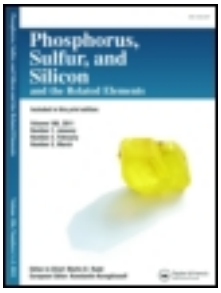

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BASE CATALYSED LOSSEN REARRANGEMENT OF N-SULPHONYLOXY-2,3-NORBORN-5-ENEDICARBOXIMIDE

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BASE CATALYSED LOSSEN REARRANGEMENT OF *N*-SULPHONYLOXY-2,3-NORBORN-5-ENEDICARBOXIMIDE

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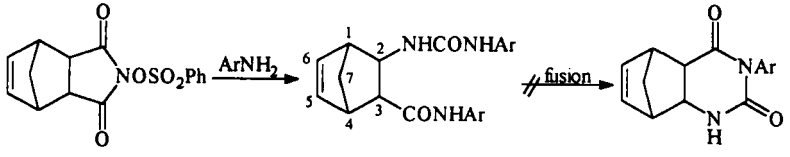
N-Sulphonyloxy-2,3-norborn-5-enedicarboximide **1** underwent Lossen rearrangement with some nucleophilic reagents, but it failed to undergo Beckmann rearrangement.

Keywords: N-Sulphonyloxynorbornene dicarboximide; amide ureas; diphenyl derivative of dicarboxylic acid anhydride

It is well known that *N*-Sulphonyloxydicarboximide derivatives undergo base-catalysed Lossen rearrangement,[1-7] so, the reaction of *cis*-*N*-phenylsulphonyloxy-5-norbornene-*endo*-2,3-dicarboximide (**1**) with amines was explored. The reaction of *cis*-*N*-phenylsulphonyloxy-5-norbornene-*endo*-2,3-dicarboximide (**1**) with aromatic amines in benzene at room temperature afforded *sym*-*N*-2-[arylcarbamoyl]-3-*endo*-norborn-5-enyl-*N*-aryl ureas **2a-c**, in yield ranging from 30% to 54%.



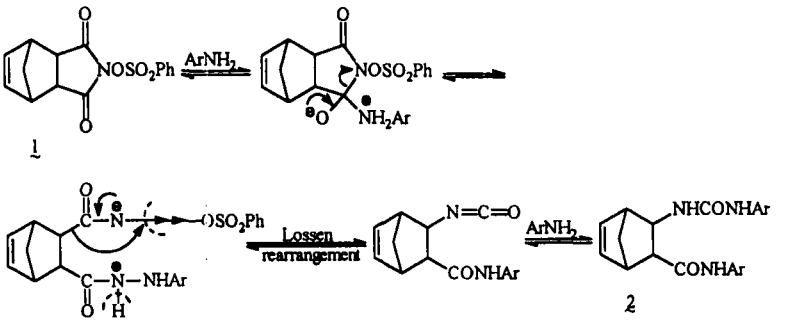
1 2 3

a, Ar=C_6H_5; b, Ar=$C_6H_4OCH_3(p)$; c,Ar=$C_6H_4CH_3(p)$

* Corresponding Author.

The structures of compounds (**2a-c**) were confirmed on the basis of elemental analyses as well as spectroscopic data. The ^{1}H-NMR spectrum of **2a** revealed a multiplet at δ 1.3–1.45 ppm assigned to the CH_2 protons at position 7, a doublet at δ 2.9–3.1 ppm integrated to CH protons at 1,4-positions, a multiplet at δ 4.7–4.85 ppm assigned to CH protons at 2,3-positions, a doublet at δ 5.8–5.9 ppm assigned to (CONH), a two multiplets at δ 6.1–6.15 and 6.4–6.5 ppm integrated to CH protons at 5,6-positions, a multiplet at δ 6.8–7.6 ppm integrated to ten protons assigned to the phenyl rings protons. Furthermore, compound **2a** showed also signals at δ 8.75 and 9.85 ppm integrated to the two protons assigned to (NHCONH). On the other hand, the ^{1}H-NMR spectra for **2b** and **2c** showed signals at δ 3.7 ppm assigned to the 6H of two -OCH_3 (**2b**) and at δ 2.2 ppm integrated to the six protons assigned to two CH_3 groups (**2c**). The other protons were detected in their expected location (cf. Experimental). Moreover, the IR spectra of **2a-c** showed the presence of ν NH in the region 3320–3340 cm^{-1}, 3240–3250 cm^{-1} and ν C=O in the region 1650–1660 cm^{-1}, 1630–1640 cm^{-1} and the mass spectrum for **2c** showed molecular ion at m/z 375. This ion underwent the fragmentation given in experimental.

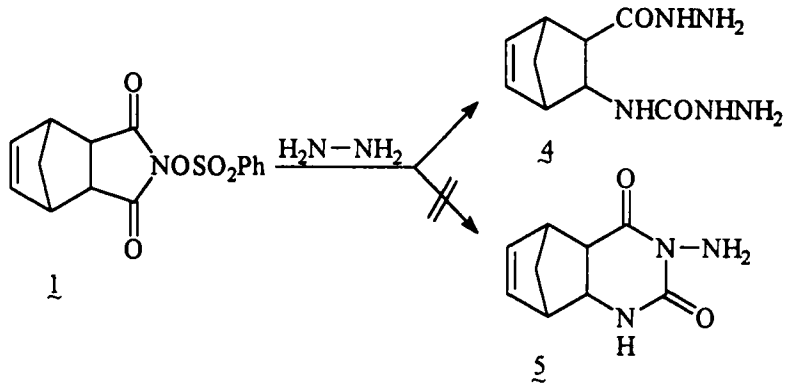
The reaction of *N*-sulphonyloxydicarboximide (**1**) with aromatic amines may be explained by the following mechanism:



Attempts to cyclize **2** by heating over its melting point to give the expected 3-aryl-*endo*-norbornene-2,4-pyrimidinones **3** were unsuccessful.[4]

Hydrazinolysis of *cis*-*N*-phenylsulphonyloxy-5-norbornene-*endo*-2,3-dicarboximide (**1**) at room temperature in benzene yielded-3-semicarbazido-*endo*-5-norbornene-2-carboxylic acid hydrazide

4 in 36% yield. This reaction was failed to give the expected 3-aminopyrimidine-2,4-dione **5** as reported previously.[4]

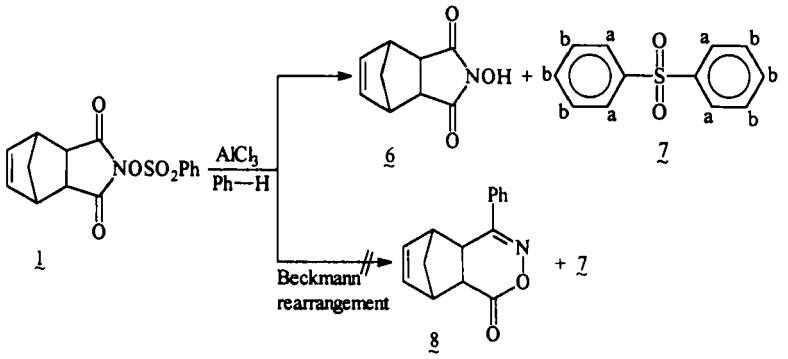


The structure of **4** was established on the basis of elemental and spectroscopic data. The ^{1}H-NMR spectrum revealed singlet signal at δ 4.0 ppm integrated to the protons assigned to the amino groups and disappeared on addition of D_2O, whereas the NHCONH and CONH are detected as a singlet signals at δ 6.4, δ 6.9 and 8.95 ppm and these signals are disappeared on addition of D_2O. The other protons were detected in their expected locations (cf. Experimental). Moreover, the mass spectrum showed molecular ion at m/z 225. This ion underwent the fragmentation given in experimental.

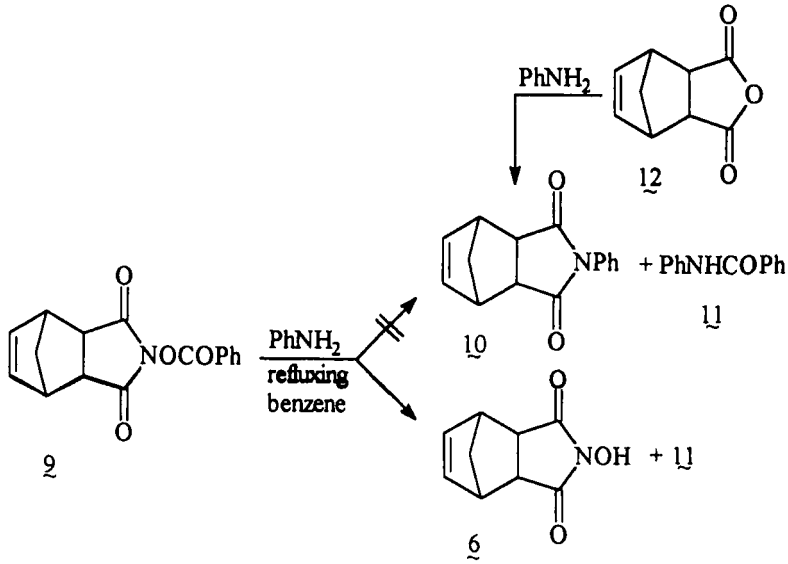
Cis-N-Phenylsulphonyloxy-5-norbornene-*endo*-2,3-dicarboximide (**1**) failed to undergo Lewis acid catalyzed Beckmann rearrangement in the presence of aromatic hydrocarbon substrate. It gave *cis-N*-hydroxy-5-norbornene-2,3-dicarboximide **6** in 9% yield and diphenylsulphone **7** in 87% yield instead of the expected aryloxazinone **8** and diarylsulphone **7** as reported previously.[6]

The structure of **6** and **7** were identical in all aspects (elemental analysis, mp, IR and ^{1}H-NMR) with that previously prepared.[1,6]

The reaction of *N*-benzoyloxy-5-norbornene-2,3-dicarboximide.[1] (**9**) with aniline to give *cis-N*-phenyl-5-norbornene-*endo*-2,3-dicaroximide (**10**) was unsuccessful.[8] Instead, **9** reacted with aniline in refluxing benzene and gave a mixture of *N*-hydroxy-5-norbornene-2,3-dicarboximide **6** and benzanilide **11**. The formation of **6** and **11** was attributed to the preferntial nucleophilic attack by an amino group on the exocyclic rather



than a ring carbonyl group, and benzene was used in this reaction as an acyl transfer agent.[9]

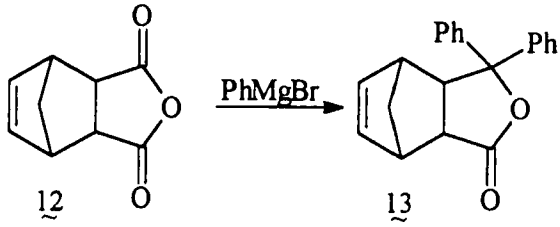


On the other hand, *cis-N*-phenyl-5-norbornene-*endo*-2,3-dicarboximide (**10**) could be prepared in 88% yield *via* the reaction of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid anhydride **12** with aniline in pyridine or by fusion at 150°C.

Structural reasonings for **10** was based on compatible analytical and spectral data. The ^{1}H-NMR spectrum revealed a multiplet at δ 7.1–7.5

ppm integrated to the five protons assigned to the phenyl ring protons. Furthermore, the mass spectrum showed molecular ion at m/z 239.

The reaction of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid anhydride **12** with phenylmagnesium bromide afforded diphenyl derivative 13 in 40% yield.



12 13

Structural reasoning for **13** was based upon elemental and spectroscopic evidences. The ^{1}H-NMR showed a multiplet signal at δ 7.15–7.55 ppm integrated to the ten protons assigned to the phenyl rings protons. The mass spectrum showed molecular ion at m/z 203.

EXPERIMENTAL

All melting points are uncorrected, the IR spectra were run on a Pye-Unicam SP 3–100 spectrophotometer using KBr disc technique (wave numbers in cm^{-1}). The ^{1}H-NMR spectra were recorded on a 250 MHz varian NMR spectrophotometer using TMS as internal standard: chemical shifts are given in ppm (δ-scale). Mass spectra on Jeol-JMS 600 spectrometer. Melting points, yields and analytical data of all newly synthesized compounds are given in Table I.

Reaction of N-sulphonyloxy-5-norbornene-endo-2,3-dicarboximide (1) with aromatic amines. Formation of 2a-c

Aromatic amine (0.04 mol) was added to a stirred suspension of *N*-sulphonyloxy derivative **1** (3.2 g, 0.01 mol) in dry benzene (30 mL). The reaction mixture was stirred for 6 h at room temperature. The solvent was removed under reduced pressure. The residue washed several times with petroleum

ether 60–80°C, then with ether and the solid product was crystallized from ethanol to give sym. *N*-2-(arylcarbamoyl)-3-*endo*-norborn-5-enyl)-*N*-aryl ureas **2a-c**. The IR spectra (KBr) showed presence of ν NH in the region 3320–3340 cm^{-1}, 3240–3250 cm^{-1}, ν C=O in the region 1650–1660 cm^{-1}, 1630–1640 cm^{-1} and ν CH, aliph. at 2960 cm^{-1} and 2830–2860 cm^{-1}.

TABLE I Melting points, Yields and Analytical Data of the Prepared Compounds

Comp. No.	*M.P, °C*	*Yield %*	*Molecular formula (M. wt)*	*Elemental Analysis Calc. / Found.*		
				% C	*% H*	*% N*
2a	246–248	30	$C_{21}H_{20}N_3O_2$	72.60	6.09	12.06
			(346)	73.04	6.08	12.10
2b	213–216	54	$C_{23}H_{25}N_3O_4$	67.80	6.18	10.31
			(407)	68.05	6.33	10.39
2c	227–229	45	$C_{23}H_{25}N_3O_2$	73.58	6.71	11.19
			(375)	73.64	6.83	11.05
4	192–194	36	$C_9H_{15}N_5O_2$	47.99	6.71	31.09
			(225)	47.59	6.36	31.03
10	139–140	88	$C_{15}H_{13}NO_2$	75.31	5.44	5.86
			(239)	75.50	5.48	6.09
13	183–185	40	$C_{21}H_{18}O_2$	83.42	5.99	–
			(302)	83.09	6.03	–

Compound 2a

^{1}H-NMR (DMSO-d_6): δ 1.3–1.45 (m, 2H, CH_2 at position 7), 2.9–3.1 (d, 2H, CH-protons at 1,4-positions), 4.7–4.85 (m, 2H, CH-protons at 2,3-positions), 5.8–5.9 (d, 1H, CONH), 6.1–6.15, 6.4–6.5 (2m, 2H, CH-protons at 5,6-positions), 6.8–7.6 (m, 10H, Ar-H), 8.75 (s, 1H, NHCONH) and 9.85 (s, 1H, NHCONH).

Compound 2b

^{1}H-NMR (DMSO-d_6): δ 1.3–1.45 (m, 2H, CH_2 at position 7), 2.9–3.05 (d, 2H, CH-protons at 1,4-positions), 3.7 (s, 6H, $2OCH_3$), 4.65–4.8 (m, 2H, CH-protons at 2,3-positions), 5.65–5.75 (d, 1H, CONH), 6.05–6.15, 6.4–

6.5 (2m, 2H, CH-protons at 5,6-positions), 6.7–7.45 (m, 8H, Ar-H), 8.55 (s, 1H, NHCONH) and 9.7 (s, 1H, NHCONH).

Compound 2c

^{1}H-NMR (DMSO-d_6): δ 1.3–1.45 (m, 2H, CH_2 at position 7), 2.2 (s, 6H, $2CH_3$), 2.9–3.1 (d, 2H, CH-protons at 1,4-positions), 4.65–4.8 (m, 2H, CH-protons at 2,3-positions), 5.7–5.8 (d, 1H, CONH), 6.05–6.15, 6.4–6.5 (2m, 2H, CH-protons at 5,6-positions), 6.9–7.45 (m, 8H, Ar-H), 8.65 (s, 1H, NHCONH) and 9.75 (s, 1H, NHCONH); MS: m/z(%) = 375(3) [M^+], 309(70), 290(7), 242(13), 218(1), 213(6), 203(76), 185(5), 176(50), 160(10), 149(11), 133(71), 119(8), 107(100), 91(49), 77(47.5), 66(47), 51(29), 39(36).

Reaction of hydtrazine hydrate with 1. Formation of 4

Hydrazine hydrate (2 mL, 0.04 mol) was added to a suspension of *N*-sulphonyloxy derivative **1** (3.2 g, 0.01 mol) in dry benzene (30 mL). The reaction mixture was stirred at room temperature for 1 h. The precipitated material was washed with petroleum ether 60–80°C and crystallized from ethanol to give 3-semicarbazido-*endo*-5-norbornene-2-carboxylic acid hydrazide **4**, IR (KBr) spectrum showed bands at 3390, 3220 cm^{-1} (NH), 2960, 2860 (CH, aliph.) and at 1650 br. (C=O's); ^{1}H-NMR (DMSO-d_6): δ 1.3 (s, 2H, 7-CH_2), 2.9 (s, 2H, 1,4-CH), 2.95 (s, 1H, 3-CH), 4.0 (s, 4H, 4NH, disappeared on addition of D_2O), 4.5 (m, 1H, 2-CH), 6.05 (m, 1H, 5-CH), 6.3 (m, 1H, 6-CH), 6.4 (d, 1H, NH, disappeared on addition of D_2O), 6.9 (s, 1H, NH, disappeared on addition of D_2O) and 8.95 (s, 1H, NH, disappeared on addition of D_2O); MS: m/z(%) = 225(2) [M^+], 207(1), 194(39), 177(2), 167(4.5), 159(23), 150(6), 141(7), 136(14), 128(100), 113(10), 101(10), 96(53), 91(31.5), 84(12), 77(25), 66(78), 53(16), 39(45).

Action of anhydrous $AlCl_3$ on N-sulphonyloxy-5-norbornene-endo-2,3-dicarboximide 1 in aromatic hydrocarbon. Formation of 6 and 7

To a suspension of *N*-sulphonyloxy derivative **1** (3.2 g, 0.01 mol) in dry benzene (30 mL), anhydrous $AlCl_3$ (2.7 g, 0.02 mol) was added with stirring during 5 min. The reaction mixture was heated under reflux for 2 h.

The complex formed was decomposed with 10 mL diluted hydrochloric acid (1:1). The solid obtained was crystallized from ethanol to give a product which it was shown to be diphenylsulphone **7**; yield 1.1 g (87%), mp 128°C; IR (KBr): 1440 cm^{-1} (SO_2), 3050 cm^{-1} (CH, arom.); ^{1}H-NMR ($CDCl_3$): δ 7.45–7.6 (m, 6H, Ar-H_b), 7.9–8.0 (m, 4H, Ar-H_a); MS: m/z(%) = 218(44) [M^+], 203(0.5), 185(2), 173(3), 152(9), 141(4), 125(100), 109(4), 97(46), 91(3), 77(60), 65(11), 51(44), 45(2), 39(7.5). The residue which does not dissolve in ethanol during crystallization to obtain **7**, was dissolved in 10 mL concentrated hydrochloric acid, neutralized with sodium bicarbonate solution and extracted with ethylacetate. The extract was evaporated under reduced pressure and the solid produced was crystallized from benzene to give 0.15 g (9%) of cis-*N*-hydroxy-5-norbornene-*endo*-2,3-dicarboximide (**6**). It was identical in all aspects (elemental analysis, mp, IR and ^{1}H-NMR) with that previously prepared.[1]

Reaction of N-hydroxy-5-norbornene-endo-2,3-dicarboximide with benzoyl chloride. Formation of N-benzoyloxy-5-norbornene-endo-2,3-dicarboximide (9)

To *N*-hydroxy derivative (1.8 g, 0.01 mol) in 10 mL dry pyridine, benzoyl chloride (1.4 mL. 0.01 mol) was added with stirring. The reaction mixture was further stirred for 20 min. The precipitate obtained was filtered off, washed with sodium bicarbonate solution then with water and dried. The product was crystallized from benzene-petroleum ether (1:4), yield 1.8 g (63%), mp 139–141°C, Lit.[1], mp 143–144°C, IR (KBr): 1793, 1770, 1738 cm^{-1} (C=O's), MS: m/z(%) = 283(2) [M^+], 249(2), 231(0.5), 218(1), 181(1), 161(1), 148(2), 139(3), 129(2), 120(11), 113(1.5), 106(30), 105(100), 96(9), 92(19), 91(30), 82(17), 78(19), 77(38), 76(15), 70(15), 66(25), 65(22), 63(14), 54(15), 52(13), 51(23), 50(18), 39(18).

Reaction of N-benzoyloxy-5-norbornene-endo-2,3-dicarboximide (9) with aniline. Formation of 6 and 11

A mixture of *N*-benzoyloxy **9** derivative (1.5 g, 0.005 mol) and aniline (1.8 mL, 0.02 mol) in 20 mL dry benzene was refluxed for 4 h. The reaction mixture was cooled whereby a precipitate was formed to give 0.9 g of benzanilide **11**. It was found that compound **11** was identical with an authentic sample[8] (elemental analysis, mp and IR). The mother liquor of

this reaction gave a product which it was shown to be N-hydroxy derivative **6**, by comparing its spectral data and mixed mp with authentic sample.[1]

Reaction of 5-norbornene-endo-2,3-dicarboxylic acid anhydride 12 with aniline. Formation of 10

Method A

A mixture of of 5-norbornene-*endo*-2,3-dicarboxylic acid anhydride **12** (1.65 g, 0.01 mol) and aniline (1 mL, ~ 0.01 mol) in 10 mL dry pyridine was refluxed for 2 h. The reaction mixture was cooled and diluted with water whereby a white precipitate was formed. The product was filtered off and it crystalllized from benzene-petroleum ether (1:4) to give 2.1 g (88%) *N*-phenyl-5-norbornene-*endo*-2,3-dicarboximide **10**, IR (KBr): 1790, 1765, 1700 (C=O's), ^{1}H-NMR ($CDCl_3$): δ 1.55–1.85 (q, 2H, 7-CH_2), 3.35–3.55 (m, 4H, CH-protons at positions 1,2,3,4), 6.3 (s, 2H, CH-protons at positions 5,6), 7.1–7.5 (m, 5H, Ar-H); MS: m/z(%) = 239(59) [M^+], 210(2), 173(100), 145(13), 136(2), 129(36), 117(21), 103(17.5), 91(42), 77(20), 66(73), 54(21), 39(34).

Method B

5-Norbornene-*endo*-2,3-dicarboxylic acid anhydride **12** (1.65 g, 0.01 mol) was heated with aniline (3.7 mL, 0.04 mol) at 150°C for 1 h. The mixture was cooled, washed with petroleum ether 40–60°C several times. The solid formed was identical as product obtained in mehod *A* in all aspects (elemental analysis, mp, IR, ^{1}H-NMR and MS).

Reaction of 5-norbornene-endo-2,3-dicarboxylic acid anhydride 12 with Grignard reagent. Formation of 13

To a well stirred solution of anhydride **12** (1.5 g, ~ 0.01 mol) in dry ether (30 mL) was added a solution of Grignard reagent; prepared by the usual way from bromobenzene (0.01 mol), at room temperature and stirring was continued for half an hour, then refluxed half an hour. The cold reaction mixture was added to crushed ice containing 5 mL concentrated hydrochloric acid, the product formed, washed with water, dried and crystallized from ethanol, yield 1.1 g (40%); IR (KBr): 1750 cm^{-1} (C=O); ^{1}H-NMR

($CDCl_3$): δ 1.4–1.7 (m, 2H, 7-CH_2), 3.15, 3.35 (2s, 2H, CH at 1,4-positions), 3.45–3.55 (m, 1H, CH at position 3), 3.85–3.95 (m, 1H, CH at position 2), 5.15–5.2, 6.05–6.15 (2m, 2H, CH at positions 5,6), 7.15–7.55 (m, 10H, Ar-H); MS: m/z(%) = 302(30) [M^+], 274(14), 258(17), 236(100), 228(6), 209(14), 191(73), 178(32), 165(42), 159(63.5), 143(33), 131(66), 120(37), 105(62), 91(55), 82(14), 77(52), 66(91), 55(13), 51(32), 39(29).

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