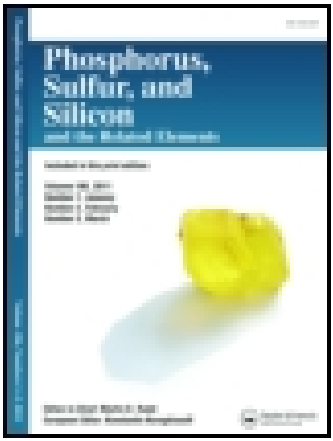

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[4 + 2] Cycloaddition Reactions Involving 2-Arylmethylidene-1-thiooxoindan Intermediates and Antimicrobial Activity Evaluation of Some Products

Mohamed I. Hegab [a], Tamer A. G. Elmalah [a] & Farouk A. Gad [a]
[a] Photochemistry Department, National Research Centre, Dokki, Cairo, Egypt
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[4 + 2] Cycloaddition Reactions Involving 2-Arylmethylidene-1-thiooxoindan Intermediates and Antimicrobial Activity Evaluation of Some Products

Mohamed I. Hegab, Tamer A. G. Elmalah, and Farouk A. Gad
Photochemistry Department, National Research Centre, Dokki, Cairo, Egypt

2-(4-Fluorophenyl)methylidene-1-thiooxoindane-, 2-(4-methoxyphenyl) methylidene-1-thiooxoindane-, 2-(4-N,N-dimethyaminophenyl)methylidene-1-thiooxoindane dimers ***5a–c*** *were prepared by the reaction of the corresponding α,β-unsaturated ketones* ***3a–c*** *with Lawesson' Reagent (LR) in refluxing benzene. When these dimers were refluxed with LR in xylene, the 1,2-thiaphospholene-2-sulfides* ***7a–c*** *were obtained. On the other hand, the thermolysis of the dimers* ***5a–c*** *in the presence of acrylamide or dichloromaleic anhydride gave the corresponding cycloadducts of Diels-Alder type* ***8a–c****, and* ***10a–c****, respectively. The 3-carbamoyl thiapyran derivatives* ***8a–c*** *showed good antimicrobial activity.*

Keywords Antimicrobial activity; 2-arylmethylidene-1-thiooxoindane dimers; Diels–Alder cycloadducts; Lawesson's reagent; 1,2-thiaphospholene-2-sulfides; α, β-unsaturated ketones

INTRODUCTION

The α,β-unsaturated thiones are little known because of their instability in the monomeric form[1–9] and tendency to undergo [4 + 2] cycloaddition in which the thione itself may serve as a dienophile or a diene. However, Karakasa and Motoki[10] reported the preparation of some thiochalcone dimers and 2-arylbenzylidene-1-thiotetralone dimers via the reaction of the corresponding α,β-unsaturated ketones with P_4S_{10}. Also, the thermolysis of thiochalcone dimers and 2-arylbenzylidene-1-thiotetralone dimers in the presence of acrylonitrile or acrylamide was reported.[10]

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Address correspondence to Mohamed I. Hegab, Photochemistry Department, National Research Centre, Dokki, 12622 Cairo, Egypt. E-mail: apmihegab65@yahoo.com

On the other hand, the reaction of some chalcones, 2-arylbenzylidene-1-tetralones and 2,2-dialkyl-3-arylbenzylidene-4-chromanones with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (Lawesson's reagent, LR) was reported.[11,12] Recently, some new chromenothiapyran derivatives have been reported.[13,14] In continuation of synthesis of some new thiapyran derivatives, it is intended to explore the reaction of 2-arylbenzylidene-1-indanones with LR in order not only to isolate the corresponding 2-arylbenzylidene-1-thiooxoindanone dimers but also, to evaluate their antimicrobial activities.

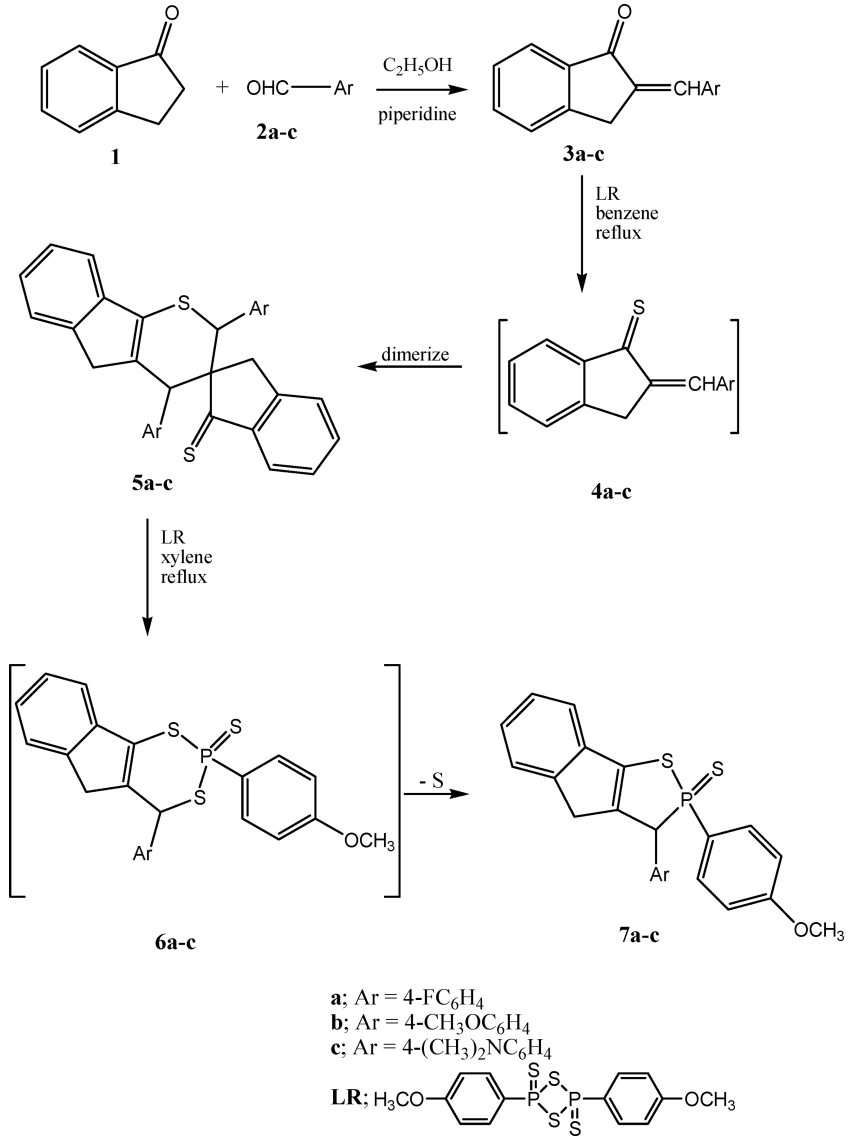
RESULTS AND DISCUSSION

In the present work, three known 2-arylbenzylidene-1-indanones, namely, 2-(4-fluorobenzylidene)indan-1-one (**3a**), 2-(4-methoxybenzylidene)indan-1-one (**3b**), and 2-(4-*N*, *N* dimethylaminobenzylidene)indan-1-one (**3c**) were prepared according to reference 15. Treatment of 2-(4-fluorobenzylidene)indan-1-one (**3a**) with LR in refluxing benzene for 3h gave the corresponding thiooxo dimmer **5a** in moderate yield (Scheme 1). In this reaction, the straightforward thionation of the carbonyl group of **3** yielded the thiooxo monomer **4** which immediately underwent cyclization with another thiooxo monomer [2 + 4] to yield the thiooxo dimer **5**. The structure of **5a** was confirmed by analytical and spectral data. The ^{1}H NMR spectrum of **5a** showed one-proton singlets at 3.70 and 5.55 ppm; these were assigned to the C-4 and the C-2 protons in the 3,4-dihydro-2*H*-thiapyran ring, respectively. The mass spectrum of **5a** exhibited the molecular ion peak at 508 (M^+, 2%) and a fragment from the thiooxo monomer **4a** (252, 100%, **4a**$^+$ – 2H) which would be formed by the cleavage of **5a**.

Similarly, 2-(4-methoxyphenyl)methylidene-1-thiooxoindan dimer (**5b**) and 2-(4-*N*, *N* dimethylaminophenyl)methylidene-1-thiooxoindan dimer (**5c**) were obtained by the reaction of **3b**, and **3c** with LR, respectively (Scheme 1). The structures of **5b,c** are supported by analytical and spectral data (cf. Experimental).

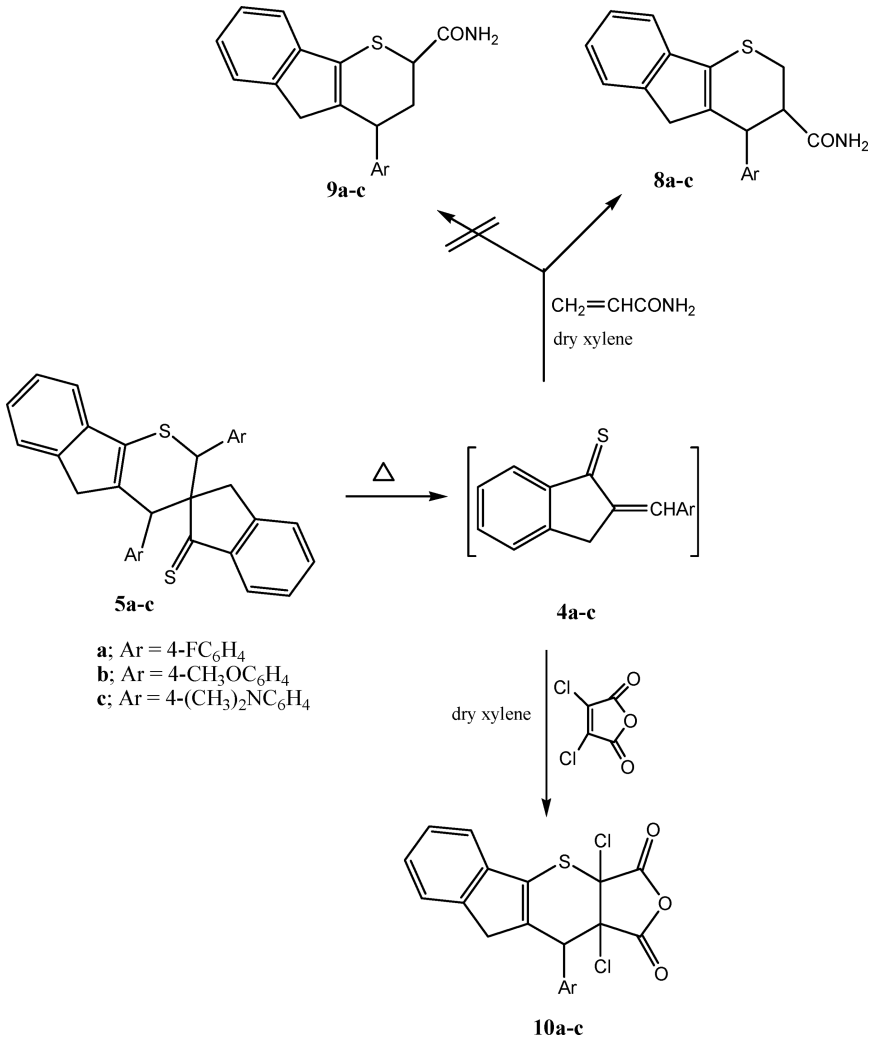
However, when the thiooxo dimers **5a–c** reacted with LR in refluxing xylene for 6 h, the phosphorus containing compounds **7a–c**, respectively, were formed (Scheme 1).

The structures of phosphorus containing compounds **7a–c** were confirmed by analytical and spectral data. The ^{1}H NMR spectrum of **7a** showed the doublet at 5.39 ppm with $J_{PH} = 15$ Hz due to the presence of an adjacent CH moiety. Its mass spectrum showed the molecular ion peak at 424 (M^+, 12%), and a base peak at 391 (M^+ – SH, 100%).



SCHEME 1

On the other hand, the thermolysis of α,β-unsaturated thioxo dimers **5a–c** in the presence of acrylamide in dry benzene for 1 h gave only adducts which were identified as **8a–c** based on ^{1}H NMR (cf. Scheme 2). In a competition reaction the unstable α,β-unsaturated thioxo monomer



SCHEME 2

4 cyclized with an external dienophile rather than with itself. This reaction proved the presence of an unstable α,β-unsaturated thioxo monomer as the intermediate. The ^{1}H NMR of **8a** showed 4-CH at 5.54 ppm as a doublet with J = 3 Hz and 3-CH at 4.79–4.89 as a multiplet. If derivative **9** would have formed, the 4-CH would appear as a triplet. Thus, according to the ^{1}H NMR data the compounds **9a–c** could be excluded. The IR spectrum of compound **8a** showed bands at 3275, 2925 (NH_2), and 1661 cm^{-1} (C=O).

Products **8a–c** show clearly the ^{1}H NMR signals of only one diasteriomer. If the minor diasteriomer is present, its concentration too small to be detected.

Similarly, the α,β-unsaturated thioxo dimers **5a–c** were heated the presence of dichloromaleic anhydride in dry xylene for 3 h to give adducts **10a–c** (cf. Scheme 2). The IR spectrum of compound **10a** showed bands at 1773, 1723 cm^{-1} [C(O)OC(O)]. Its ^{1}H NMR spectrum revealed a signal at 5.55 (1H, s, CH). The mass spectrum of compound **10a** showed the molecular ion peak at 424 (M^+ $2Cl^{37}$,1), 422 (M^+ $Cl^{37,35}$, 9), and 420 (M^+ $2Cl^{35}$, 50).

ANTIMICROBIAL ACTIVITY

The in vitro antimicrobial activity of the new synthesized thiapyran derivatives was investigated against several pathogenic representative Gram-negative bacteria, Gram-positive bacteria, fungi, and yeast. All microorganisms used were obtained from the culture collection of the Department of Natural and Microbial Products, National Research Centre, Dokki, Cairo, Egypt.

Medium[16–18]

The cap-assay method containing (g/L): peptone 6, yeast extract 3, meat extract 1.5, glucose 1, and agar 20 was used. The medium was sterilized and divided while hot (50–60°C) in 15-mL portions among sterile 9-cm diameter Petri dishes. One mL of the spore suspension of each microorganism was spread all over the surface of the cold solid medium placed in the Petri dish.

Method

0.5 g of each of the tested compounds was dissolved in 5 mL of *N*, *N*-dimethylformamide, an amount of 0.1 mL of test solution was placed on a 9-mm diameter Whatman paper disc, and the solvent was left to evaporate. These saturated discs were placed carefully on the surface of the incubated solid medium; each Petri dish contains at least 3 discs. The Petri dishes were incubated at 5°C overnight, then examined. The results were then recorded by measuring the inhibition zone diameters.

TABLE I The Antimicrobial Activity of Some Newly Synthesized Compounds

Tested Compounds and Standards	Inhibition zone (mm)			
	Microorganism			
	Bacteria			
	Gram-negative	Gram-positive	Fungi	Yeast
	Escherichia Coli	*Bacillus Subtilis*	*Aspergillus Niger*	*Candida Albicans*
Streptomycin	+++	+++	+	+++
Fusidic Acid	—	—	+++	+++
5a	—	—	—	++
5b	—	—	—	+
5c	—	—	—	+
8a	+	+	—	+++
8b	+	+	—	++
8c	+	+	—	++
10a	—	—	—	++
10b	—	—	—	+
10c	—	—	—	+

+++ Highly sensitive (21–25 mm); ++ Fairly sensitive (16–20 mm); + Slightly sensitive (15–10 mm); —Not sensitive.

RESULTS

The antimicrobial activity of the tested compounds (**5a–c**, **8a–c**, and **10a–c**) was evaluated by measuring the zone diameters and their results were compared with those of well-known drugs as shown in Table I. 3-Carbamoyl thiapyran derivatives **8a–c** showed good antimicrobial activity. However, 3-carbamoyl-4-(4-fluorophenyl)-2,3,4-trihydroindeno[1,2-*e*]thiapyran (**8a**) demonstrated inhibitory activity more than **8b** and **8c**.

EXPERIMENTAL

Melting points are uncorrected and recorded on a digital Electrothermal IA 9000 SERIES melting point apparatus (Electrothermal, Essex, U.K.). Microanalyses were performed with all final compounds on Elementar-Vario EL, Microanalytical Unit, Central Services Laboratory, National Research Centre, Cairo, Egypt. The ^{1}H NMR spectra were taken for samples in $CDCl_3$ as solvent (unless otherwise mentioned) with Jeol EX-270 and Jeol EX-500 MHz NMR spectrometers, Central Services Laboratory, National Research Centre, Cairo, Egypt.

Chemical shifts are quoted in δ and were referenced to that of the solvents. Splitting patterns were designated as follow: s singlet; d doublet; t triplet; m multiplet. Mass spectra were recorded on Shimadzu GCMS-QP 1000 EX EI (70 eV) spectrometers (Micro-Analytical Center of Cairo University). IR spectra were obtained with Brucker-Vector 22 for KBr wafers (Micro-analytical Center of Cairo University). Compounds **3a–c**[15] were prepared according to the literature procedure.

Reaction of Arylbenzylidene-1-indanone Derivatives 3 with Lawesson's Reagent (LR)

A mixture of **3** (2 mmol) and LR (0.4 g, 1.1 mmol) in dry benzene (20 mL) was refluxed for 3 h. After cooling, the reaction mixture was filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel (Fluka 60, particle size 0.06–0.20 mm) using diethyl ether:petroleum ether 40–60°C 1:10 (v/v) as an eluent. The solvent was evaporated and the residue was recrystallized from ethanol to give thiapyran derivatives **5**.

2,4-Di(4-fluorophenyl)spiroindan-2′,3-inden[1,2-b]-2,4-dihydrothiapyran-1′-thione (5a)

From **3a** (0.46 g). Green crystals, m.p. 223–226°C, yield 55% (0.5 g). IR: υ = 2915, 1690, 1605, 1510, 1460, 1250, 1171, 1031, 835, 759, 715 cm^{-1}. ^1H NMR: δ = 3.44 (2H, s, CH_2), 3.52 (2H, s, CH_2), 3.70 (1H, s, CH), 5.55 (1H, s, CH), 6.97–7.57 (16H, m, Ar-H). MS (EI): m/z (%) = 508 (M^+, 2), 475 (24), 424 (2), 394 (5), 367 (15), 254 (29), 252 (100), 219 (9), 139 (43), 126 (19), 115 (15). Anal. calcd. for $C_{32}H_{22}F_2S_2$ (508.62): C, 75.56; H, 4.36; S, 12.60%. found: C, 75.34; H, 4.22; S, 12.29.

2,4-Di(4-metoxyphenyl)spiroindan-2′,3-inden[1,2-b]-2,4-dihydrothiapyran-1′-thione (5b)

From **3b** (0.50 g). Green crystals, m.p. 109–111°C, yield 57% (0.57 g). IR: υ = 2923, 1701, 1607, 1509, 1459, 1249, 1176, 1033, 833, 758, 717 cm^{-1}. ^1H NMR: δ = 3.43 (2H, s, CH_2), 3.53 (2H, s, CH_2), 3.70 (1H, s, CH), 3.85 (6H, s, OCH_3), 5.75 (1H, s, CH), 6.50–7.35 (16H, m, Ar-H). MS (EI): m/z (%) = 266 (1/2M^+, 74), 265 (100), 251 (29), 235 (53), 221 (22), 189 (20), 151 (44), 121 (25), 110 (8). Anal. calcd. for $C_{34}H_{28}O_2S_2$ (532.68): C, 76.65; H, 5.29; S, 12.03%. found: C, 76.34; H, 5.12; S, 11.79.

2,4-Di(4-N,N-dimethylaminophenyl)spiroindan-2′,3-inden[1,2-b]-2,4-dihydrothiapyran-1′-thione (5c)

From **3c** (0.52 g). Dark green crystals, m.p. 223–226°C, yield 50% (0.55 g). IR: υ = 2918, 1610, 1586, 1569, 1521, 1465, 1323, 1265, 1162,

1094, 1029, 947, 814, 758, 718 cm^{-1}. ^1H NMR: δ = 2.84 (12H, s, 2 $N(CH_3)_2$), 3.43 (2H, s, CH_2), 3.50 (2H, s, CH_2), 3.71 (1H, s, CH), 5.65 (1H, s, CH), 6.70–7.85 (16H, m, Ar-H). MS (EI): m/z (%) = 279 (1/2M^+, 61), 278 (100), 263 (11), 235 (21), 221 (2), 189 (3), 164 (49), 148 (17), 139 (25), 132 (14), 121 (17), 115 (14). Anal. calcd. for $C_{36}H_{34}N_2S_2$ (558.77): C, 77.37; H, 6.13; N, 5.01%. found: C, 77.04; H, 5.98; N, 4.79.

Heating of Thioxo Dimers 5 with Lawesson's Reagent (LR)

A mixture of **5** (2 mmol) and LR (0.8 g, 2.1 mmol) in dry xylene (20 mL) was refluxed for 6 h. After cooling, the reaction mixture was filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel (Fluka 60, particle size 0.06–0.20 mm) using diethyl ether:petroleum ether 40–60°C 1:10 (v/v) as an eluent. The solvent was evaporated and the residue was recrystallized from ethanol to give phosphorus compounds **7**.

3-(4-Fluorophenyl)-2-(4-methoxyphenyl)indeno[1,2-d]-3H-1,2-thiaphospholene-2-sulfide (7a)

From **5a** (1.0 g). Colorless crystals, m.p. 201–204°C, yield 60% (0.48 g). ^1H NMR: δ = 3.51 (2H, s, CH_2), 3.79 (3H, s, OCH_3), 5.39 (1H, d, J_{PH} = 15Hz, 3-CH), 6.77–7.67 (12H, m, Ar-H). MS (EI): m/z (%) = 424 (M^+, 12), 391 (100), 345 (50), 254 (29), 222 (19), 139 (33), 126 (29), 115 (16). Anal. calcd. for $C_{23}H_{18}FOPS_2$ (424.48): C, 65.07; H, 4.27; S, 15.10%. found: C, 64.81; H, 4.07; S, 14.93.

2,3-Di(4-methoxyphenyl)indeno[1,2-d]-3H-1,2-thiaphospholene-2-sulfide (7b)

From **5b** (1.0 g). Colorless crystals, m.p. 91–94°C, yield 63% (0.54 g). ^1H NMR: δ = 3.50 (2H, s, CH_2), 3.68 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 5.39 (1H, d, J_{PH} = 15Hz, 3-CH), 6.77–7.67 (12H, m, Ar-H). MS (EI): m/z (%) = 436 (M^+, 12), 404 (100), 379 (50), 266 (19), 222 (39), 139 (23), 126 (19), 115 (15). Anal. calcd. for $C_{24}H_{21}O_2PS_2$ (436.52): C, 65.03; H, 4.85; S, 14.68%. found: C, 64.85; H, 4.57; S, 14.43.

3-(4-N,N-Dimethylphenyl)-2-(4-methoxyphenyl)indeno[1,2-d]-3H-1,2-thiaphospholene-2-sulfide (7c)

From **5c** (1.1 g). Colorless crystals, m.p. 198–201°C, yield 45% (0.20 g). ^1H NMR: δ = 2.86 (6H, s, $N(CH_3)_2$), 3.52 (2H, s, CH_2), 3.81 (3H, s, OCH_3), 5.40 (1H, d, J_{PH} = 15Hz, 3-CH), 6.97–7.77 (12H, m, Ar-H). MS (EI): m/z (%) = 449 (M^+, 10), 416 (100), 279 (50), 221 (20), 139 (33), 126 (29). Anal. calcd. for $C_{25}H_{24}NOPS_2$ (449.56): C, 66.78; H, 5.38; N, 3.11; S, 14.26%. found: C, 66.46; H, 5.19; N, 2.98; S, 14.03.

The Thermolysis of α,β-unsaturated thioxo dimers 5 in the Presence of Acrylamide

A solution of α,β-unsaturated thioxo dimers **5** (1 mmol) and acrylamide (0.15 g, 2.1 mmol) in dry benzene (10 mL) was refluxed for 1 h. The solvent was evaporated and the residue was chromatographed on silica gel (Fluka 60, particle size 0.06–0.20 mm) using petroleum ether 40–60°C as an eluent. The solvent was evaporated and the residue was recrystallized from ethanol to give the adduct **8**.

3-Carbamoyl-4-(4-fluorophenyl)-2,3,4-trihydroindeno[1,2-e] thiapyran (8a)

From **5a** (0.5 g). Colorless crystals, m.p. 108–110°C, yield 30% (0.1 g). IR: υ = 3275, 2925, 1661, 1625, 1515, 1464, 1250, 1173, 1031, 833, 761, 715 cm^{-1}. ^1H NMR: δ = 3.50 (2H, s, CH_2), 3.85 (2H, d, J = 3Hz, CH_2), 4.79–4.89 (1H, m, CH), 5.45 (1H, d, J = 3Hz, CH), 5.85 (2H, br. s, NH_2), 6.95–7.35 (8H, m, Ar-H). MS (EI): m/z (%) = 325 (M^+, 25), 254 (19), 235 (100), 189 (9), 118 (43). Anal. calcd. for $C_{19}H_{16}FNOS$ (325.38): C, 70.13; H, 4.95; N, 4.30; S, 9.85%. found: C, 69.84; H, 4.82; N, 4.18; S, 9.64.

3-Carbamoyl-4-(4-methoxyphenyl)-2,3,4-trihydroindeno [1,2-e]thiapyran (8b)

From **5b** (0.5 g). Colorless crystals, m.p. 65–68°C, yield 38% (0.12 g). IR: υ = 3275, 2926, 1665, 1627, 1515, 1462, 1250, 1171, 1031, 835, 763, 717 cm^{-1}. ^1H NMR: δ = 3.50 (2H, s, CH_2), 3.83 (3H, s, OCH_3), 3.86 (2H, d, J = 3Hz, CH_2), 4.77–4.85 (1H, m, CH), 5.45 (1H, d, J = 3Hz, CH), 5.84 (2H, br. s, NH_2), 6.95–7.55 (8H, m, Ar-H). MS (EI): m/z (%) = 337 (M^+, 45), 266 (39), 235 (100), 189 (19), 118 (23). Anal. calcd. for $C_{20}H_{19}NO_2S$ (337.41): C, 71.89; H, 5.67; N, 4.14; S, 9.50%. found: C, 71.54; H, 5.82; N, 3.88; S, 9.24.

3-Carbamoyl-4-(4-N,N-dimethylaminophenyl)-2,3,4-trihydroindeno[1,2-e]thiapyran (8c)

From **5c** (0.5 g). Colorless crystals, m.p. 112–115°C, yield 32% (0.11 g). IR: υ = 3275, 2926, 1660, 1625, 1517, 1460, 1250, 1171, 1031, 837, 763, 715 cm^{-1}. ^1H NMR: δ = 2.85 (6H, s, $N(CH_3)_2$), 3.51 (2H, s, CH_2), 3.85 (2H, d, J = 3Hz, CH_2), 4.78–4.87 (1H, m, CH), 5.45 (1H, d, J = 3Hz, CH), 5.85 (2H, br. s, NH_2), 6.95–7.55 (8H, m, Ar-H). MS (EI): m/z (%) = 350 (M^+, 15), 234 (100), 189 (29), 118 (14). Anal. calcd. for $C_{21}H_{22}N_2OS$ (350.45): C, 71.96; H, 6.32; N, 7.99; S, 9.14%. found: C, 71.64; H, 6.22; N, 7.68; S, 8.84.

The Thermolysis of α,β-unsaturated Thioxo Dimers 5 in the Presence of Dichloromaleic Anhydride

A solution of α,β-unsaturated thioxo dimers **5** (1 mmol) and dichloromaleic anhydride (3.32 g, 2.1 mmol) in dry xylene (10 mL) was refluxed for 3 h. The solvent was evaporated and the residue was chromatographed on silica gel (Fluka 60, particle size 0.06–0.20 mm) using petroleum ether 40–60°C as an eluent. The solvent was evaporated and the residue was recrystallized from ethyl acetate to give the adduct **10**.

3a,10a-Dichloro-10-(4-fluorophenyl)-3a,9,10,10a-tetrahydroindeno[1,2-e]thiapyran[2,3-d]furan-1,3-dione (10a)

From **5a** (0.5 g). Colorless crystals, m.p. 118–121°C, yield 25% (0.2 g). IR: $\upsilon = 2925, 1773, 1723, 1606, 1511, 1463, 1250, 1177, 1032, 916, 834, 757\ cm^{-1}$. ^1H NMR: $\delta = 3.50$ (2H, s, CH_2), 5.55 (1H, s, CH), 6.95–7.55 (8H, m, Ar-H). MS (EI): m/z (%) = 424 (M^+ $2Cl^{37}$, 1), 422 (M^+ $Cl^{37,35}$,9), 420 (M^+ $2Cl^{35}$, 50), 350 (19), 306 (9), 235 (100), 189 (19), 152 (15). Anal. calcd. for $C_{20}H_{11}Cl_2FO_3S$ (421.26): C, 57.01; H, 2.63; S, 7.61%. found: C, 56.88; H, 2.55; S, 7.34.

3a,10a-Dichloro-10-(4-methoxphenyl)-3a,9,10,10a-tetrahydroindeno[1,2-e]thiapyran[2,3-d]furan-1,3-dione (10b)

From **5b** (0.5 g). Colorless crystals, m.p. 78–81°C, yield 27% (0.2 g). IR: $\upsilon = 2924, 1771, 1723, 1604, 1509, 1461, 1248, 1175, 1030, 915, 832, 755\ cm^{-1}$. ^1H NMR: $\delta = 3.50$ (2H, s, CH_2), 3.84 (3H, s, OCH_3), 5.53 (1H, s, CH), 6.97–7.58 (8H, m, Ar-H). MS (EI): m/z (%) = 436 (M^+ $2Cl^{37}$, 2), 434 (M^+ $Cl^{37,35}$, 18), 432 (M^+ $2Cl^{35}$, 50), 399 (3), 397 (15), 384 (100), 369 (20), 363 (4), 265 (49), 250 (12), 235 (20), 221 (8), 189 (8), 151 (19). Anal. calcd. for $C_{21}H_{14}Cl_2O_4S$ (433.29): C, 58.20; H, 3.25; S, 7.39%. found: C, 57.98; H, 3.05; S, 7.14.

3a,10a-Dichloro-10-(4-N,N-dimethylaminophenyl)-3a,9,10,10a-tetrahydroindeno[1,2-e]thiapyran[2,3-d]furan-1,3-dione (10c)

From **5c** (0.5 g). Colorless crystals, m.p. 123–125°C, yield 25% (0.2 g). IR: $\upsilon = 2924, 1775, 1725, 1606, 1507, 1465, 1248, 1175, 1030, 917, 832, 757\ cm^{-1}$. ^1H NMR: $\delta = 2.86$ (6H, s, $N(CH_3)_2$), 3.52 (2H, s, CH_2), 5.51 (1H, s, CH), 6.96–7.57 (8H, m, Ar-H). MS (EI): m/z (%) = 449 (M^+ $2Cl^{37}$, 2), 447 (M^+ $Cl^{37,35}$, 18), 445 (M^+ $2Cl^{35}$, 50), 412 (3), 410 (16), 375 (10), 360 (5), 331 (39), 250 (15), 235 (21), 221 (7), 189 (10), 151 (20). Anal. calcd. for $C_{22}H_{17}Cl_2NO_3S$ (446.33): C, 59.19; H, 3.84; N, 3.13%. found: C, 58.88; H, 3.65; N, 2.79.

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