

Bromination of *N*-(*o*-Aminophenyl)-*cis*-4-cyclohexene-1,2-dicarboximide and *cis*-2-(2-Benzimidazolyl)-4-cyclohexene-1-carboxylic Acid

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Abstract—Exhaustive oxidative bromination of *N*-(*o*-aminophenyl)-*cis*-4-cyclohexene-1,2-dicarboximide and 2-(2-benzimidazolyl)-*cis*-4-cyclohexene-1-carboxylic acid results in bromine addition at the double bond. Under more severe conditions, the addition of bromine at the double bond is accompanied by bromination of the aromatic ring. The latter process does not occur in the exhaustive bromination of *cis*-2-(2-benzimidazolyl)-4-cyclohexene-1-carboxylic acid.

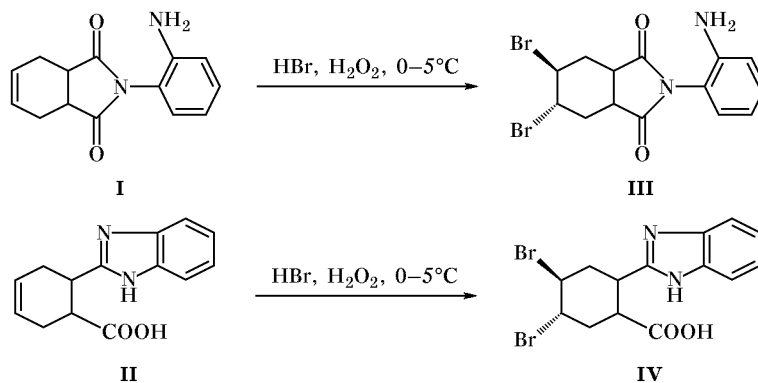
It was shown in [1] that exhaustive oxidative bromination of *N*-phenyl-*cis*-4-cyclohexene-1,2-dicarboximide is not accompanied by substitution in the aromatic ring but results only in bromine addition at the cyclohexene double bond, yielding *N*-phenyl-*trans*-4,5-dibromocyclohexane-1,2-dicarboximide. The present communication reports on the bromination of *N*-(*o*-aminophenyl)-*cis*-4-cyclohexene-1,2-dicarboximide (**I**) and *cis*-2-(2-benzimidazolyl)-4-cyclohexene-1-carboxylic acid (**II**). A mixture of 40% hydrobromic acid and 28% hydrogen peroxide was used as oxidant. The oxidative bromination of compounds **I** and **II** was carried out under mild conditions (substrate–HBr–H₂O₂ molar ratio 1:2:1, 0–5°C); as a result, *trans*-4,5-dibromo derivatives **III** and **IV** were obtained (see table; Scheme 1).

Exhaustive oxidative bromination of compound **I** (substrate–HBr–H₂O₂ molar ratio 1:6:1, 15–20°C)

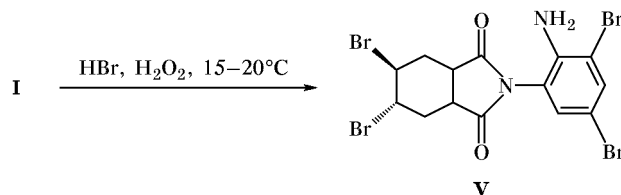
leads to both bromine addition at the double bond and substitution in the aromatic ring to afford tetrabromo derivative **V** (see table; Scheme 2); under the same conditions, acid **II** undergoes only addition of bromine at the cyclohexene double bond to give dibromide **IV**.

The orienting ability of the amino group was verified by a model reaction. For this purpose, exhaustive oxidative bromination was carried out under analogous conditions with *N*-(*o*-aminophenyl)-phthalimide (**VI**) and 2-(2-benzimidazolyl)benzoic acid. In the first case, the product was dibromide **VII** (see table; Scheme 3), whereas in the latter case no reaction occurred. These data indicate a high orienting potency of the amino group. Exhaustive oxidative bromination of *N*-(*p*- and *m*-aminophenyl)-*cis*-4-cyclohexene-1,2-dicarboximides **VIII** and **IX** (substrate–HBr–H₂O₂ molar ratio 1:6:3, 15–20°C) gave

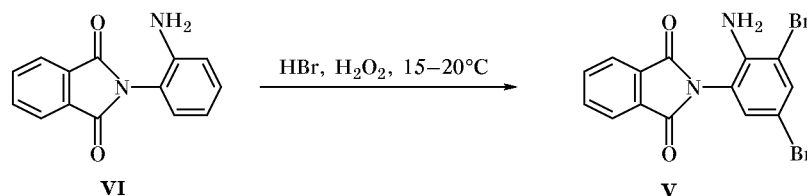
Scheme 1.



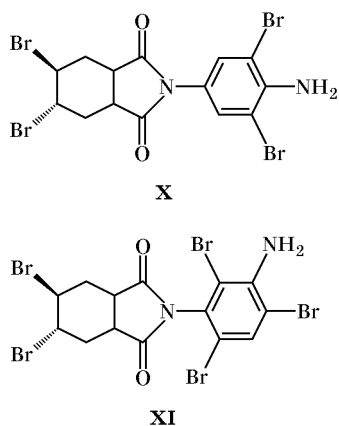
Scheme 2.



Scheme 3.



products of both bromine addition at the double bond and substitution in the aromatic ring, tetra- and penta-bromo derivatives **X** and **XI**, respectively (see table).



The structure of tetrabromide **V** was proved by independent synthesis, by oxidative bromination of dibromide **III** (substrate–HBr–H₂O₂ molar ratio 1:6:3, 15–20°C). Dibromide **IV** failed to react under the same conditions.

The structure of the products was confirmed by their elemental analyses (see table) and IR spectra. In the IR spectra we observed absorption bands at 640–680 cm⁻¹ due to stretching vibrations of the C–Br bonds, while no absorption typical of C=C bonds was present (1600, 1602 cm⁻¹).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The purity of the products was checked by TLC on Silufol

Yields, melting points, *R_f* values, and elemental analyses of compounds **II**–**XI**

Comp. no.	Yield, %	mp, °C (solvent)	<i>R_f</i>	Found, %		Formula	Calculated, %		<i>M</i>	
				Br	N		Br	N	found	calcd.
II	60	236 (benzene)	0.68	–	11.52	C ₁₄ H ₁₄ N ₂ O ₂	–	11.57	240.2	241.0
III	97	252 (ethanol)	0.51	39.42	6.67	C ₁₄ H ₁₄ Br ₂ N ₂ O ₂	39.80	6.96	400.0	402.0
IV	60	150 (benzene)	0.70	39.70	6.92	C ₁₄ H ₁₄ Br ₂ N ₂ O ₂	39.80	6.97	400.9	402.0
V	96	201 (benzene)	0.63	55.26	4.74	C ₁₄ H ₁₄ Br ₄ N ₂ O ₂	55.36	4.84	576.5	578.0
VI	94	230 (ethanol)	0.70	–	11.71	C ₁₄ H ₁₀ N ₂ O ₂	–	11.76	236.8	238.0
VII	73	161 (ethanol)	0.63	39.88	6.81	C ₁₄ H ₈ Br ₂ N ₂ O ₂	40.40	7.07	394.8	396.0
VIII	81	172 (ethanol)	0.56	–	11.11	C ₁₄ H ₁₄ N ₂ O ₂	–	11.57	240.8	242.0
IX	93	240 (ethanol)	0.65	–	11.08	C ₁₄ H ₁₄ N ₂ O ₂	–	11.57	238.4	242.0
X	100	246 (benzene)	0.86	56.79	4.62	C ₁₄ H ₁₂ Br ₄ N ₂ O ₂	57.14	5.00	558.6	560.0
XI	76	301	0.58	62.11	4.00	C ₁₄ H ₁₁ Br ₅ N ₂ O ₂	62.60	4.38	638.4	639.0

plates using benzene–dichloroethane–acetic acid (4:1.5:1, by volume); spots were visualized under UV light. The molecular weights were determined by cryoscopy in camphor.

Compounds **III–V** and **VII–IX** were synthesized by the procedure described in [2].

Oxidative bromination of imides I and VI and acid II. A solution of 0.22 mol of 28% hydrogen peroxide was added dropwise over a period of 30 min to a mixture of 0.1 mol of compound **I**, **II**, or **VI** and 0.2 mol of 40% hydrobromic acid (substrate–HBr–H₂O₂ molar ratio 1:2:1) under vigorous stirring at 0–5°C. When the addition was complete, the mixture was stirred for 1.5–2 h at 0–5°C. The precipitate was

filtered off and repeatedly washed with distilled water to remove traces of the acid.

Exhaustive oxidative bromination of compounds **I**, **VI**, **VIII**, and **IX** was carried out in a similar way, but the substrate–HBr–H₂O₂ molar ratio was 1:6:3, and the reaction temperature was 15–20°C.

REFERENCES

1. Salakhova, R-S.M., *Cand. Sci. (Chem.) Dissertation*, 1974.
2. Salakhov, M.S., Umaeva, V.S., Salakhova, Ya.S., and Idrisova, S.Sh., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 397.