

Reaction of Endic Anhydride with Hydrazines and Acylhydrazines

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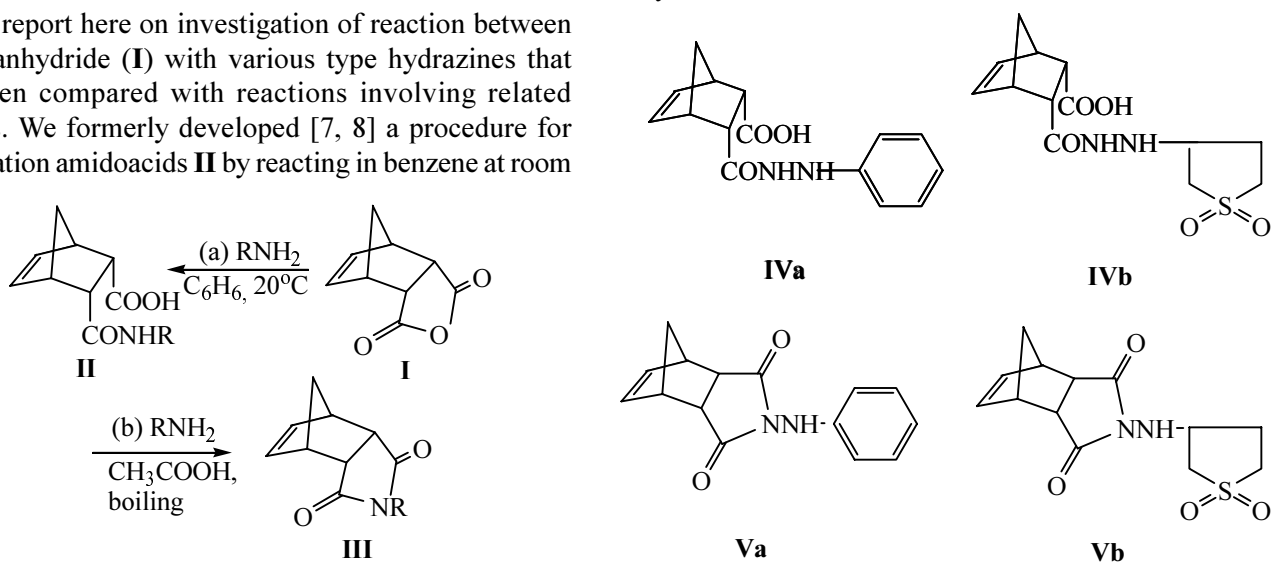
Abstract—Reaction products of bicyclo[2.2.1]hept-2-ene-*endo*,*endo*-5,6-dicarboxylic (endic) acid with hydrazines and acylhydrazines were prepared. The features distinguishing of these reactions from those with amines were revealed. The compounds obtained were characterized by ¹H, ¹³C NMR, and IR spectra. The assignment of the signals in NMR spectra was done with the use of quantum-chemical calculations of chemical shifts performed by the density functional method. The structure of one among compounds synthesized, *N*-(*m*-hydroxybenzoylamino)-bicyclo[2.2.1]hept-2-ene-*endo*,*endo*-5,6-dicarboxamide, was proved by X-ray diffraction analysis.

Organic hydrazine derivatives are widely applied as synthons in manufacturing pharmaceuticals possessing tuberculocidal, antitumor, psychoterapeutic, and other activity. They are used in agriculture as plant growth regulators and stimulators, and as chemical protecting agents for plants [1]. Among hydrazine derivatives the products of their acylation with endic anhydride [bicyclo[2.2.1]hept-2-ene-*endo*,*endo*-5,6-dicarboxylic acid anhydride (**I**)] were investigated [2]. Some of them also function as plant growth regulators [3], herbicides [4], activators of antitumor drugs [5], and synthons for preparation of new antibiotics [6].

We report here on investigation of reaction between endic anhydride (**I**) with various type hydrazines that has been compared with reactions involving related amines. We formerly developed [7, 8] a procedure for preparation amidoacids **II** by reacting in benzene at room

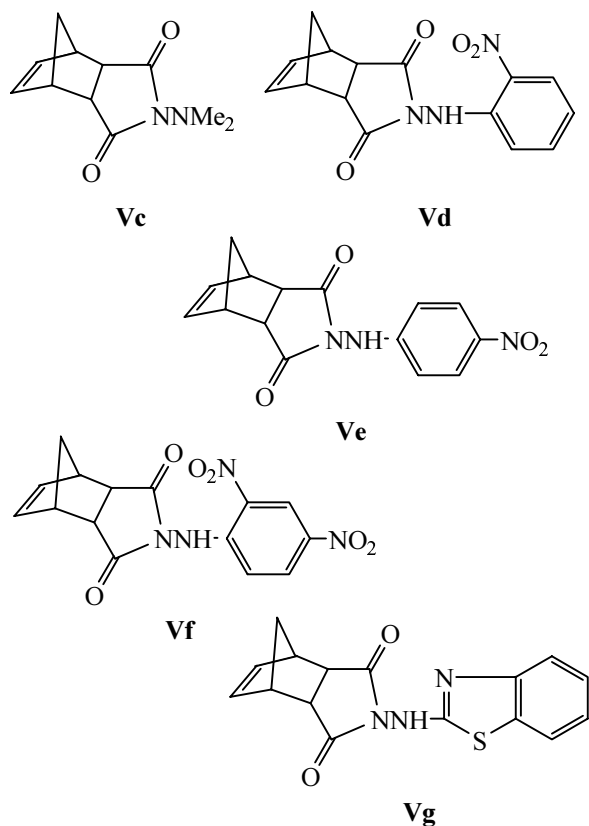
temperature equimolar amounts of endic anhydride (**I**) with alkyl-amines, arylamines, amines containing cage-like norbornene, norbornane, and adamantane fragments. Amido-acids by boiling with acetic acids were transformed into carboximides **III** that under similar conditions were obtained directly from anhydride **I** and amines although in lower yields.

Unlike the aminolysis of anhydride (**I**) its reactions with alkyl- and- arylhydrazines under mild conditions pre-vaillingly afforded compounds with imide fragments. Reactions products with phenylhydrazine **IVa** and 3-hydrazinethiolane dioxide **IVb** formed an exclusion



for they had structures of hydrazidoacids. The latter compounds were converted into imides **Va, b** by heating in acetic acid.

Other hydrazines (1,1-dimethylhydrazine, *o*-nitro-, *p*-nitro-, *o,p*-dinitrophenylhydrazines, 2-benzothiazolylhydrazine) both under mild conditions (reaction *a*) and at boiling the reagents with acetic acid (reaction *b*) furnished imides **Vc–g**.



The discovered trend to cyclic imide formation in the reactions of endic anhydride with hydrazines in contrast to similar reactions with amines affording under the same conditions amidoacids [7, 8] apparently originates from increase in the acidity of hydrogens in the NH group at the carbonyl in the intermediates (hydrazidoacids) caused by the effect of the adjacent amino group.

In the IR spectrum of amidoacid **IVa** several bands of stretching vibrations of carbonyl groups were observed corresponding to carboxy and carboxamide groups; the presence of the latter was proved by absorption bands at 3250 [$\nu(\text{NH})$], 2750–2300 [$\nu(\text{OH})$], 1500 [$\delta(\text{NH})$] cm^{-1} [9].

In the ^1H NMR spectra of hydrazidoacids **IVa, b** two features were observed confirming their structure. Firstly, “twin” protons in the framework part of the molecules

are nonequivalent, in particular, H^5 and H^6 , and also H^2 and H^3 in compound **IVa**. Secondly, two signals from protons attached to nitrogen are present whose position is affected by their environment. In the spectrum of amidoacid **IVa** the proton signal from the carboxy group appeared at 11.36 ppm. In the ^1H NMR spectra of compounds **Va–e, g** the protons H^1 and H^4 , H^2 and H^3 , H^5 and H^6 are equivalent, and their signals are located downfield with respect to the corresponding signals in the spectra of amidoacids. The bridge protons (H^{7s} and H^{7a}) resonate as doublets with a coupling constant 8.7–9.3 Hz. In all imide spectra save that of compound **Vc** one-proton signals are present at 3.50–10.80 ppm belonging to hydrogens linked to nitrogen. The ^{13}C NMR spectra of aminoimides **Vd, e, g** demonstrate as well as the proton spectra the equivalence of skeleton carbon atoms C^1 and C^4 , C^2 and C^3 , C^5 and C^6 . The signals from carbon atoms in imide groups appear in a narrow range 173.9–175.7 ppm. The assignment of signals in the NMR spectra was done on the strength of quantum-chemical calculations of the chemical shifts in the ^1H and ^{13}C NMR spectra of compound **Vb** (Table 1). The calculations were performed by methods GIAO [10] and IGAIM [11] in PBE1PBE approximation using a set of basis functions 6-31G**(II) physically adapted to the calculation of magnetic properties[12]. The geometry of hydrazide **Vc** was preliminary optimized in the B3LYP/6-311G* approximation. The calculation results revealed an important feature of protons shielding in the molecule of imide **Vc**: the signals from protons H^1 and H^4 and from the corresponding carbons are located downfield from the signals of H^5 and H^6 and C^5 and C^6 .

The reactions of endic anhydride with hydrazines were compared with its reactions with hydrazides of carboxylic acids from the aromatic series (benzoic, *o*-chloro-, *m*-hydroxy-, *m*-nitro-, *p*-nitrobenzoic acids), with

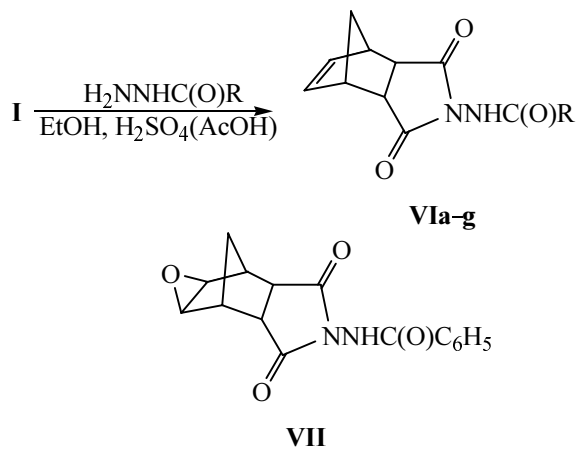
Table 1. Chemical shifts (ppm) in ^1H and ^{13}C NMR spectra of compound **Vc** calculated in PBE1PBE/6-31G**(II)

Atom	Calculation method		Atom	Calculation method	
	GIAO	IGAIM		GIAO	IGAIM
H^1	3.13	3.00	C^1	52.12	52.08
H^2	6.35	6.21	C	146.50	145.86
H^3	6.37	6.21	C^3	146.20	145.48
H^4	3.11	3.00	C^4	52.02	51.91
H^5	2.70	2.52	C^5	48.99	48.78
H^6	2.79	2.60	C^6	49.63	49.45
H^{7s}	1.42	1.42	C^7	56.74	56.85
H^{7a}	1.10	1.07			

Table 2. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($E^2 \times 10^3$) of nonhydrogen atoms in the structure of compound **VId**

Atom	x	y	z	U_{eq}
N ¹	-175 (2)	8860 (2)	5942 (2)	35 (1)
N ²	-421 (2)	7755 (2)	5467 (2)	40 (1)
O ¹	-1249 (2)	8410 (2)	7436 (2)	50 (1)
O ²	698 (2)	9825 (2)	4547 (2)	55 (1)
O ³	1787 (2)	7362 (2)	5388 (2)	49 (1)
O ⁴	2095 (2)	3995 (2)	2788 (2)	68 (1)
C ¹	-630 (2)	9117 (2)	6918 (2)	33 (1)
C ²	-213 (2)	10408 (2)	7158 (2)	35 (1)
C ³	-1390 (3)	11339 (2)	7278 (2)	44 (1)
C ⁴	-2304 (3)	11163 (2)	6376 (3)	48 (1)
C ⁵	-1676 (3)	11586 (2)	5556 (3)	49 (1)
C ⁶	-312 (3)	12036 (2)	5889 (2)	44 (1)
C ⁷	-652 (3)	12510 (2)	6957 (2)	49 (1)
C ⁸	501 (2)	10874 (2)	6185 (2)	35 (1)
C ⁹	398 (2)	9853 (2)	5425 (2)	36 (1)
C ¹⁰	639 (2)	7071 (2)	5171 (2)	33 (1)
C ¹¹	306 (2)	5965 (2)	4556 (2)	33 (1)
C ¹²	1323 (2)	5447 (2)	3974 (2)	36 (1)
C ¹³	1055 (3)	4447 (2)	3356 (2)	42 (1)
C ¹⁴	-236 (3)	3964 (2)	3328 (2)	47 (1)
C ¹⁵	-1228 (2)	4460 (2)	3927 (3)	51 (1)
C ¹⁶	-974 (2)	5460 (2)	4541 (3)	44 (1)

1-adamantanecarboxylic acid hydrazide, and with semi-carbazide hydrochloride. All hydrazides were inert to endic anhydride in reactions performed by procedure *a* and at heating at reflux in benzene, but the process occurred under conditions of procedure *b* or at heating



VI, R = NH₂ (**a**), C₆H₅ (**b**), *o*-C₆H₄Cl (**c**), *m*-C₆H₄OH (**d**), *m*-C₆H₄NO₂ (**e**), *p*-C₆H₄NO₂ (**f**), 1-Ad (**g**).

in alcohol in the presence of catalytic quantity of concn. sulfuric acid (procedure *c*). The identity of products obtained by both methods was demonstrated by an example of compound **Vd**. More severe conditions of reaction between endic anhydride and carboxylic acids hydrazides are apparently due to the lack of the α -effect ensuring the supernucleophilicity of hydrazines [13].

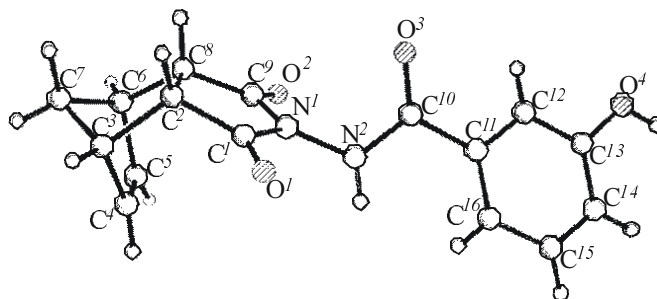
The IR spectra of compounds **VIa-g** contain no absorption bands of carboxy groups but appear the bands of asymmetrical and symmetric stretching vibrations of imide carbonyl groups (1790–1770, 1733–1716 cm⁻¹) and of a carbonyl group belonging to the amide moiety (1680–1660 cm⁻¹). The spectra contain absorption bands from vibrations of N–H bonds in the regions 3475–3265 and 1590–1530 cm⁻¹ [ν (NH), δ (NH)], and also from the aromatic fragments of compounds **VIb-f**.

On comparison of the ¹H NMR spectra of compounds **Va** and **VIb** stands out the difference in positions of proton signals from H² and H³ (6.20 and 5.95 ppm respectively). In the ¹³C NMR spectra of compounds **VIa-g** appears a signal from a carbon atom of the exocyclic carboxy group. In the spectra of compounds **VIb,c** these signals are displaced to 132.61 and 131.99 ppm respectively testifying to the existence in solution of tautomer forms of aminoimides acyl derivatives [NH–C=O \rightleftharpoons N=C(OH)].

Single crystals of compound **VId** were subjected to X-ray diffraction study that proved its amide structure (see figure, Table 2). The five-membered heterocycle exists in an *envelop* conformation.

The deviation of atom N¹ from the mean-square plane of the other atoms in the ring is 0.09 Å. The nitrogen atom is planar (the sum of bond angles equals to 359.6°). The bicycloheptene fragment and the five-membered heterocycle are in a *cis*-junction (torsion angle H²C²C⁸H⁸ is 2.6°).

Atom C¹⁰ is in the *ac* conformation with respect to C¹–N¹ bond [torsion angle C¹N¹N²C¹⁰ –120.6(2)°].



Structure of compound **VId** according to X-ray diffraction study.

Phenyl substituent is in close to *ap* conformation with respect to N¹–N² bond [torsion angle N¹N²C¹⁰C¹¹ – 173.1(2)°] and is turned relative to N²–C¹⁰ bond by 160.5(2)° [torsion angle N²C¹⁰C¹¹C¹²]. The carbonyl group and aromatic system are acoplanar [torsion angle O³C¹⁰C¹¹C¹² – 18.5(4)°]. This results in lack of conjugation between these fragments as revealed in the length of C¹⁰–C¹¹ bond equal to 1.491(3) Å.

Formation of intermolecular hydrogen bonds N²–H···O³ (*x* – 1/2, –*y* + 3/2, *z*), H···O 1.98 Å, NH···O 155.3° and O⁴–H···O¹ (–*x*, 1 – *y*, *z* – 1/2), H···O 2.02 Å, OH···O 159.6° results in elongation of bonds N¹–C¹ 1.385(3) Å (Average value 1.372 Å [14]), N¹–C⁹ 1.401(3) (1.372) Å, N²–C¹⁰ 1.350(3)(1.334) Å.

We demonstrated by an example of one hydrazide the possibility of their epoxidation. Treating hydrazide **Vb** with performic acid *in statu nascendi* obtained from 98% formic acid and 30–35% solution of hydrogen peroxide gave the corresponding epoxide **VII**. The assumed structure of compound **VII** is confirmed by the presence in its IR spectrum by a band in the region 855 cm^{–1} characteristic of epoxynorbomanes [15]. In the ¹H NMR spectrum the indicative features are the position of signals from protons H² and H³ attached to the epoxy ring (3.12 ppm) and the upfield shift of one of bridge protons (H^{7a}) (1.05 ppm). This proton is located just over the plane of the epoxy ring and is subject to magnetic anisotropic effect thereof.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord IR75 from samples in KBr pellets. ¹H NMR spectra were registered on spectrometers Varian VXR-300 (operating frequency 300 MHz) and Gemini-BB (operating frequency 500 MHz) from solutions in deuteriochloroform, deuterodimethyl sulfoxide, or deuteromethanol using HMDS as internal reference. ¹³C NMR spectra were measured on spectrometer Gemini-BB (operating frequency 100.58 MHz). The reaction progress was monitored and the purity of compounds synthesized was checked by TLC on Silufol UV-254 plates, eluent ethyl ether, development in iodine vapor. Elemental analysis was performed on a Karlo Erba analyzer.

Crystals of compounds **VId** rhombic, at 20°C *a* 9.942(3), *b* 10.942(4), *c* 13.103(4) Å, *V* 1425.4(8) Å³, C₁₆H₁₄N₂O₄, *M_r*, 298.29, *Z* 4, space group *Pna*2₁, *d_{calc}*

1.390 g/cm³, μ(MOK_α) 0.102 mm^{–1}, F(000) 624. Unit cell parameters and intensities of 1783 reflections (1783 independent, R_{int} 0.00) were measured on an automatic four-circle diffractometer Siemens P3/PC (MOK_α, graphite monochromator, 2θ/θ-scanning, 2θ_{max} 56°).

The structure was solved by the direct method with the use of software package SHELX97 [16]. Position of hydrogen atoms was revealed from the difference synthesis of electron density and taken into account with the use of *rider* model with *U*_{iso} = *nU*_{eq} (*n* is 1.5 for hydroxy group and 1.2 for the other hydrogen O atoms). The structure was refined by *F*² in full-matrix least-squares procedure in anisotropic approximation for nonhydrogen atoms till *wR*₂ 0.088 for 1783 reflections (*R*₁ 0.033 for 1262 reflections with *F* > 4σ(*F*), *S* 1.001). Final values of atomic coordinates are given in Table 2.

Reaction of endic anhydride with substituted hydrazines. (a) Equimolar amounts of endic anhydride and substituted hydrazine were mixed in benzene solution, and the mixture was left standing till separated a precipitate. The latter was filtered off, dried, and subjected to further purification. Compounds **IVa, b, Vc–g** were prepared by this procedure.

(b) Equimolar amounts of endic anhydride and substituted hydrazine were heated at reflux in glacial acetic acid till completion of reaction (TLC monitoring). The acetic acid was removed in a vacuum, ice water was added to the residue, the separated precipitate was filtered off, dried, and subjected to further purification. Compounds **Vc–g** and **VId** were prepared by this procedure.

(c) Equimolar amounts of endic anhydride and an appropriate hydrazide were dissolved in ethanol, 2–3 drops of concn. sulfuric acid were added to the mixture, and it was heated at reflux till completion of reaction (TLC monitoring). The ethanol was removed in a vacuum, ice water was added to the residue, the separated crystals were filtered off, washed with water on the filter, dried, and subjected to further purification. Compounds **Vla–g** were prepared by this procedure.

Compounds **Va, b** were prepared by heating at reflux in the glacial acetic acid of the corresponding amidoacids **IVa, b** till completion of reaction (TLC monitoring). After the usual workup of the reaction mixture the reaction products were subjected to further purification

endo-5-(N'-Phenylhydrazinocarbonyl)bicyclo-[2.2.1]hept-2-ene-endo-6-carboxylic acid (IVa). Yield 85%, mp 163–165°C. IR spectrum, cm^{–1}: 3250, 1700,

1680, 1500, 1350, 1150. ^1H NMR spectrum, δ , ppm: 9.40 d (1H, NH), 7.24 d (1H, NH), 7.10–6.70 (5H, H arom), 6.16 d (1H, H²), 5.92 d (1H, H³), 3.24 m (1H, H¹), 3.20 m (1H, H⁴), 3.00 m (2H, H⁵, H⁶), 1.32 m (2H, H^{7s}, H^{7a}). Found, %: C 66.24; H 5.81; N 10.33. C₁₅H₁₆N₂O₃. Calculated, %: C 66.18; H 5.88; N 10.29.

endo-5-[N'-(1,1-Dioxotetrahydrothiophen-3-yl)hydrazinocarbonyl]bicyclo[2.2.1]hept-2-ene-endo-6-carboxylic acid (IVb). Yield 83%, mp 185–187°C. ^1H NMR spectrum, δ , ppm: 5.65 d (1H, NH), 3.78 d.d (1H, NH), 6.10 m (2H, H², H³), 3.36 m (1H, H¹), 3.33 m (1H, H⁴), 3.12 m (2H, H⁵, H⁶), 1.65 d (1H, H^{7s}), 1.56 d (1H, H^{7a}). Found, %: C 49.63; H 5.75; N 8.94. C₁₃H₁₈N₂O₅S. Calculated, %: C 49.68; H 5.73; N 8.92.

N-(Anilino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (Va). Yield 69%, mp 180–182°C. IR spectrum, cm⁻¹: 3050, 1700, 1500, 1350, 1150, 712. ^1H NMR spectrum, δ , ppm: 7.10–6.70 (5H, H arom), 5.95 s (1H, NH), 6.20 m (2H, H², H³), 3.46 m (2H, H¹, H⁴), 3.32 m (2H, H⁵, H⁶), 1.75 d (1H, H^{7s}), 1.49 d (1H, H^{7a}). Found, %: C 70.85; H 5.54; N 11.08. C₁₅H₁₄N₂O₂. Calculated, %: C 70.87; H 5.51; N 11.02.

N-(1,1-Dioxotetrahydrothiophen-3-ylamino)-bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (Vb). Yield 73%, mp 185–187°C. IR spectrum, cm⁻¹: 3250, 1750, 1350, 1250, 1150, 1050, 720. ^1H NMR spectrum, δ , ppm: 4.46 s (1H, NH), 6.15 m (2H, H², H³), 3.80 m (2H, H¹, H⁴), 3.26 m (2H, H⁵, H⁶), 1.70 d (1H, H^{7s}), 1.45 d (1H, H^{7a}). Found, %: C 52.73; H 5.44; N 9.49. C₁₃H₁₆N₂O₄S. Calculated, %: C 52.70; H 5.40; N 9.46.

N-(Dimethylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (Vc). Yield 65%, mp 139–141°C. IR spectrum, cm⁻¹: 1700, 1450, 1359, 1200, 790, 725. ^1H NMR spectrum, δ , ppm: 6.09 m (2H, H², H³), 3.40 m (2H, H¹, H⁴), 3.12 m (2H, H⁵, H⁶), 1.72 d (1H, H^{7s}), 1.49 d (1H, H^{7a}). Found, %: C 64.01; H 6.83; N 13.49. C₁₁H₁₄N₂O₂. Calculated, %: C 64.08; H 6.80; N 13.59.

N-(O-Nitrophenylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (Vd). Yield 95%, mp 153–155°C. ^1H NMR spectrum, δ , ppm: 8.09, 7.75 (4H, H arom), 6.15 m (2H, H², H³), 3.48 m (2H, H¹, H⁴), 3.38 m (2H, H⁵, H⁶), 1.72 d (1H, H^{7s}), 1.63 d (1H, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 174.42 (C=O), 133.61, 131.74, 129.52, 124.50 (C arom), 134.59 (C², C³), 51.46 (C⁷), 45.13 (C¹, C⁴), 44.40 (C⁵, C⁶). Found, %: C 60.25; H 4.29; N 14.11. C₁₅H₁₃N₃O₄. Calculated, %: C 60.20; H 4.35; N 14.05.

N-(p-Nitrophenylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (Ve). Yield 70%, mp 230–232°C. IR spectrum, cm⁻¹: 3359, 3081, 1720, 1602, 1518, 1336, 1193, 752. ^1H NMR spectrum, δ , ppm: 9.48 s (1H, NH), 8.09, 6.76 (4H, H arom), 6.26 m (2H, H², H³), 3.52 m (2H, H¹, H⁴), 3.35 m (2H, H⁵, H⁶), 1.64 d (1H, H^{7s}), 1.60 d (1H, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 175.66 (C=O), 126.40, 112.07 (C arom), 139.86 (C², C³), 52.44 (C⁷), 45.14 (C¹, C⁴), 44.53 (C⁵, C⁶). Found, %: C 60.26; H 4.41; N 14.03. C₁₅H₁₃N₃O₄. Calculated, %: C 60.20; H 4.35; N 14.05.

N-(o,p-Dinitrophenylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (Vf). Yield 68%, mp 236–238°C. IR spectrum, cm⁻¹: 3353, 1727, 1610, 1587, 1323, 1180, 842, 733. Found, %: C 52.25; H 3.41; N 16.30. C₁₅H₁₂N₄O₆. Calculated, %: C 52.32; H 3.49; N 16.28.

N-(Benzothiazol-2-ylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (Vg). Yield 93%, mp 180–182°C. ^1H NMR spectrum, δ , ppm: 10.84 s (1H, NH), 7.68–7.10 (4H, H arom), 6.18 m (2H, H², H³), 3.45 m (2H, H¹, H⁴), 3.30 m (2H, H⁵, H⁶), 1.58 d (1H, H^{7s}), 1.52 d (1H, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 173.92 (C=O), 128.21, 126.13, 122.21, 121.67, 117.18 (C arom), 134.75 (C², C³), 51.35 (C⁷), 44.41 (C¹, C⁴), 43.56 (C⁵, C⁶). Found, %: C 61.69; H 4.25; N 13.45. C₁₆H₁₃N₃O₂S. Calculated, %: C 61.74; H 4.18; N 13.50.

N-Ureidobicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (VIa). Yield 79%, mp 203–205°C. ^1H NMR spectrum, δ , ppm: 9.77 s (1H, NH), 8.11 s (1H, NH), 7.80 s (1H, NH), 5.99 m (2H, H², H³), 3.35 m (2H, H¹, H⁴), 3.25 m (2H, H⁵, H⁶), 1.54 m (2H, H^{7s}, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 174.20 (C=O), 134.11 (C², C³), 50.83 (C⁷), 44.11 (C¹, C⁴), 43.61 (C⁵, C⁶). Found, %: C 54.26; H 5.02; N 19.05. C₁₀H₁₁N₃O₃. Calculated, %: C 54.30; H 4.98; N 19.00.

N-(Benzoylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (VIb). Yield 96%, mp 106–108°C. IR spectrum, cm⁻¹: 3450, 1790, 1716, 1668, 1552, 1339, 1308, 707. ^1H NMR spectrum, δ , ppm: 7.85–7.47 (5H, H arom), 5.95 m (2H, H², H³), 3.46 m (2H, H¹, H⁴), 3.32 m (2H, H⁵, H⁶), 1.75 d (1H, H^{7s}), 1.49 d (1H, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 174.96 (C=O), 132.61 (C=O), 128.57, 127.64 (C arom), 134.58 (C², C³), 51.57 (C⁷), 45.10 (C¹, C⁴), 44.36 (C⁵, C⁶). Found, %: C 68.03; H 4.89; N 9.94. C₁₆H₁₄N₂O₃. Calculated, %: C 68.09; H 4.96; N 9.93.

N-(o-Chlorobenzoylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (VIc). Yield 72%,

mp 192–194°C. IR spectrum, cm^{-1} : 3267, 3067, 1786, 1733, 1685, 1591, 1351, 872. ^1H NMR spectrum, δ , ppm: 7.58, 7.47, 7.38 (4H, H arom), 6.15 m (2H, H^2 , H^3), 3.47 m (2H, H^1 , H^4), 3.38 m (2H, H^5 , H^6), 1.71 d (1H, H^{7s}), 1.62 d (1H, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 174.49 (C=O), 131.99 (C=O), 131.52, 130.20, 129.41, 128.13, 126.89 (C arom), 134.58 (C^2 , C^3), 51.48 (C^7), 45.13 (C^1 , C^4), 44.41 (C^5 , C^6). Found, %: C 60.72; H 4.05; N 8.81. $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}_3$. Calculated, %: C 60.66; H 4.11; N 8.85.

***N*-(*m*-Hydroxybenzoylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (VI_d)**. Yield 88%, mp 238–240°C. IR spectrum, cm^{-1} : 3366, 3009, 1792, 1728, 1662, 1584, 1359, 838. ^1H NMR spectrum, δ , ppm: 7.29–7.00 (4H, H arom), 6.16 m (2H, H^2 , H^3), 3.45 m (2H, H^1 , H^4), 3.36 m (2H, H^5 , H^6), 1.71 d (1H, H^{7s}), 1.61 d (1H, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 174.96 (C=O), 157.75 (C=O), 133.57, 132.98, 130.20, 126.95, 114.48 (C arom), 134.57 (C^2 , C^3), 51.56 (C^7), 45.10 (C^1 , C^4), 44.38 (C^5 , C^6). Found, %: C 64.48; H 4.74; N 9.43. $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$. Calculated, %: C 64.43; H 4.70; N 9.40.

***N*-(*m*-Nitrobenzoylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (VI_e)**. Yield 92%, mp 114–116°C. IR spectrum, cm^{-1} : 3476, 3010, 1783, 1718, 1670, 1534, 1375, 1350, 1304, 740. ^1H NMR spectrum, δ , ppm: 8.70, 8.43, 8.21, 7.75 (4H, H arom), 6.18 m (2H, H^2 , H^3), 3.50 m (2H, H^1 , H^4), 3.39 m (2H, H^5 , H^6), 1.72 d (1H, H^{7s}), 1.63 d (1H, H^{7a}). ^{13}C NMR spectrum, δ , ppm: 174.78 (C=O), 148.44 (C=O), 133.57, 132.98, 130.22, 126.95, 122.54 (C arom), 134.61 (C^2 , C^3), 51.97 (C^7), 45.16 (C^1 , C^4), 44.37 (C^5 , C^6). Found, %: C 58.77; H 4.05; N 12.89. $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_5$. Calculated, %: C 58.72; H 3.98; N 12.84.

***N*-(*p*-Nitrobenzoylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (VI_f)**. Yield 51%, mp 127–129°C. IR spectrum, cm^{-1} : 3452, 3010, 1770, 1674, 1606, 1526, 1358, 854, 708. Found, %: C 58.67; H 4.08; N 12.88. $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_5$. Calculated, %: C 58.72; H 3.98; N 12.84.

***N*-(1-Adamantanecarbonylamino)bicyclo[2.2.1]hept-2-ene-endo,endo-5,6-dicarboximide (VI_g)**. Yield 68%, mp 214–216°C. Found, %: C 70.31; H 7.09; N 8.33. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_3$. Calculated, %: C 70.59; H 7.06; N 8.24.

***N*-(Benzoylamino)-exo-2,3-epoxybicyclo-[2.2.1]heptane-endo,endo-5,6-dicarboximide (VII)**. To a solution of 0.1 g (0.355 mmol) of hydrazide VI_b in 3 ml of 98% formic acid at 35–40°C while stirring was added

0.05 ml (0.43 mmol) of 30% hydrogen peroxide solution, and stirring was continued till completion of the reaction (TLC monitoring). The formic acid was removed in a vacuum, ice water was added to the residue, the precipitated crystals were filtered off, washed with water on the filter, dried, and recrystallized from 2-propanol. Yield 72%, mp 132–133°C. IR spectrum, cm^{-1} : 3410, 1705, 1655, 1540, 1310, 1290, 1190, 855. ^1H NMR spectrum, δ , ppm: 8.05 (NH), 7.80–7.45 (5H, H arom), 3.45 m (2H, H^1 , H^4), 3.25 m (2H, H^5 , H^6), 3.12 m (2H, H^2 , H^3), 1.71 d (1H, H^{7s}), 1.05 d (1H, H^{7a}). Found, %: C 64.54; H 4.79; N 9.31. $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$. Calculated, %: C 64.43; H 4.70; N 9.39.

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