2-BENZOPYRYLIUM SALTS

XV.* SYNTHESIS OF 4,5,8,9-TETRAMETHOXY-11-ARYL-11H-INDENO[1,2-c]-2-BENZOPYRYLIUM SALTS

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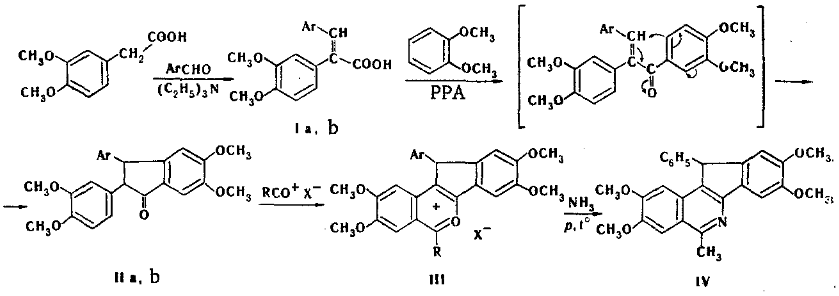
α-Veratrylindanones were obtained by reaction of α-veratrylcinnamic acid with veratrole in polyphosphoric acid (PPA). A method for the synthesis of indeno-2-benzopyrylium salts based on acylation of the indanones with the free acids and their anhydrides was developed. It was shown that indeno-2-benzopyrylium salts can be converted to the little-studied indeno-[1,2-c]isoquinoline bases.

Currently one of the most convenient methods for the synthesis of isoquinolines is based on the ability of 2-benzopyrylium salts to exchange an oxygen heteroatom for nitrogen and undergo conversion to the corresponding nitrogen bases [2, 3]. In connection with the fact that this sort of transformation does not generally cause serious difficulties, the effectiveness of this method depends primarily on the accessibility of the starting 2-benzopyrylium salts.

In the present paper we describe the synthesis of the previously practically unknown indeno[1,2-c]-2-benzopyrylium salts by acylation of α-veratrylindanones (II).

It is known that in the reaction of α,β-unsaturated acids with aromatic compounds [4] or cyclic olefins [5] in the presence of polyphosphoric acid (PPA) cycloaddition may also occur immediately after acylation. In fact, α-veratrylindanones (II) are formed in yields close to quantitative when α-veratrylcinnamic acids are heated with veratrole in PPA.



II a Ar = C$_6$H$_5$; b Ar = 3,4-(CH$_3$O)$_2$C$_6$H$_3$

We have obtained indeno-2-benzopyrylium salts (III) as brightly colored high-melting substances by acylation of indanones II with aliphatic acid anhydrides in the presence of 70% $HClO_4$ and aromatic or aliphatic-aromatic acids in PPA. Like the spectra of 3-aryl-2-benzopyrylium salts [3], the spectra of the products contain a number of characteristic bands at 1610-1620, 1540-1546, 1470-1480, and 1230-1240 cm^{-1}.

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*See [1] for communication XIV.

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Like 3-aryl-2-benzopyrylium salts [3], the indeno[1,2-c]benzopyrylium salts exchange the oxygen heteroatom for a nitrogen only on treatment with alcoholic ammonia solution under pressure. This method was used to give 1-methyl-4,5,8,9-tetramethoxy-11-phenyl-11H-indeno-[1,2-c]isoquinoline in quantitative yield. This sort of structure is a component of the opium alkaloid cryptopine [6]. The synthesis of 11H-indeno[1,2-c]isoquinolines was previously realized by double cyclization of benzylhomophthalic acid and conversion of the resulting isocoumarins to the corresponding isocarbostyrils [7], by accidental synthesis from o-phthalaldehyde [8], and recently from 4-benzylisoquinolines [6, 9].

EXPERIMENTAL

The IR spectra of the compounds in mineral oil were recorded with a UR-20 spectrometer.

α-(3,4-Dimethoxyphenyl)cinnamic Acid. This compound was obtained by a method similar to that in [10]. The product was obtained in 51% yield as light-yellow crystals with mp 182-183° (alcohol). IR spectrum: 1690, 1630, 1608, and 1550 cm^{-1}. Found, %: C 71.6; H 5.9. $C_{17}H_{16}O_4$. Calculated, %: C 71.8; H 5.6.

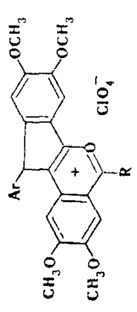
α-(3,4-Dimethoxy-2-(3,4-dimethoxyphenyl)-3,4-dimethoxycinnamic Acid. This compound was similarly obtained in 50% yield and had mp 213-214° (from alcohol) (mp 215-217° [11]). IR spectrum: 1692, 1630, 1610, and 1552 cm^{-1}.

5,6-Dimethoxy-2-(3,4-dimethoxyphenyl)-3-phenylindanone (IIa). A mixture of 1.42 g (0.005 mole) of α-veratrylcinnamic acid, 0.7 g of veratrole, and 10 g of PPA was heated at 100° with vigorous stirring for 10 min. After hydrolysis of the reaction mixture, the resulting precipitate was removed by filtration and dried to give 1.8 g (90%) of colorless crystals with mp 170-171° (from alcohol). Found, %: C 74.4; H 6.1. $C_{25}H_{24}O_5$. Calculated, %: C 74.3; H 5.9. IR spectrum: 1670, 1600, and 1530 cm^{-1}.

5,6-Dimethoxy-2,3-di(3,4-dimethoxyphenyl)-indanone (IIb). This compound was similarly obtained in 80% yield as colorless crystals with mp 120° (from alcohol). Found,%: C 69.4; H 6.2. $C_{27}H_{28}O_7$. Calculated, %: C 69.8; H 6.0. IR spectrum: 1674, 1610, and 1532 cm^{-1}.

1-Methyl-4,5,8,9-tetramethoxy-11-phenyl-11H-indeno[1,2-c]-2-benzopyrylium Perchlorate. A 0.5 ml sample of 70% perchloric acid was added dropwise with cooling and stirring to a solution of 0.4 g (0.001 mole) of α-veratryl-β-phenylindanone (IIa) in 5 ml of acetic anhydride. The resulting precipitate was removed by filtration and washed with acetic acid and ether to give 0.5 g (95%) of orange crystals with mp 229-230° (after recrystallization from acetic acid and reprecipitation from nitromethane by the addition of ether). Salts Nos. 2, 3, and 4 (see Table 1) were similarly synthesized.

TABLE 1.



No.	R	Ar	Color	mp,* deg C	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	Cl	C	H	Cl	
1	CH_3	C_6H_5	Orange	229	$C_{27}H_{25}ClO_9$	61,0	5,0	6,6	61,2	4,8	6,7	95
2	C_2H_5	C_6H_5	"	233	$C_{28}H_{27}ClO_9$	62,0	5,0	6,0	62,0	5,0	6,6	83
3	CH_3	3,4-$(CH_3O)_2C_6H_3$	"	222	$C_{29}H_{29}ClO_{11}$	59,5	4,8	5,9	59,1	4,9	6,0	93
4	C_2H_5	3,4-$(CH_3O)_2C_6H_3$	"	232	$C_{30}H_{31}ClO_{11}$	59,3	5,5	6,0	59,7	5,2	5,9	88
5	4-CH_3O—C_6H_4	C_6H_5	Violet	226	$C_{33}H_{29}ClO_{10}$	63,8	5,0	6,1	63,8	4,7	5,7	50
6	$C_6H_5CH_2$	C_6H_5	Bright-red	236	$C_{33}H_{29}ClO_9$	66,0	5,0	6,3	65,5	4,8	5,9	73
7	3,4-$(CH_3O)_2C_6H_3$	C_6H_5	Bright-red	243	$C_{34}H_{31}ClO_{11}$	63,0	4,7	5,3	62,7	4,8	5,5	30

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* To avoid the formation of solvated molecules, all of the synthesized salts were reprecipitated from nitromethane (by the addition of ether) after recrystallization from glacial acetic acid.

1-Benzyl-4,5,8,9-tetramethoxy-11-phenyl-11H-indeno[1,2-c]-2-benzopyrylium Perchlorate. A mixture of 0.4 g (1 mmole) of α-veratryl-β-phenylindanone (IIa) and 0.14 g (1.2 mmole) of phenylacetic acid in 5 g of PPA was heated with vigorous stirring at 120° for 1 h. The mixture was poured into cold water, and the aqueous mixture was acidified with 30% $HClO_4$. The precipitated product was removed by filtration, dried, and reprecipitated from a small amount of acetic acid containing a few drops of 70% $HClO_4$ by the addition of ether to give 0.44 g (73%) of bright-red crystals with mp 236-237° (after recrystallization from acetic acid and reprecipitation from nitromethane by the addition of ether). Salts Nos. 6 and 7 (see Table 1) were similarly obtained.

1-Methyl-4,5,8,9-tetramethoxy-11-phenyl-11H-indeno[1,2-c]isoquinoline (IV). A suspension of 0.53 g (0.001 mole) of 1-methyl-4,5,8,9-tetramethoxy-11-phenyl-11H-indeno[1,2-c]-2-benzopyrylium perchlorate in 10 ml of alcohol in an ampule was cooled to −10° and saturated with ammonia. The sealed ampule was heated at 100° for 6 h, after which it was cooled, and the solvent was removed at reduced pressure. The residue was treated with 25 ml of water, and the resulting precipitate was removed by filtration and dried to give 0.36 g (84%) of colorless needles with mp 199-200° (from benzene) and R_f 0.6 [Al_2O_3, chloroform–benzene (3:2)]. Found, %: C 75.6; H 5.8; N 3.3. $C_{27}H_{25}NO_4$. Calculated, %: C 75.9; H 5.6; N 3.3. IR spectrum: 1625, 1610, and 1590 cm^{-1}.

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