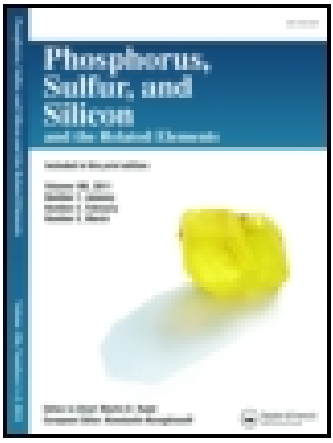

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A CONVENIENT METHOD FOR BROMOSULFENYLATION: REACTIONS OF SULFENAMIDES WITH OLEFINS IN THE PRESENCE OF $POBr_3$

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A general method for the one-pot transformation of alkenes into abromoalkyl-arylsulfides has been proposed based on the sulfenylation reaction by means of sulfenamides in the presence of phosphorus oxibromide. The plausible reaction mechanism and the results of reactions with a number of model alkenes such as cyclohexene, 1-heptene, norbornene and other from the bicyclo[2.2.1]heptane series are discussed.

Keywords: sulfenamides; sulfenylation; phosphorus oxohalides

INTRODUCTION

The sulfenylation reactions, the processes of electrophilic incorporation of the RS fragment to a molecule, are known for more than 100 years[1]. The most useful as sulfenylating agents are sulfenyl halides; other derivatives of sulfenic acid, such as sulfenyl carboxylates, sulfenamides and sulfenates are less frequently used[2–6]. Sulfenyl halide addition to C=C double bond is a classical model AdE reaction. There is a variety of works dealing with investigation of the mechanism and products of these reactions[7]. However, with some exceptions, all works on the issue are con-

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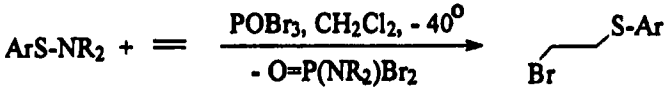
cerned with arylsulfenyl chlorides, and the data about other haloanhydrides of sulfenic acid are presented by few articles. Perhaps, this selection is due to availability and higher stability of sulfenyl chlorides as compared with the corresponding fluorides[6], iodides[9], and, to a lesser degree, bromides[10].

RESULTS AND DISCUSSION

We have found that arylsulfenamides can react with POBra at –40 °C to form complexes which are capable of electrophilic addition to alkene double bonds. After the phosphorus-containing products were removed on a silica gel column, the reaction mixture was identified as the bromosulfenylation product, based on the ^{1}H NMR spectra. The products were further purified by preparative TLC method.



1a-d **2-8**

1a, Ar = C_6H_5, R_2 = $(CH_2)_2O(CH_2)_2$;

1b, Ar = 2-NO_2-C_6H_4, R_2 = $(CH_2)_2O(CH_2)_2$;

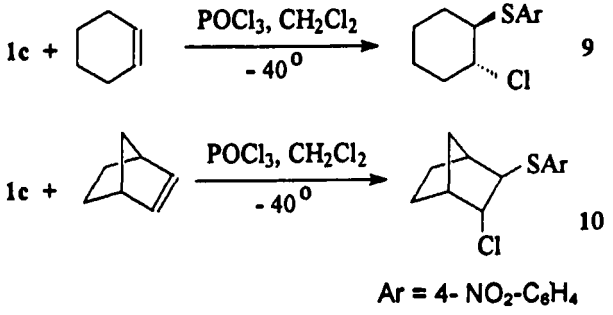
1c, Ar = 4- NO_2-C_6H_4, R_2 = $(CH_2)_2O(CH_2)_2$;

1d, Ar = 4- NO_2-C_6H_4, R = CH_3

The structures and yields of products obtained are presented in table I.

The same reaction of sulfenamides with olefins, activated by $POCl_3$, give chlorosulfides which are the analogs of arylsulfenyl chloride addition products.

The reaction is the alternative to the ArS-Hal addition to olefins in its result. Nevertheless, the details of the reaction proceeding allow us to reject the sulfenyl halide intermediate formation in the process under investigation. First, sulfenyl halide formation upon mixing of POBrs and sulfenamide in the absence of olefin was not detected by means of TLC. Second, sulfenyl halides addition to olefins, as a rule, is a slow process (taking several hours at room-temperature or upon heating) and is accom-



panied by formation of considerable amounts of diaryldisulfides, which are products of radical degradation of sulfenylating agents[11]. At the same time, the reaction was competed within several minutes at – 40 °C and the formation of by-products was virtually negligible.

The reagent, arylsulfenamide- $POBr_3$ complex, is stable at room temperature for several hours in the CH_2Cl_2 solution. Complex Ib-$POBr_3$ was isolated as the spreading solid after mixing of reactant solutions in THF. In the CH_2Cl_2 solution, the reagent slowly degrades to form diaryldisulfide, Br_2 and $O{=}P(NR_2)Br_2$.

The structure of the formed complex was examined by ^{13}P NMR method In the spectrum of sulfenamide 1c and $POBr_3$ mixture additional signals were found (-50.2 and –28.0 ppm) besides the $POBr_3$ signal at –101.3 ppm. In another synthesis using $POBr_3$ and morpholine it has been proved that the peak at –28 0 ppm is the signal due to $0{=}P(NF_2)Br_2$. The signal at –50.2 disappeared after olefin addition to the reaction mixture, thus being attributed to the sulfenylation complex.

We assume that, first, the reaction proceeds as acid-base interaction between POBrs as a Lewis acid and the nitrogen atom of sulfenamide, yielding B or C (see chart 1). Using AM-1 method the structure of the phenylthiomorpholine- $POBr_3$ complex was calculated. The structure with the optimised geometry was shown to be close to C.

Further, the complete substitution of a bromine atom at the phosphorus atom takes place, forming the ammonium salt D. After this, intermediate D can add to olefin giving trans – 1,2-bromo-sulfide. The following finding testifies that it is the D species which attacks the olefin: calculated charges on the sulfur atom are 0.059 and 0.064 for structures B and C, respectively, which are nearly the same as that for the starting sulfenamide (0.052). Cal-

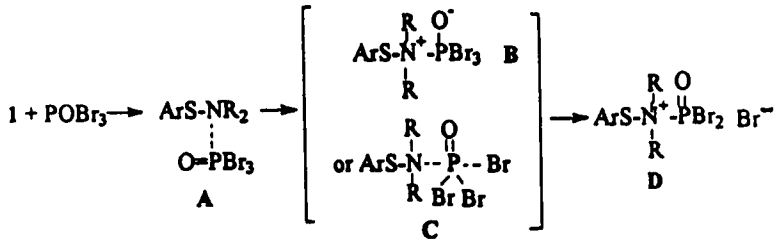
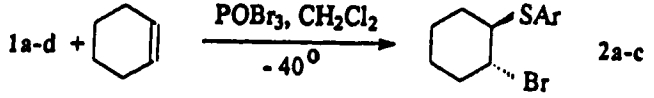


CHART 1

culation made for structure D gives the much greater positive charge on sulfur, namely 0.182 and, which is more surprising, the sulfur (not nitrogen) atom is the electrophilic site of the molecule. Moreover, the semi-empirical calculations show that LUMO is localised on the O-P-Br fragment for all of the structures B, C, D and, therefore, the reaction under consideration is not an orbital-controlled process.

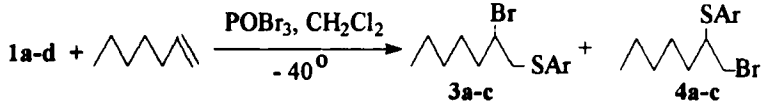
Cyclohexene is a convenient model for studying the stereochemistry of addition reactions. The addition of sulfenamides **1a-d** to this olefin in the presence of $POBr_3$ have been found to occur stereoselectively and results in trans-1,2-adducts, in agreement with the electrophilic addition mechanism. The broadening of the ^1H NMR signals for a-protons at both arylthio- and bromo- groups on transition from nonpolar (C_6D_6) to more polar ($CDCl_3$) solvent unequivocally suggests the trans-configuration of bromosulfide 1c..



2a, Ar = C_6H_5, 2b, Ar = 2-NO_2-C_6H_4, 2c, Ar = 4-NO_2-C_6H_4

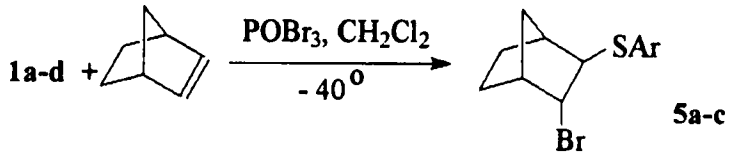
1-Heptene as a terminal olefin, was chosen for determination of reaction regioselectivity. It is known that addition of sulfenyl chlorides to terminal olefins usually proceed without regioselectivity, with the formation of both possible products The addition products formed in accordance with the Markovnikov rule is assumed to be more thermodynamically stable. In the same time, the anti-Markovnikov product is formed under the conditions

reaction kinetically controlled [12]. After the reaction of sulfenamide **1a-d** with 1-heptene at −40°C, the mixture of both Markovnikov **3a-c** and anti-Markovnikov **4a''c** products has been isolated. In the case of compounds 3c and 4c their NMR spectra were measured again one month after their preparation and only the adduct 3c (Markovnikov's) was found. This means that compounds 3 and 4 can be transformed into each other.



3a, 4a, Ar = C_6H_5, **3b, 4b**, Ar = 2-NO_2-C_6H_4, **3c, 4c**, Ar = 4-NO_2-C_6H_4

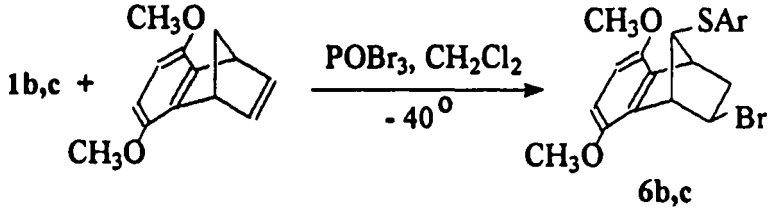
To study the addition to norbornene was interesting for determination of the reagent's effective electrophilicity, the ability to cause a carbon skeleton rearrangements and the other phenomena typical of carbocation processes[13]. In this reaction only formation of 1,2-addition adducts **5a-c** has been observed. Neither the reaction conducted in the presence of $LiClO_4$ nor the interaction in a more polar solvent (CH_3CN) lead to formation of the rearrangement products. The attempt to isolate the conjugated addition products were made by means of $Hg(OCOCH_3)_2$ adding to the reaction mixture. But this reaction was resulted in the formation only bromsulfide **5.**



5a, Ar = C_6H_5, **5b**, Ar = 2-NO_2-C_6H_4, **5c**, Ar = 4-NO_2-C_6H_4

However, the products of the Wagner-Meerwein rearrangement have been obtained when an other olefin from the bicyclo[2.2.1]heptane series, namely, 3,6-dimethoxy-benzonorbornadiene, was put into reaction. The interaction of sulfenamides **1b** and **1c** with this olefin in the presence of $POBr_3$ results in the formation of corresponding bromosulfides, having the structure of 2,7-disubstituted norbornanes. The reduction of yields in these

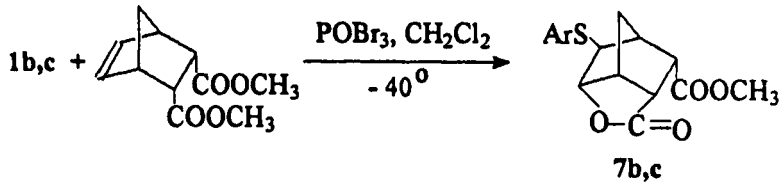
cases, perhaps, connected with the formation of by-products of sulfenylation of the substrate aromatic ring, activated by the methoxy substitution.



6b,c

6b, Ar = 2-NO_2-C_6H_4, **6c**, Ar = 4-NO_2-C_6H_4

Products of the conjugated addition we can obtain using as a substrate other olefin from the bicyclo[2.2.1]heptane series, 5,6-diendo-norborn-2-enedimethylcarboxylate. The own carbomethoxy group of the substrate in this example acts as external nucleophile and γ-lactones **7b, c** have been isolated as the products.

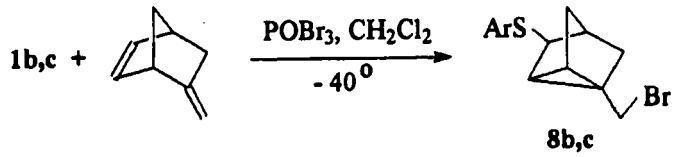


7b,c

7b, Ar = 2-NO_2-C_6H_4, **7c**, Ar = 4-NO_2-C_6H_4

The stereochemistry of electrophilic agents addition to 5-methylenenorbornene has not been yet established. It is known that its sulfenylation by arylsulfenyl chlorides results in nortricyclene structure product, besides, the authors supposed the beginning endo-attack of electrophile to the endocyclic double bond as the most likely[14]. We have made a careful NMR investigation of the methylenenorbornene bromosulfenylation products with the use of the nuclear Overhauser effect (NOE). Under the irradiation of the HCS-proton signal (3.42 ppm) the significant increasing of H_6 (1.67 ppm) and H_3 (1.53 ppm) signals intensity and the absence of the response on the H_7 (2.02 and 1.50 ppm) were observed. The irradiation of the CH_2Br-group multiple (3.37 ppm) results in the increasing of the H_3H_4

(1.49 ppm) and H_6 (2 protons, 1.67 and 1.62 ppm) signals intensity. These data demonstrated that, at least in the this reaction, not *endo,* but exo-attack of sulfenylating species to norbornene double bond and the final formation of the nortricyclane structure take place.



8b,c

8b, Ar = 2-NO_2-C_6H_4, **8c**, Ar = 4-NO_2-C_6H_4

TABLE I The products of arylsulfenamides reactions with alkenes in the presence of $POBr_3$

Alkene	*ArS-NR$_2$*	*Product*	*Yield, %*
Cyclohexene	**1a**	**2a**	72
	1b	**2b**	95
	1c	**2c**	80
	1d	**2c**	85
1-Heptene	**1a**	**3a + 4a**	81
	1b	**3b + 4b**	92
	1c	**3c + 4c**	95
	1d	**3c + 4c**	62
Norbornene	**1a**	**5a**	79
	1b	**5b**	99
	1c	**5c**	75
	1d	**5c**	76
2,6-dimethoxy-benzonorbornadiene	**1b**	**6b**	69
	1c	**6c**	45
5,6-diendo-norborn-2-ene-dimethyl-carboxylate	**1b**	**7b**	86
	1c	**7c**	98
5-methylene-norbornene	**1b**	**8b**	92
	1c	**8c**	78

In conclusion we would noted that the proposed method for alkenes bromosulfenylation via generating of high-reactive arylsulfenamide-$POBr_3$ complexes can be a convenient synthetical method. The stability of the starting compounds and the simplicity of the experimental procedure make this method a suitable one for practical use.

EXPERIMENTAL

General

The purity of the reaction products was monitored by TLC. The preparative separation of the reaction product was carried out by TLC with Silufol plates using ethyl acetate – petroleum ether (1:3) as the eluent. All solvents were dried by standart technics. NMR spectra were recorded in $CDCl_3$.. IR spectra were obtained in nujol.

Reactions between arylsulfenamides and alkenes in the presence of $POHal_3$ (general procedure)

An equivalent amount of $POHal_3$ in absolute $CH_2Cl_2$was slowly added to a solution of sulfenamide in CH_2Cl_2 at –40 °C and then 1.5-fold excess of alkene in the same solvent was added. The mixture was heated to the room temperature, passed through a column-filter with silica gel (h = 5 cm). After evaporation of the solvent the residue was chromatographed.

trans-2-Phenylthio-cyclohexylbromide (2a)

R_f 0.92. ^1H NMR δ 7.5–7.15 (m, 5H), 4.28 (m, 1H), 3.52 (m, 1H), 2.45–0.90 (m, 8H). Anal. Calcd. for $C_{12}H_{15}BrS$: C 53.14; H 5.57. Found: C 53.09; H 5.70.

trans-2-(2-Nitrophenylthio)-cyclohexylbromide (2b)

R_f 0.85. ^1H NMR δ 8.08 (m, 1H), 7.58 (m, 1H), 7.43 (m, 1H), 7.30 (m, 1H), 4.40 (m, 1H), 3.75 (m, 1H), 2.50–1.20 (m, 8H). Anal. Calcd. for $C_{12}H_{14}BrNO_2S$: C 45.58; H 4.46; N 4.43. Found: C 45.53; H 3.98; N 4.00.

trans-2-(4-Nitrophenylthio)-cyclohexylbromide (2c)

R_f 0.92. ^{1}H NMR δ 8.15 (d, 2H, J = 9 Hz), 7.38 (d, 2H, J = 9 Hz) 4.28 (m, 1H), 3.72 (m, 1H), 2.45–0.90 (m, 8H). ^{13}C NMR δ 22.28, 22.51, 28.66, 32,30, 50.43, 53.25, 123.70, 124.00, 128.4. Anal. Calcd. for $C_{12}H_{14}BrNO_2S$: C 45.58; H 4.47; N 4.43. Found: C 45.43; H 4.58; N 4.28.

1-Phenylthio-hexyl-2-bromide (3a) and 2-Phenylthio-hexyl-1-bromide (4a)

R_f 0.90. ^{1}H NMR (for mixture) δ 7.38–7.10 (m, 5H of comp. **3a** and **4a**), 3.98 (m, 1H of comp. **3a**), 3.47 (dd, 2H of comp. **3a**, J = 4.9, 13.9 Hz), 3.17 (dd, 2H of comp. **4a**, J = 9.6, 13.8 Hz), 3.12 (m, 1H of comp. **4a**), 2.08–1.10 (m, 8H of comp. **3a** and **4a**), 0.82 (q, 3H of comp. **3a** and **4a**, J = 7.0 Hz). ^{1}H NMR (for **3a**) δ 7.38–7.10 (m, 5H), 3.98 (m, 1H), 3.47 (m, 2H, J = 4.9, 13.9 Hz), 2.08–1.10 (m, 8H), 0.82 (q, 3H). Anal. Calcd. for $C_{13}H_{19}BrS$: C 54.36; H 6.67. Found: C 54.11; H 6.18.

1-(2-Nitrophenylthio)-hexyl-2-bromide (3b) and 2-(2-Nitrophenylthio)-hexyl-1-bromide (4b)

R_f 0.94. ^{1}H NMR δ 8.15 (m, 1H of comp. **3b** and **4b**), 7.58 (m, 1H of comp. **3b** and **4b**), 7.43 (m, 1H of comp. **3b** and **4b**), 7.25 (m, 1H of comp. **3b** and **4b**), 4.07 (m, 1H of comp. **3b**), 3.55 (dd, 2H of comp. **3b**, J = 4.0, 10.2 Hz), 3.32 (m, 1H of comp. **4b**), 3.23 (dd, 2H of comp. **4b**, J = 3.8, 13.5 Hz), 2.50–1.20 (m, 8H of comp. **3b** and **4b**), 1.08 (q, 3H, of comp. **3b** and **4b**, J = 7.0 Hz). Anal. Calcd. for $C_{13}H_{18}BrNO_2S$: C 46.99; H 5.46; N 4.21. Found: C 46.50; H 4.98; N 4.20.

1-(4-Nitrophenylthio)-hexyl-2-bromide (3c) and 2-(4-Nitrophenylthio)-hexyl-1-bromide (4c)

R_f 0.90. ^{1}H NMR δ 8.12 (d, 2H of comp. **3c** and **4c**, J = 9.0 Hz). 7.38 (d, 2H of comp. **3c** and **4c**, J = 9.0 Hz), 4.05 (m, 1H of comp. **3c**), 3.63 (dd, 2H of comp. **3c**, J = 5.0, 13.9 Hz), 3.56 (dd, 2H of comp. **4c**, J = 3.5, 10.0 Hz), 3.51 (m, 1H of comp. **4c**), 2.15–1.20 (m, 8H of comp. **3c** and **4c**), 0.90 (q, 3H of comp. **3c** and **4c**, J = 7.0 Hz). Anal. Calcd. for $C_{13}H_{18}BrNO_2S$: C 46.99; H 5.46; N 4.21. Found: C 47.18; H 5.50; N 4.21.

exo-2-Phenylthio-endo-3-norbornylbromide (5a)

R_f 0.93. ^{1}H NMR δ 7.25–6.95 (m, 5H), 3.88 (m, 1H), 3.00 (dd, 1H, J = 2.7, 4.0 Hz), 2.51 (m, 1H), 2.45 (m, 1H), 2.30–1.14 (m, 6H). Anal. Calcd. for $C_{13}H_{15}BrS$: C 55.13; H 5.34. Found: C 55.14; H 5.48.

exo-2-(2-Nitrophenylthio)-endo-3-norbornylbromide (5b)

R_f 0.93. ^{1}H NMR δ 8.10 (d, 1H, J = 7.5 Hz), 7.50–7.05 (m, 3H), 4.05 (m, 1H), 3.15 (dd, 1H, J = 2.3, 4.2 Hz), 2.60 (m, 1H), 2.48 (m, 1H), 2.37–1.10 (m, 6H). Anal. Calcd. for $C_{13}H_{14}BrNO_2S$: C 47.56; H 4.30; N 4.27. Found: C 48.00; H 4.29; N 3.99.

exo-2-(4-Nitrophenylthio)-endo-3-norbornylbromide (5c)

R_f 0.84. ^{1}H NMR δ 8.01 (d, 2H, J = 8.8 Hz), 7.20 (d, 2H, J = 8.8 Hz), 3.95 (m, 1H) 3.24 (dd, 1H, J = 3.8, 8.0 Hz), 2.46 (m, 1H), 2.40 (m, 1H), 2.30–1.14 (m, 6H). Anal. Calcd. for $C_{13}H_{14}BrNO_2S$: C 47.56; H 4.30; N 4.27. Found: C 47.78; H 4.33; N 4.24.

3, 6-Dimethoxy-sin-1 1-(2-nitrophenylthio)-tricyclo[6.0.1.0$^{[2, 7]}$] undeca-2(7), 3, 5-trienyl-exo-9-bromide (6b)

M.p. 60–61 °C, yellow crystals from heptane. R_f 0.53. ^{1}H NMR δ 8.09 (m, 1H), 7.51 (m, 2H), 7.25 (m, 1H), 6.15 (dd, 2H, J = 10.7, 16.0 Hz), 3.99 (m, 1H), 3.78 (s, 1H), 3.76 (m, 1H), 3.73 (m, 1H), 3.72 dd, 1H, J = 4.5, 8.0 Hz), 3.65 (d, 1H, J = 4.5 Hz), 2.79 (dt, 1H, J = 4.5, 14.0 Hz), 2.17 (dd, 1H, J = 8.0, 14.0 Hz). ^{13}C NMR δ 36.58, 45.09, 45.64, 52.31, 55.58, 55.62, 61.92, 110.49, 110.73, 124.98, 125.70, 128.02, 132.90, 133.29, 134.20, 138.20, 147.26, 147.67. Anal. Calcd. for $C_{19}H_{18}BrNO_4S$: C 52.30; H 4.16; N 3.21. Found: C 52.69: H 4.07; N 3.30.

3,6-Dimethoxy-sin-1 1-(4-nitrophenylthio)-tricyclo[6.0.1.0$^{[2, 7]}$] undeca-2(7), 3, 5-trienyl-exo-9-bromide (6c)

R_f 0.40. ^{1}H NMR δ 8.20 (d, 2H, J = 9.0 Hz), 7.45 (d, 2H, J = 9.0 Hz), 6.66 (d, 2H, J = 9.0 Hz), 6.62 (d, 2H, J = 9.0 Hz), 3.98 (m, 1 H), 3.81 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.73 (m, 1H), 3.71 (m, 1H), 2.77 (dt, 1H, J = 4.0, 12.0 Hz), 2.20 (dd, 1H, J = 7.0, 12.0 Hz). Anal. Calcd. for $C_{19}H_{18}BrNO_4S$: C 52.30; H 4.16; N 3.21. Found: C 52.42: H 4.12; N 3.64.

endo-3-Methoxycarbonyl-exo-5-(2-nitrophenylthio)-bicyclo[2.2.1] heptan- 2-carboxylic acid γ-lactone (7b)

M.p. 115–117 °C, yellow crystals from heptane. R_f 0.06. ^{1}H NMR δ 8.12 (m, 1H), 7.98 (m, 2H), 7.55 (m, 1H), 4.89 (dd, 1H, J = 3.2, 5.6 Hz), 4.76 (d, 1H, J = 3.2 Hz), 3.50 (s, 3H), 3.48 (dd, 1H, J = 5.6, 14.4 Hz), 2.89 (dd, 1H, J = 5.6, 14.4 Hz). IR 1790 (C=0, lactone), 1730 (COOMe) Anal. Calcd. For $C_{16}H_{15}NO_6S$: C55.01; H4.33; N4.01. Found: C55,31; H4,27; N: 4,24.

endo-3-Methoxycarbonyl-exo-5-(4-nitrophenylthio)-bicyclo[2.2.1] heptan-2-carboxylic acid y-lactone (7c)

M.p. 147–149 °C, yellow crystals from heptane (lit. m.p. 146 °C [15]). Rf 0.09. ^{1}H NMR § 8.23 (d, 2H, J = 9.0 Hz), 7.53 (d, 2H, J = 9.0 Hz), 4.77 (dd, 1H, J = 3.2, 5.7 Hz), 4.28 (d, 1H, J = 2.5 Hz), 3.83 (s, 3H), 3.57 (dd, 1H, J = 2.5, 5.7 Hz), 3.37 (dd, 1H, J = 3.6, 10.0 Hz), 3.07 (dd, 1H, J = 5.5, 10.0 Hz). IR 1800 (C=0, lactone), 1745 (COOMe). Anal. Calcd. for $C_{16}H_{15}NO_6$ S: C 55.01; H 4.33; N 4.01. Found: C 55.36; H 4.43; N 4.33,

2-Bromomethyl-5-(2-nitrophenylthio)-tricyclo[2.2.1.0$^{[2,6]}$]heptane (8b)

R_f 0.94. ^{1}H NMR δ 3.42 (bs, 1H), 3.37 (m, 2H), 2.25 (bs, 1H), 2.02 (d, 1H, J = 10.8 Hz), 1.67 (d, 1H, J = 10.8 Hz), 1.62(d, 1H, J = 10.8 Hz), 1.53 (d, 1H, J = 5.3 Hz), 1.50 (d, 1H, J = 10.8 Hz), 1.49 (d, 1H, J = 5.3 Hz). ^{13}C NMR δ 21.67, 24.68, 28.40, 31.99, 36.03, 36.26, 36.58, 51.25, 124.39, 126.01, 127.43, 132.95, 137.38, 146.56. Anal. Calcd. for $C_{14}H_{15}BrNO_2S$: C 49.28; H 4.43; N 4.10. Found: C 49.08; H 3.91; N 4.39.

2-Bromomethyl-5-(4-nitrophenylthio)-tricyclo[2.2.1.0$^{[2,6]}$]heptane (8c)

R_f 0.88. ^{1}H NMR δ 7.95 (d, 2H, J = 9.0 Hz), 7.25 (d, 2H, J = 9.0 Hz), 3.83 (dd 2H, J = 5.1, 11.0 Hz), 3.66 (bs, 1H), 2.30 (s, 1H), 1.90–1.37 (m, 6H). Anal. Calcd. for $C_{14}H_{15}BrNO_2S$: C 49.28; H 4.43; N 4.10. Found: C 49.55; H 3.98; N 4.00.

trans-2-(4-Nitrophenylthio)-cyclohexylchloride (9)

M.p. 68 °C, yellow crystals from heptane (lit. m.p. 66 °C [16]). R_f 0.80. ^{1}H NMR δ 8.02 (d, 2H, J = 9.0 Hz), 7.34 (d, 2H, J = 9.0 Hz), 3.99 (m, 1 H), 3.60 (m, 1 H), 2.50–1.30 (m, 8H).

exo-2-(4-Nitrophenylthio)-endo-3-norbornylchloride (10)

R_f 0.80. ^{1}H NMR δ 8.05 (d, 2H, J = 9.0 Hz), 7.25 (d, 2H, J = 9.0 Hz), 3.95 (m, 1H), 3.15 (m, 1H), 2.60–1.12 (m, 8H). Anal. Calcd. for $C_{13}H_{14}ClNO_2S$: C 55.02; H 4.97; N 4.94. Found: C 54.80; H 4.88; N 4.66.

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