position ortho to the donor group can occur in the region 105-110 ppm [13]. In the polycyclic compounds II there is a shift of the signal to even higher field.

TABLE 1. Electronic and IR Spectra of Quinone Imines Synthesized

Compound	Electronic spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}			
		C=O	C=N	$C=C_{quinoid}$	$C=C_{enamine}$
II a	231 (4,23), 260 (4,08), 460 (3,57)	1634	1612	1590, 1558	1648
II b	232 (4,24), 272 (4,08), 457 (3,60)	1640	1618	1596, 1562	1645
II c	232 (4,62), 272 (4,51), 468 (4,10)	1638	1610	1590, 1550	1653
II d	241 (4,11), 282 (3,62), 493 (3,61)	1638	1606	1582, 1550	1672
II e	247 (4,50), 284 (4,05), 489 (4,07)	1634	1608	1584, 1550	1664
II f	225 (4,51), 270 (4,37), 473 (3,90)	1636	1608	1588, 1550	1646
II g	232 (4,40), 267 (4,32), 476 (3,82)	1634	1610	1590, 1554	1650
II h	215 (4,47), 258 (4,51), 468 (4,07)	1644	1606	1580, 1556	—
II i	213 (4,52), 258 (4,41), 468 (3,91)	1644	1614	1586, 1554	—
II j	226 (4,54), 275 (3,95), 464 (3,68)	1642	1608	1588, 1556	—
III a	240 (4,23), 284 (4,02), 476 (3,30)	1644	1608	1588, 1559	—

TABLE 2. PMR Spectra of Quinone Imines Synthesized

Compound	Chemical shifts, ppm (spin-spin coupling constant, Hz)					
	2-H	3-H	5-H, d	7-H, d.d	8-H, d	Ar—H, m
II a		5,57 d.d (5; 3)	4,85 (2)	6,57 (10; 2)	7,19 (10)	7,36—7,70
II b	3,46 q. d (12; 6; 3)	5,60 d (3)	4,94 (2)	6,58 (10; 2)		7,18—7,74
II c	3,86 d. d (10; 3,5)	5,50 (3,5)	4,76 (2)	6,60 (10; 2)		7,18—7,40
II d			5,74 (2)	6,63 (10; 2)	7,14 (14)	
II e	3,35 d (10)		5,83 (2)	6,68 (10; 2)		7,05—7,34
II f	3,58 d (10)		5,25 (2)	6,68 (10; 2)		7,05—7,36
II g			5,30 (2)	6,64 (10; 2)		7,05—7,30
II h	3,25 d,d (−18; 12); 2,93 d.d (−18; 6)		6,13 (2)	6,72 (10; 2)	7,16 (10)	7,23—7,40
II i	4,35 d (10)		6,18 (2)	6,74 (10; 2)		6,88—7,43
II j	4,34 d (10)		5,38 (2)	6,73 (10; 2)	7,00 (10)	7,10—7,85
II k			5,38 (2)	6,69 (10; 2)		7,10—7,91
III a	6,16 s		6,08 (2)	6,68 (10; 2)		7,10—7,30
III b	5,75 s		5,42 (2)	6,59 (10; 2)		7,13—7,72
III c	6,32 s		5,45 (2)	6,64 (10; 2)		7,15—8,00

TABLE 3. ^{13}C NMR Spectra of Quinone Imines II

Compound	Chemical shifts, ppm						
	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8a)}$	$C_{(9a)}$
II b	119,0	142,8	100,1	182,7	138,6	159,4	98,6
II c	118,4	142,5	98,7	186,0	138,6	159,5	96,6
II d	120,5	128,5	95,5	185,9	138,8	159,5	96,7
II e	123,7	128,6	95,7	186,0	138,8	159,7	96,2
II f	123,9	143,7	98,1	185,7	138,9	159,5	96,6
II i	—*	—*	94,5	186,9	138,8	159,5	96,4

*Overlapping with signals from aromatic carbon atoms.

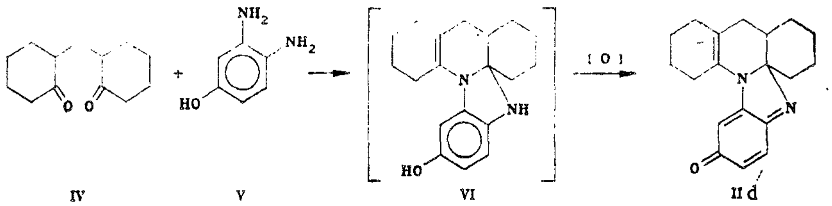
According to the mass spectral data, the values of the molecular ions of all the quinone imines synthesized correspond to the calculated molecular weights. The molecular ion peaks have the greatest intensity. In all the mass spectra there are peaks with m/z of M — 28 and M — 29, which are characteristic of the mass spectra of quinoid compounds. In the mass spectra of compounds IIc-f, h, j and IIIa there are quite intense peaks from $[M - C_4H_9]^+$ ions, which results from the separation of a side-chain tetramethylene fragment ($R + R^1$).

Using compound IId as a model we attempted to synthesize an enaminoquinone imine from the corresponding 1,5-diketone (IV) and 3,4-diaminophenol (V). We have improved the existing method [14] for the synthesis of the latter (as its hydrochloride) from 3-nitro-4-aminophenol. (Formula, following page, below Table.)

Reaction of diketone IV and diamine V gives a complex mixture of products, evidently as a result of the lack of selectivity of the reaction and the very ready oxidizability of the products being formed. From the mixture was isolated in low yield product IId, which is formed when the unstable initial product VI is oxidized.

TABLE 4. Conditions of Synthesis and Yields of Quinone Imines II and III

Synthesized compound	Compound being oxidized	Quantity of compound, g	Quantity of MnO_2, g	Type of MnO_2	Solvent	T, °C	Reaction time, h	Yield of oxidation product, %
IIa	Ia	0,25	2,15	A	Benzene	20	2	97
IIb	Ib	1,0	6,6	A	Benzene	20	2	93
IIc	Ic	1,0	2,6	A	Benzene	20	1	95
IId	Id	0,5	7,4	C	Ether	20	4	67
IIe	Ie	0,5	2,5	B	Benzene	20	0,5	96
IIf	If	0,55	1,7	B	Benzene	20	3	98
IIg	Ig	0,5	2,5	B	Benzene	20	5	93
IIh IIIa	Id	0,2	2,5	A	CH_2Cl_2	40	5	29 (IIh), 15 (IIIa)
IIi	Ie	0,2	1,5	A	Benzene	80	4	82
IIj	If	0,25	0,87	A	Benzene	80	2	99
IIg+IIk IIIb+IIIc	Ig	0,2	1,85	A	CH_2Cl_2	40	4	6 (IIg), 4 (IIk), 24 (IIIb), 6 (IIIc)



EXPERIMENTAL

Electronic spectra were recorded on a Hitachi-220A instrument; IR spectra were recorded on a Specord IR-75 instrument in chloroform; NMR spectra were recorded on Bruker HX-90E and Bruker WM-250 instruments in deuterochloroform, with TMS as internal standard. Mass spectra were obtained on an LKB-9000 instrument with ionizing voltage 70 eV and using direct introduction of samples. The course of the reactions and the purity of the products obtained were monitored by TLC on Silufol plates.

2,4,9a-Triphenyl-4a,9-diaza-1,2,4a,9a-tetrahydrofluorene (Ib). A solution of 65.6 g (0.2 mole) of 1,3,5-triphenylpentane-1,5-dione, 24 g (0.22 mole) of o-phenylenediamine, and 0.5 g of p-toluenesulfonic acid in 600 ml of xylene was boiled with a Dean-Stark column for 4 h until the evolution of water had ceased, and was then cooled. After 12 h the precipitate that had formed was filtered off and washed with xylene and ethanol. The solvent was evaporated from the residue at reduced pressure, 100 ml of ethanol was added to the residue, and after 12 h a crystalline product was filtered off and washed with ethanol. The two fractions of compound Ib were identical; yield 75%. Compounds Id, e were obtained according to [1], compounds Ia, c, f, g were obtained according to [2].

Oxidation of 4a,9-Diaza-1,2,4a,9a-tetrahydrofluorene Derivatives. The reaction conditions are given in Table 4. To obtain compounds IIa-c, e-g, j, MnO_2 was rapidly added to an agitated solution of the appropriate compound I. In the remaining cases, to an agitated suspension of MnO_2 in the solvent used was added dropwise a solution of compound I in the same solvent. The mixture obtained was agitated until the TLC spot due to the initial compound had disappeared; the MnO_2 was filtered off (after cooling if necessary), the mixture was washed with chloroform until the washing liquid showed no more coloration, and the solvent was evaporated. In the preparation of compounds IIa-c, e-g, i, j the residue proved to be an almost pure end product. In the remaining cases the residue was chromatographed on silica gel SL 40/100 plates (350 × 250 mm) for isolation of compound IId and silica gel SL 5/40 for isolation of compounds IIh, IIIa, and mixtures IIg + IIk and IIIb + IIIc; the eluant was a hexane–ethyl acetate mixture (1:1). The ratios of the components in the mixtures isolated were determined from the PMR spectral data (ratio of intensities of signals from 5-H and 6-H protons, and for the mixture of IIIb + IIIc the signal intensity from the 2-H proton was also used).

TABLE 5. Properties of Compounds Synthesized

Compound	mp, °C*	Found, %			Empirical formula	Calculated, %		
		C	H	N		C	H	N
I b	204—206	86,7	6,0	7,1	$C_{29}H_{24}N_2$	87,0	6,0	7,0
II a	76—78	81,4	5,5	8,3	$C_{23}H_{18}N_2O$	81,7	5,3	8,3
II b	206—207	84,3	5,4	6,7	$C_{29}H_{22}N_2O$	84,0	5,3	6,8
II c	229—231	82,6	6,5	7,0	$C_{24}H_{24}N_2O$	82,6	6,1	7,1
II d	169—170	77,3	7,9	9,8	$C_{19}H_{22}N_2O$	77,6	7,5	9,5
II e	205—206	81,2	7,0	7,8	$C_{25}H_{26}N_2O$	81,1	7,0	7,6
II f	260—261	83,4	6,4	7,2	$C_{29}H_{26}N_2O$	83,3	6,2	7,2
II g	244—245	83,0	6,0	7,2	$C_{27}H_{22}N_2O$	83,1	5,6	7,5
II h	172—174	78,9	6,0	9,8	$C_{19}H_{18}N_2O$	78,6	6,2	9,7
II i	249—250	82,0	6,2	7,8	$C_{25}H_{22}N_2O$	82,0	6,0	7,7
II a	256—258	83,6	6,2	6,7	$C_{29}H_{24}N_2O$	83,7	5,8	6,7
III j	129—131	79,0	5,5	9,9	$C_{19}H_{16}N_2O$	79,2	5,6	9,7

*Compounds were recrystallized as follows: Ib) from an ethanol—DMF mixture; IIa, b, e, h, j) from a hexane—benzene mixture; IIc, d, f, g, i) from a hexane—acetone mixture. Compound IIIa was not recrystallized.

All the quinone imines obtained were crystalline products (prismatic crystals) of a red or orange color, readily soluble in chloroform, fairly soluble in benzene, ethanol, and acetone, and very sparingly soluble (except for IId and IIIa) in hexane. Their properties are given in Table 5.

3,4-Diaminophenol Hydrochloride. Concentrated HCl (150 ml) was added to 10 g (65 mmole) of 3-nitro-4-aminophenol, the mixture was heated to boiling, 23 g (83 mmole) of tin was added in the form of small fragments, and a small length of platinum gauze was placed in the mixture. After 2 h the evolution of hydrogen had ceased, and 3,4-diaminophenol hydrochloride (V•HCl) was filtered off. Yield was 12 g (81%) of almost pure product.

Reaction of 2,2'-Methylenedicyclohexanone with 3,4-Diaminophenol. To a solution of 0.8 g (3.8 mmole) of diketone IV and 0.5 g (2.5 mmole) of V•HCl in 10 ml of ethanol with argon bubbled through was added 0.3 g (4 mmole) of diethylamine. The mixture was kept for 3 h at room temperature in an atmosphere of argon, then air was passed through for 2 h, the mixture was diluted with 20 ml of water, and extracted with hexane (5 × 15 ml). Hexane was evaporated from the residue, which was chromatographed on silica gel SL 40/100 in the system hexane–ethyl acetate (1:1.2). Compound IId was isolated (37 mg, 5%) and identified from its melting point and IR spectrum in a mixed sample with a known specimen.

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THIONATION OF IMIDAZOPYRIDINES

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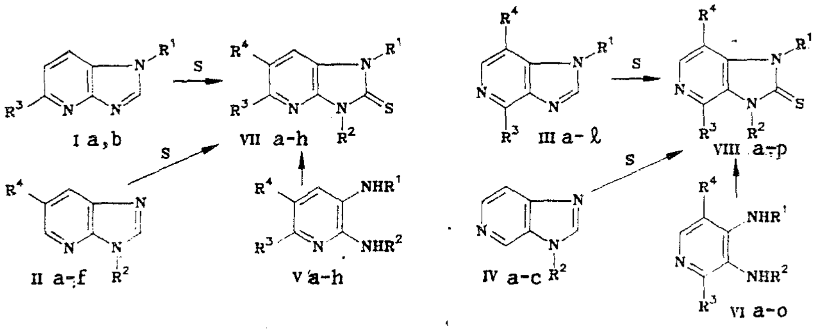
Direct thionation of imidazo[4,5-b]pyridines and imidazo[4,5-c]pyridines results in the formation of their 2-thioxo derivatives, usually in high yield. The thione structure of the imidazopyridines obtained has been confirmed from their IR spectra in the solid state and in solution. The general nature of the thionation of imidazole, benzimidazole, imidazo[4,5-b]pyridine, imidazo[4,5-c]pyridine, and purine has been noted as one of the distinctive chemical properties of compounds in this series of nitrogen heterocycles.

Imidazole when heated with sulfur is converted to its 2-mercapto derivative in "very good" yield [1]. Benzimidazole and its substituted derivatives [2, 3] and also purine [3] react with sulfur in a similar manner. Thionation of desazapurines such as imidazo[4,5-b]pyridine (IIa) and imidazo[4,5-c]pyridine (IIIa), which in structural terms are intermediate betweeen benzimidazole and purine, has not previously been studied.

We have shown [4] that when equivalent amounts of imidazopyridines I-IV are melted with sulfur, 1,3-dihydro-2H-imidazopyridine-2-thiones VII and VIII (Table 1) are formed, usually with high yields. Using the information in [5, 6] the same compounds were obtained from diamines V and VI and potassium ethylxanthate (method A) or carbon disulfide (method B) in the presence of pyridine (Table 2). Samples of compounds VIIa-h and VIIIa-n obtained by the two routes were found to be identical from the absence of any depression in the melting point of a mixed specimen and from their IR spectra. Other possible reaction products such as imidazo[4,5-c]pyridine-4-thiones are probably not formed, at least not to any noticeable extent.



I a $R^1=CH_3$, $R^3=H$; b $R^1=CH_3$, $R^3=NO_2$; II a $R^2=R^4=H$; b $R^2=CH_3$, $R^4=H$; c $R^2=CH_2C_6H_5$, $R^4=H$; d $R^2=C_6H_5$, $R^4=H$; e $R^2=H$, $R^4=Cl$; f $R^2=H$, $R^4=Br$; III a $R^1=R^3=R^4=H$; b $R^1=CH_3$, $R^3=R^4=H$; c $R^1=i\text{-}C_3H_7$, $R^3=R^4=H$; d $R^1=C_4H_9$, $R^3=R^4=H$; e $R^1=C_6H_{11}$, $R^3=R^4=H$; f $R^1=CH_2C_6H_5$, $R^3=R^4=H$; g $R^1=C_6H_5$, $R^3=R^4=H$; h $R^1=R^4=H$; $R^3=Cl$; i $R^1=R^3=H$, $R^4=Br$; j $R^1=R^3=H$, $R^4=NO_2$; k $R^1=CH_3$, $R^4=H$, $R^3=Cl$; ℓ $R^1=CH_3$, $R^3=OCH_3$, $R^4=H$; IV a $R^2=CH_3$; b $R^2=CH_2C_6H_5$; c $R^2=C_2H_5$; V, VII a $R^1=R^2=R^3=R^4=H$; b $R^2=CH_3$, $R^1=R^3=R^4=H$; c $R^2=CH_2C_6H_5$, $R^1=R^3=R^4=H$; d $R^2=C_6H_5$, $R^1=R^3=R^4=H$; e $R^1=R^2=R^3=H$, $R^4=Cl$; f $R^1=R^2=R^3=H$, $R^4=Br$; g $R^1=CH_3$, $R^2=R^3=R^4=H$; h $R^1=CH_3$, $R^2=R^4=H$; $R^3=NO_2$; VI, VIII a $R^1=R^2=R^3=R^4=H$; b $R^1=CH_3$, $R^2=R^3=R^4=H$; c $R^1=i\text{-}C_3H_7$, $R^2=R^3=R^4=H$; d $R^1=C_4H_9$, $R^2=R^3=R^4=H$; e $R^1=C_6H_{11}$, $R^2=R^3=R^4=H$; f $R^1=CH_2C_6H_5$, $R^2=R^3=R^4=H$; g $R^1=C_6H_5$, $R^2=R^3=R^4=H$; h $R^1=R^2=R^4=H$, $R^3=Cl$; i $R^1=R^2=R^3=H$, $R^4=Br$; j $R^1=R^2=R^3=H$, $R^4=NO_2$; k $R^1=CH_3$, $R^2=R^4=H$, $R^3=Cl$; ℓ $R^2=CH_3$, $R^1=R^3=R^4=H$; m $R^2=CH_2C_6H_5$, $R^1=R^3=R^4=H$; n $R^2=C_2H_5$, $R^1=R^3=R^4=H$; o $R^1=C_{18}H_{37}$, $R^2=R^3=R^4=H$; p $R^2=R^3=R^4=H$; $R^1=CH_3$, $R^2=R^4=H$, $R^3=OCH_3$

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