# TRANSFORMATIONS OF SUBSTITUTED TETRAHYDRO-8H-INDENO[1,2-d]IMIDAZOLES IN CONCENTRATED SULFURIC ACID

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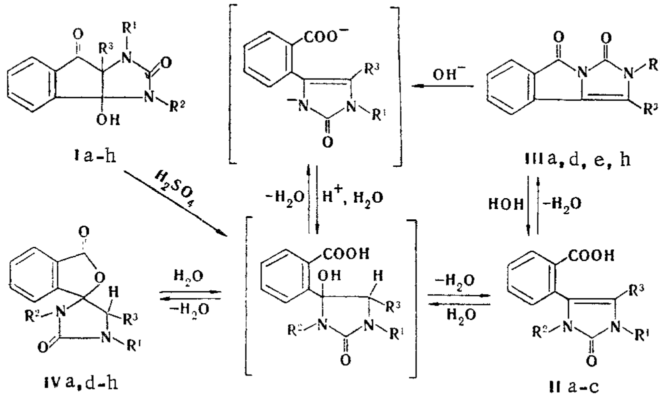
The five-membered ring of the indene system in 2,8-dioxo-3a-hydroxy-8a-R-1,2,3a,8a-tetrahydro-8H-indeno[1,2-d]imidazoles is hydrolytically cleaved in concentrated sulfuric acid solutions. Depending on the reaction conditions, compounds for which substituted 4-(o-carboxyphenyl)imidazol-2-one (II), 1,8-dioxo-1,2-dihydro-8H-imidazo[4,3-a]isoindole (III), and spiro[imidazolidine-4,3'-phthalide] structures were assumed were isolated.

Under the influence of strong acids (concentrated sulfuric and polyphosphoric acids), 8-oxo-2-thioxo-1,2,3a,8a-tetrahydro-8H-indeno[1,2-d]imidazoles can be converted to 2-thioxo-4-(o-carboxyphenyl)imidazolines and 8-oxo-1-thioxo-1,2-dihydro-8H-imidazo[4,3-a]isoindoles [1-3]. In concentrated sulfuric acid, indeno[1,2-d]imidazoles (I) are altered in the same manner. Various transformation products – 4-(o-carboxyphenyl)imidazol-2-ones (II), dihydroimidazo[4,3-a]isoindoles (III), or spiro[imidazolidine-4,3'-phthalides] (IV) – are isolated, depending on the reaction conditions.



I—IV a $R^1=R^2=H$; $R^3=OH$; I, II b $R^1=CH_2C_6H_5$; $R^2=R^3=C_6H_5$; I, II c $R^1=H$; $R^2=R^3=C_6H_5$; I, III, IV d $R^1=CH_3$; $R^2=H$; $R^3=OH$; I, III, IV e $R^1=CH_3$; $R^2=H$; $R^3=OCH_3$; I, IV f $R^1=H$; $R^2=C_6H_5$; $R^3=OCH_3$; I, IV g $R^1=H$; $R^2=C_6H_5$; $R^3=OH$; I, III, IV h $R^1=R^2=H$; $R^3=OCH_3$

On brief treatment of I with concentrated sulfuric acid, the five-membered ring of the indane grouping opens to give substituted imidazolones II. Cleavage of the five-membered ring in acidic media commences with protonation of the carbonyl group, promoting hydrolytic cleavage of the ring [4]. Compounds II are colorless crystalline substances that are quite soluble in alkalis. The IR spectra of these compounds contain a characteristic absorption band at 1695-1702 $cm^{-1}$ that corresponds to the vibrations of the carbonyl group of aromatic acids [5]. The vibrational frequency of imidazolinone is observed at 1666-1677 $cm^{-1}$. The $\nu_{C=C}$ bands of the imidazolinone ring at 1631-1644 $cm^{-1}$ [6] and the stretching vibrations of aromatic rings at 1572-1600 $cm^{-1}$ show up distinctly in the spectra of almost all of the 2-imidazolones (II). In some cases the $\nu_{C=O}$ and $\nu_{C=C}$ bands of imidazolinone overlap. The UV spectra of II contain absorption

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maxima at ~285 nm (log ε 4.15); this is in complete agreement with the absorption of 4-(o-carboxyphenyl)-4-imidazoline-2-thione [1, 2].

Yellow crystalline substances that are soluble in polar solvents but insoluble in nonpolar solvents are isolated in the case of more prolonged action of concentrated sulfuric acid on I and subsequent addition of ice to the solution. Compounds that have identical physical and chemical properties were also synthesized by intramolecular cyclization of II. The substituted dihydroimidazo[4,3-a]isoindole structure (III) was adopted for these compounds on the basis of their chemical and spectral properties and also in analogy with the transformations of the thio derivatives of indeno[1,2-d]imidazoles in solution in dehydrating acids [3]. Of course, III can be only formed from those indeno[1,2-d]imidazoles (I) or 4-(o-carboxyphenyl)imidazol-2-ones (II) that do not have a substituent attached to the nitrogen atom in the 3-position ($R^2 = H$).

An intense broad absorption band at 1745-1769 $cm^{-1}$, which is often split into a doublet at 1745-1751 and 1707-1723 $cm^{-1}$, is characteristic for the IR spectra of solid III. This absorption should be assigned to the vibrations of the CO—N—CO grouping [5]. In addition, the absorption frequencies of a double bond at 1651-1669 $cm^{-1}$ and three low-intensity absorption maxima of an aromatic ring at 1579-1608, 1556-1558, and 1530 $cm^{-1}$ are observed in the spectra of III. Absorption at 239 (log ε ~4.19), 306 (log ε 4.12), and 394-398 nm (log ε 3.68) is characteristic for the UV spectra of III.

In alkaline media compounds III undergo cleavage; this confirms the different character of the UV spectra of solutions of III in neutral and alkaline ethanol. The hypsochromic shift of the absorption bands and the disappearance of the maximum at 394 nm provide evidence for disruption of the π—p conjugation during cleavage of the III system. Spiro[imidazolidine-4,3'-phthalides] (IV) are isolated when alkaline solutions of III are acidified.

Compounds IV are formed like isoindoles III and imidazolones II in solutions of imidazoles I in concentrated sulfuric acid and also on successive alkaline-acidic hydrolysis of isoindoles III. Two absorption bands at 230-240 nm (log ε ~ 4.15) and 280 nm (log ε ~3.30) appear in the UV spectra of IV. The absorption of a phthalide grouping at 1751-1776 $cm^{-1}$ and the $\nu_{C=O}$ band of imidazolidone at 1660-1669 $cm^{-1}$ are observed in the IR spectra of IV. The characteristic low-intensity bands of the benzene ring appear at 1599-1608 and 1580-1583 $cm^{-1}$.

## EXPERIMENTAL

**1-Benzyl-4-(o-carboxyphenyl)-3,5-diphenyl-4-imidazolin-2-one (IIb).** A 2-g (5 mmole) sample of 2,8-dioxo-3a-hydroxy-benzyl-3,8a-diphenyl-1,2,3a,8a-tetrahydro-8H-indeno[1,2-d]imidazole (Ib) was dissolved in 10 ml of concentrated $H_2SO_4$, and the mixture was poured over ice after 15 min. The resulting white precipitate was removed by filtration, washed thoroughly with cold water, and recrystallized from ethanol to give 1.1 g (52%) of IIb with mp 273°. Found: C 77.9; H 5.1; N 6.1%. $C_{29}H_{22}N_2O_3$. Calculated: C 78.0; H 5.0; N 6.3%.

Compounds IIa, c were similarly obtained (Table 1).

**1,8-Dioxo-3-hydroxy-1,2-dihydro-8H-imidazo[4,3-a]isoindole (IIIa).** A 0.44-g (2 mmole) sample of Ia was dissolved in 5 ml of concentrated $H_2SO_4$, and the mixture was poured over ice after 30 min. The resulting yellow precipitate was removed by filtration, washed with cold water, and recrystallized from ethanol—dioxane (1 : 1) to give 0.3 g (64%) of IIIa with mp 289°. Found: C 59.2; H 3.2; N 13.7%. $C_{10}H_6N_2O_3$. Calculated: C 59.5; H 3.0; N 13.7%. The same compound was obtained in 72% yield by similar treatment of IIa.

TABLE 1. Characteristics of the Synthesized Compounds

| Compound | $R^1$ | $R^2$ | $R^3$ | mp, °C | Empirical formula | N, % | | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | | | | | found | calc. | |
| If | H | $C_6H_5$ | $OCH_3$ | 159 | $C_{17}H_{14}N_2O_4$ | 8,9 | 9,0 | 51 |
| Ih | H | H | $OCH_3$ | 194 | $C_{11}H_{10}N_2O_4$ | 11,7 | 12,0 | 42 |
| IIa | H | H | OH | 170—171 | $C_{10}H_8N_2O_4$ | 12,6 | 12,7 | 49 |
| IIc | H | $C_6H_5$ | $C_6H_5$ | 265 | $C_{22}H_{16}N_2O_3$ | 7,5 | 7,8 | 61 |
| IIIe | $CH_3$ | H | OH | 295 | $C_{11}H_8N_2O_3$ | 13,2 | 13,0 | 80 |
| IVd | $CH_3$ | H | $OCH_3$ | 284—285 | $C_{12}H_{10}N_2O_3$ | 12,3 | 12,9 | 72 |
| IVe | $CH_3$ | H | OH | 179—180 | $C_{11}H_{10}N_2O_4$ | 11,7 | 12,0 | 49 |
| IVf | $CH_3$ | H | $OCH_3$ | 169—170 | $C_{12}H_{12}N_2O_4$ | 11,2 | 11,3 | 38 |
| IVg | H | $C_6H_5$ | $OCH_3$ | 225—226 | $C_{17}H_{14}N_2O_4$ | 9,1 | 9,0 | 35 |
| IIId | H | $C_6H_5$ | OH | 269—270 | $C_{16}H_{12}N_2O_4$ | 9,2 | 9,5 | 34 |

Spiro[2-oxo-5-hydroxyimidazolidine-4,3'-phthalide] (IVa). A 0.44-g (2 mmole) sample of Ia was dissolved in 5 ml of concentrated $H_2SO_4$, and the mixture was allowed to stand overnight. The following day it was poured over ice, and the resulting white precipitate was removed by filtration, washed with cold water, and recrystallized from ethanol to give 0.26 g (60%) of IVa with mp 229-230°. Found: C 54.4; H 3.8; N 12.5%. $C_{10}H_8N_2O_4$. Calculated: C 54.5; H 3.7; N 12.7%.

Compounds IVd-g (Table 1) were similarly obtained from Id-g. Compound IVe was also obtained from IIIe. A 0.92-g (4 mmole) sample of IIIe was dissolved in 20 ml of 5% KOH, and the solution was neutralized after 1 h with 10% hydrochloric acid. The resulting white crystals were removed by filtration and recrystallized from ethanol to give 0.41 g (41%) of IVe.

2,8-Dioxo-3a-hydroxy-1-methyl-8a-methoxy-1,2,3a,8a-tetrahydro-8H-indeno[1,2-d]imidazole (Ie). A 1.17-g (5 mmole) sample of 2,8-dioxo-3a,8a-dihydroxy-1-methyl-1,2,3a,8a-tetrahydro-8H-indeno[1,2-d]-imidazole (Id) was dissolved in 15 ml of 5% KOH, and the mixture was cooled to 5° and treated with 0.47 ml (5 mmole) of dimethyl sulfate with stirring. The mixture was then stirred for 2 h without cooling, and the resulting white crystals were removed by filtration. Recrystallization from ethanol gives 1.0 g (81%) of Ie with mp 179°. Found: C 72.8; H 4.9; N 11.0%. $C_{12}H_{12}N_2O_4$. Calculated: C 73.1; H 4.9; N 11.3%.

Compounds If, h (Table 1) were similarly obtained from Ig and Ia.

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