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ORIGINAL PAPER

Formation of dioxospiroindene[1,3]thiazine and thioxoindeno[2,1-*d*]imidazolone derivatives from alkenylidene-hydrazinecarbothioamides

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The reaction of (substituted) alkenylidene-hydrazinecarbothioamides with 2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile led to the formation of 1,3-dioxospiroindene[1,3]-thiazine and thioxoindeno[2,1-*d*]imidazolone derivatives in modest yields. In addition, 1,3-dihydroxyindan-2-ylidenepropanedinitrile was found. Explanations of these conversions involving nucleophilic reactions and condensations are presented.

Keywords: alkenylidene-hydrazinecarbothioamides, dioxospiroindene[1,3]thiazine, thioxoindeno [2,1-*d*]imidazolone

Introduction

2-(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile ((2-dicyanomethylidene)indan-1,3-dione, *II*) is the weakest acceptor (Bespalov et al., 1980) in the series of related organic π-acceptors such as tetracyanoethene and (2,5-cyclohexadiene-1,4-diylidene)-dimalononitrile, 7,7,8,8-tetracyanoquinodimethane (tetracyanoquinodimethane) which also readily form addition products with organic nucleophiles (Junek et al., 1972; Rappoport & Ladkani, 1973; Boila-Göckel et al., 1996; Hanefeld et al., 1996; Junek et al., 1990; Döpp et al., 2002, 2006, 1996; Hassan & Shehatta, 2007; Hassan et al., 2009). *N*,*N*′-diarylacetamidines reacted with *II* to form indenoazepine-6-ones during nucleophilic attack by N-2 of acetamidines on a cyano group of *II* (Döpp et al., 1996). The reaction of *II* with 1-substituted-2,5-dithiobiureas (Hassan et al., 2007), acylthiosemicarbazides (Hassan et al., 2008a), thiocarbohydrazides (Hassan et al., 1997), and substituted carbohydrazides (Hassan et al., 2009) were reported. The aroyl thiourea derivatives and *II* in acetic acid (100 %) afforded indenothiazepine derivatives rather than spiroindolothiazines (Aly et al., 2010). Heterocyclisation of thiosemicarbazones is induced by various metallic salts (Noto et al., 1996, 1995, 1999; Gruttadauia et al., 1993; Ernst et al., 1995; Invidiata et al., 1997) or by dienophilic reagents (Gomaa et al., 2006; Darehkordi et al., 2007).

On other occasions, the cyclisation mechanism involves a plain oxidation step (electron abstraction or dehydrogenation) prior to the actual ring closure step (Tsoungas & Diplas, 2003). These intriguing transformations prompted us to investigate the reactions of alkenylidene-hydrazinecarbothioamides *Ia*–*Ie* (bearing substituents), a selection of aryl, alkenyl, and alkyl substituents with *II* to synthesise important spiro- and fused heterocyclic systems.

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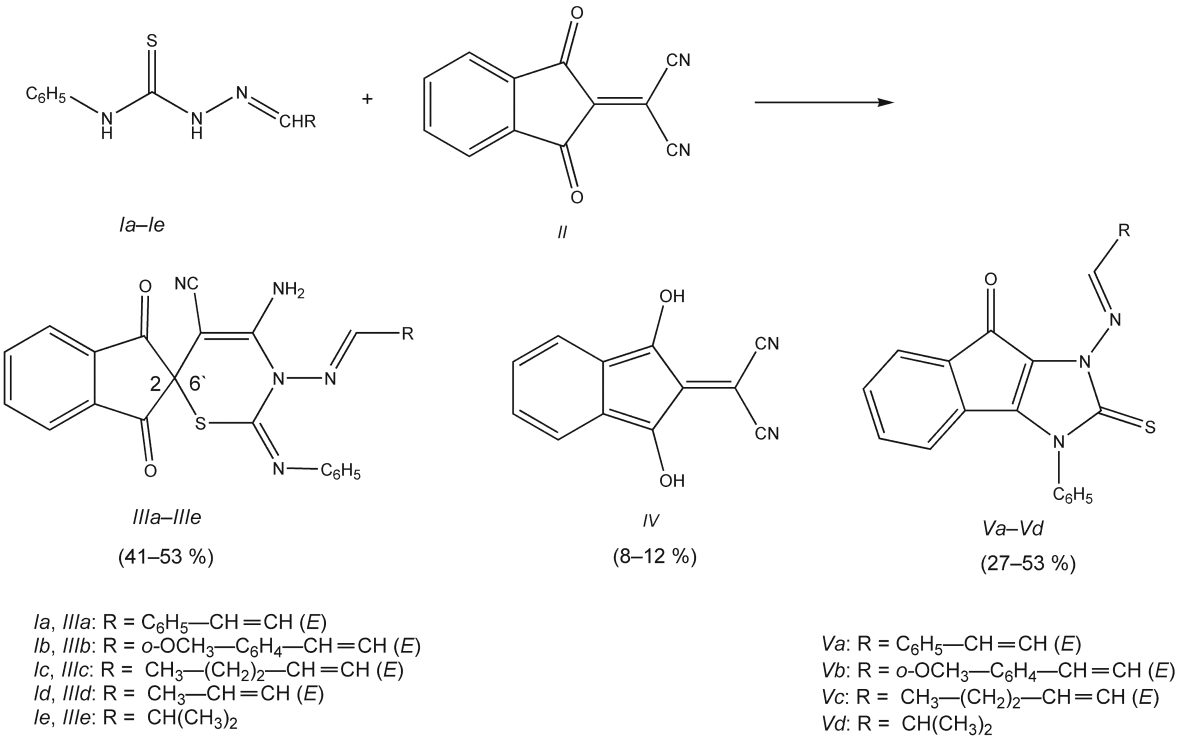

Fig. 1. The products from the reaction between *Ia–Ie* and *II*.

Experimental

Melting points were determined using open glass capillaries on a Gallenkamp melting point apparatus (Gallenkanp, UK) and the values remain uncorrected. Elemental analyses were determined by the Microanalytical Center, Cairo University, Egypt using Elmyer 306, (Germany). The IR spectra were recorded on a Shimadzue 408 instrument (Japan), using potassium bromide discs. The ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.6 MHz) spectra were observed on a Bruker AM400 spectrometer (Germany) with tetramethylsilane as the internal standard; chemical shifts are expressed as δ. The ^{13}C NMR signals were assigned on the basis of DEPT 135/90 spectra. The mass spectra were obtained on a Finnigan MAT 312 (Germany) instrument using electron impact ionisation (70 eV). Air-dried 1.0 mm thick layers of the silica gel slurry applied (Merck PF254, Germany) onto 48 cm wide and 20 cm high glass plates using the solvents listed were used in preparative layer chromatography (plc). Zones were eluted with acetone and detected by fluorescence indicator quenching upon 254 nm light.

Preparation of substituted alkenylidene-hydrazinecarbothioamides (Ia–Ie)

A solution of the respective aldehyde (1.0 mmol) in 5 mL dimethylsulphoxide was added drop-wise into a solution of 4-substituted thiosemicarbazide (1.0 mmol) in the same solvent with two drops of acetic anhydride upon stirring at room temperature. The solution mixture was stirred for 3 h, left to stand overnight and poured into 250 mL of ice/water. The precipitate was removed by filtration and allowed to crystallise from ethanol to give colourless crystals of *Ia–Ie*. (2-Dicyanomethylidene)indan-1,3-dione (*II*) was prepared following the method described by Chaterjee (1969).

Reaction of alkenylidene-hydrazinecarbothioamides (Ia–Ie) with (2-dicyanomethylidene) indan-1,3-dione (II)

To a solution of *II* (208 mg, 1 mmol) in dry ethyl acetate (20 mL), a solution of *Ia–Ie* (1 mmol) in dry ethyl acetate, (10 mL) was added with stirring. The mixture was refluxed for 4–6 h until the starting materials were consumed (as monitored by TLC). The precipitate was filtered, washed with cold ethyl acetate and identified as 1,3-dihydroxyindan-2-ylidenepropanedinitrile *IV*. The filtrate was preconcentrated, applied to 5 plc plates and developed using toluene/ethyl acetate ($\varphi_r = 1:1$ for the reactions with *Ia*, *Ib*, *Ie* and $\varphi_r = 2:1$ for *Ic*, *Id*) to give a number of coloured zones. Two intense zones were extracted with acetone. The fastest migrating (reddish brown) zone contained compounds *Va–Vd*; the slowest orange zone contained *IIIa–IIIe*. The products so obtained were re-crystallised.

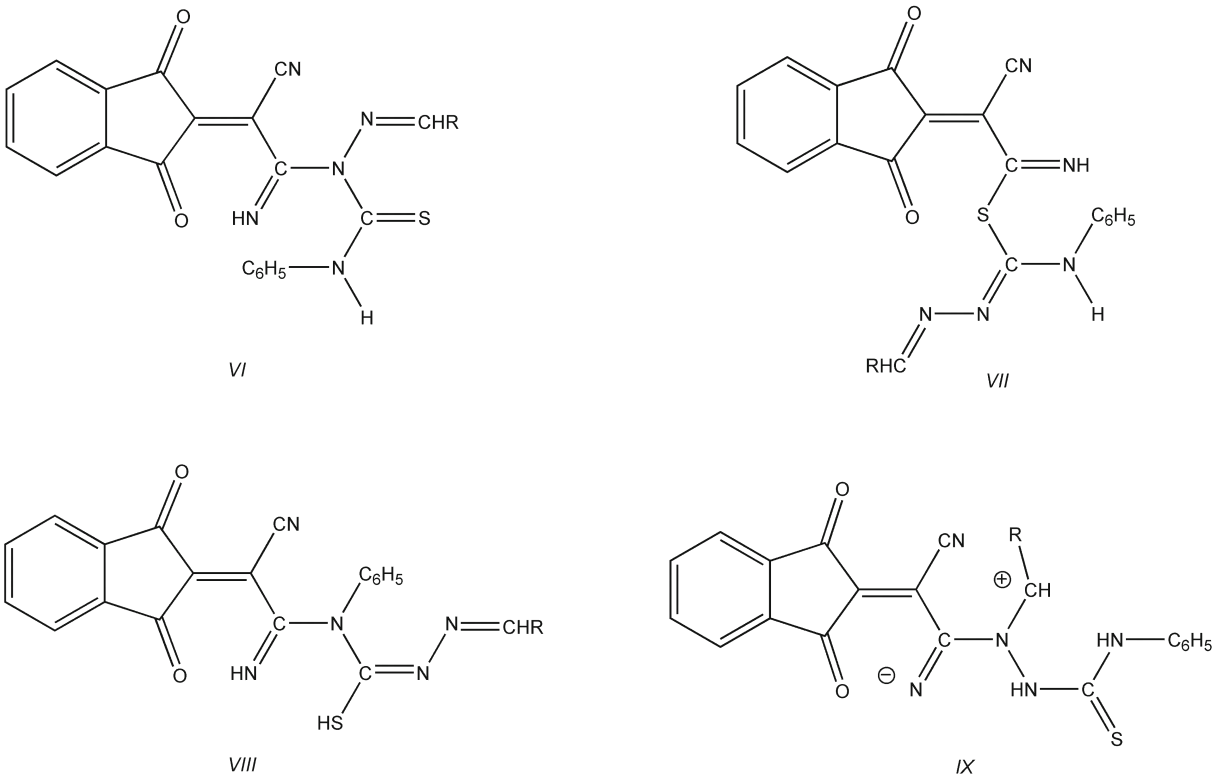

Fig. 2. Four labile (1 : 1) adducts (*VI–XI*) from the reaction between *I* and *II*.

Results and discussion

Solutions of *Ia–Ie* (1 mmol) in dry ethyl acetate (10 mL) were added into a solution of *II* (1 mmol) in dry ethyl acetate (20 mL); the mixtures were refluxed for 4–6 h with the admission of air; the chromatographic separation of the residue afforded a number of coloured zones from which products *III* and *V* could be isolated (Fig. 1).

4′-Amino-1,3-dioxo-3′-(substituted)-2′-(phenylimino)-1,2′,3,3′-tetrahydrospiro(indene-2,6′-[1,3]thiazine)-5′-carbonitriles (*IIIa–IIIe*) were assigned on the basis of the elemental analysis and spectral data. The IR spectra of *IIIa–IIIe* showed strong absorption signals between 1730 cm^{-1} and 1720 cm^{-1} for the carbonyl group, and between 3370–3290 cm^{-1} for NH_2, 2220–2210 cm^{-1} (C≡N), and 1655–1645 cm^{-1} (C=N). ^{1}H NMR spectra showed broad exchangeable signals with (D_2O) between δ 6.72–6.50 due to the amino group, in addition to the aromatic protons. The ^{1}H NMR of *IIIa* showed the presence of multiplet δ at 6.60–6.85 due to CH═CH. In its ^{13}C NMR spectrum, the (Ar—*C*H═*C*H—) group resonated at δ 124.9 and at δ 136.1. Also, ^{13}C NMR of *IIIa* showed signals at δ 57.6 (spiro–C-2,6′), δ 158.0 (C-2′), and δ 192.2 (C-1,3). The ^{13}C NMR data of *IIIa* are in line with the ^{1}H NMR data insofar as the distinctive appearance of carbon signals representing CH═N at δ 143.7. Thiazine-C-5′ and C-4′ resonated at δ 53.7 and δ 168.4, respectively, in accordance with the trends in δ values for C-atoms observed in push-pull alkenes (Kalinowski et at., 1984; Gewald & Schindler, 1990).

In addition, in the ^{13}C NMR of *IIIa–IIIe*, spiro C-2,6′ is regularly shifted up-field at δ 57.7–56.6 and so is in a range close to that found in the related systems (*Va*, *Vc*, and *Vd*, Hafez et al. (1986) and compounds *Xa–Xc*, Gomaa and Döpp (1998)) compared with spiro C-2,4′ in the alternative structures *X* and *XII*.

The mass spectrometry fragmentation of isolated compounds was studied under electron ionisation. The following common features of the fragmentation patterns are strong evidence for the assigned structures: loss of PhN═C═S giving rise to the ion m/z = 135 common in the spectra of all five compounds. The resulting fragment ions undergo loss of RCH═N—N═C═S, m/z = 104 (C_6H_4CO), and m/z = 66 (H_2N—C═C—CN). The analytical data of compound *III* would also match other isomers of products *X–XV* (Figs. 3–5).

Compounds *Ia–Ie* may react at least with their sulphur atom, N-2 and N-4 as nucleophilic sites. On the other hand, it was reported that the methine carbon of *I* acted as a nucleophile in the sense of a polarity inversion (Diez et al., 1997; Aziz et al., 2007; El-Kaïm et al., 2003; Hassan et al., 2008b). Thus, several options for the interaction between *Ia–Ie* and *II* may be envisaged.

It is probable that all the products observed are formed from one of the four labile (1 : 1) adducts *(VI–*

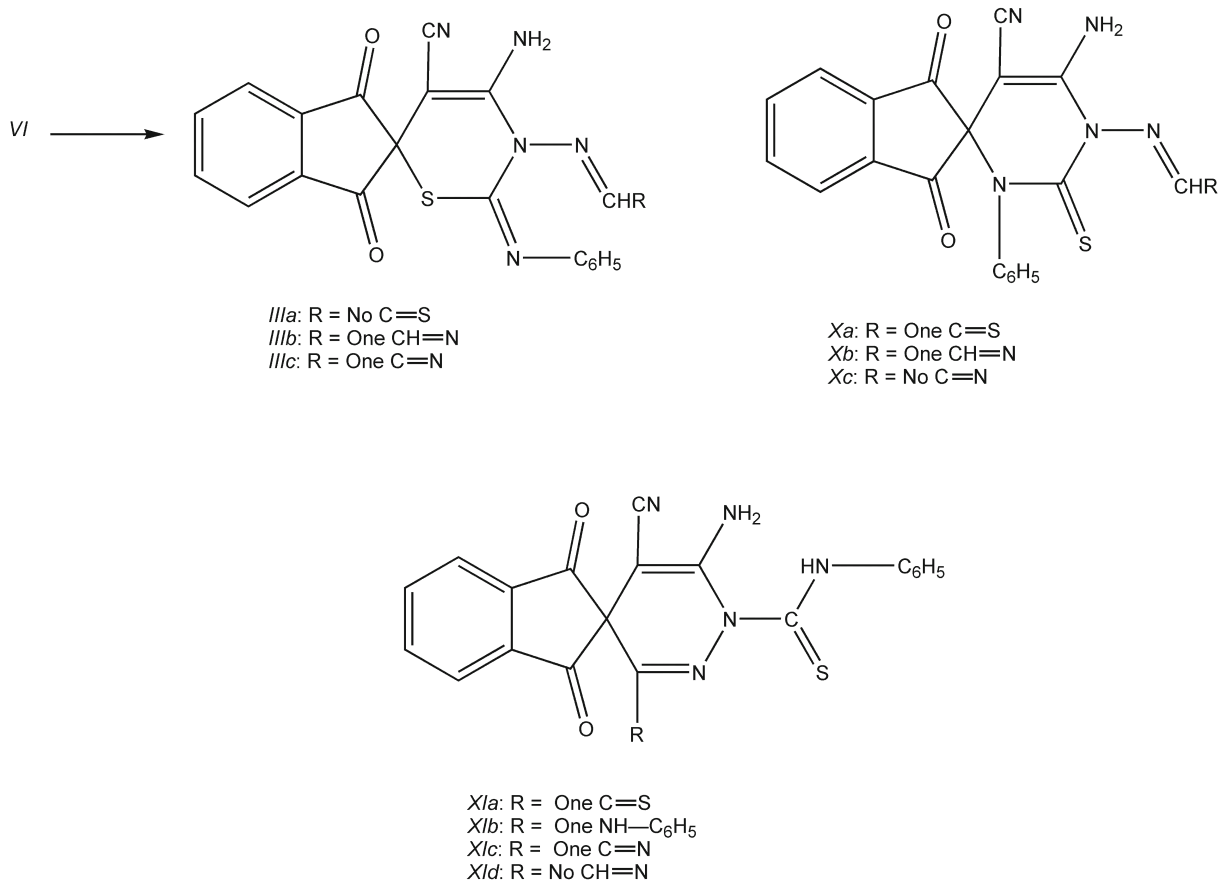

Fig. 3. The isomeric products from the intermediate *VI*.

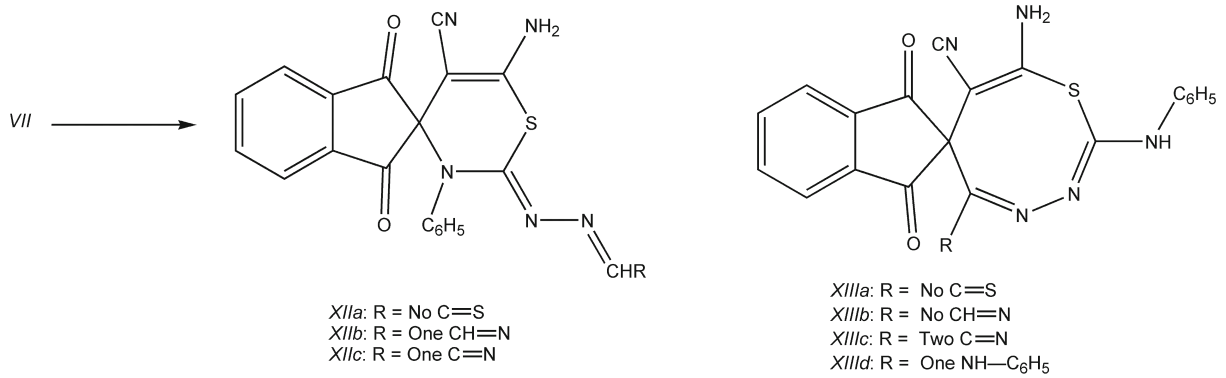

Fig. 4. The isomeric products from the intermediate *VII*.

IX) of *II* to *I* (Fig. 2). The isomeric products would be *III, X*, and *XI*, if the reaction took place through (N-2 and SH), (N-2 and N-4), and (N-4 and azomethine–CH), respectively, via the intermediate *VI* (Fig. 3).

Products *XII* and *XIII* could be isolated if the reaction involved the participation of SH and N-4 or SH and azomethine–CH, respectively via the adduct *VII* (Fig. 4).

If N-4 attacked the C≡N of *II*, adduct *VIII* was observed followed by inter-molecular nucleophilic attack either by SH or azomethine–CH, products *XIV* and *XV* could be isolated (Fig. 5).

Structures *X*, *XI*, *XIII*, *XIV*, and *XV* could be excluded on the basis of ^{1}H NMR as well as ^{13}C NMR spectra. For the alternative structures *XII,* the spiro–C-2,4′ ^{13}C-resonances are considerably down-field to those which were observed (Gomaa & Döpp, 1998; Hassan et al., 2006). Structures *XII* and *XIV* could be excluded on the basis of fragmentation ions in the mass spectra of isolated products and formation of PhN═C═S as well as R—CH═N—N═C═S as fragments, for example *IIIa* at m/z = 489, 447, 354, 210,

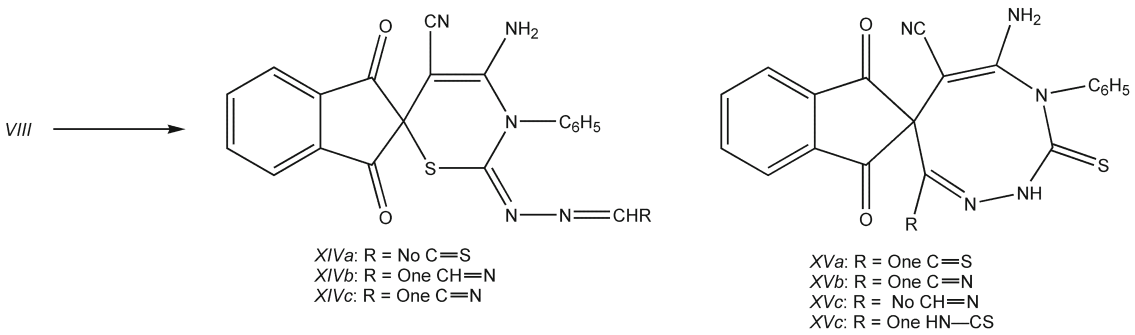

Fig. 5. The isomeric products from the intermediate *VIII*.

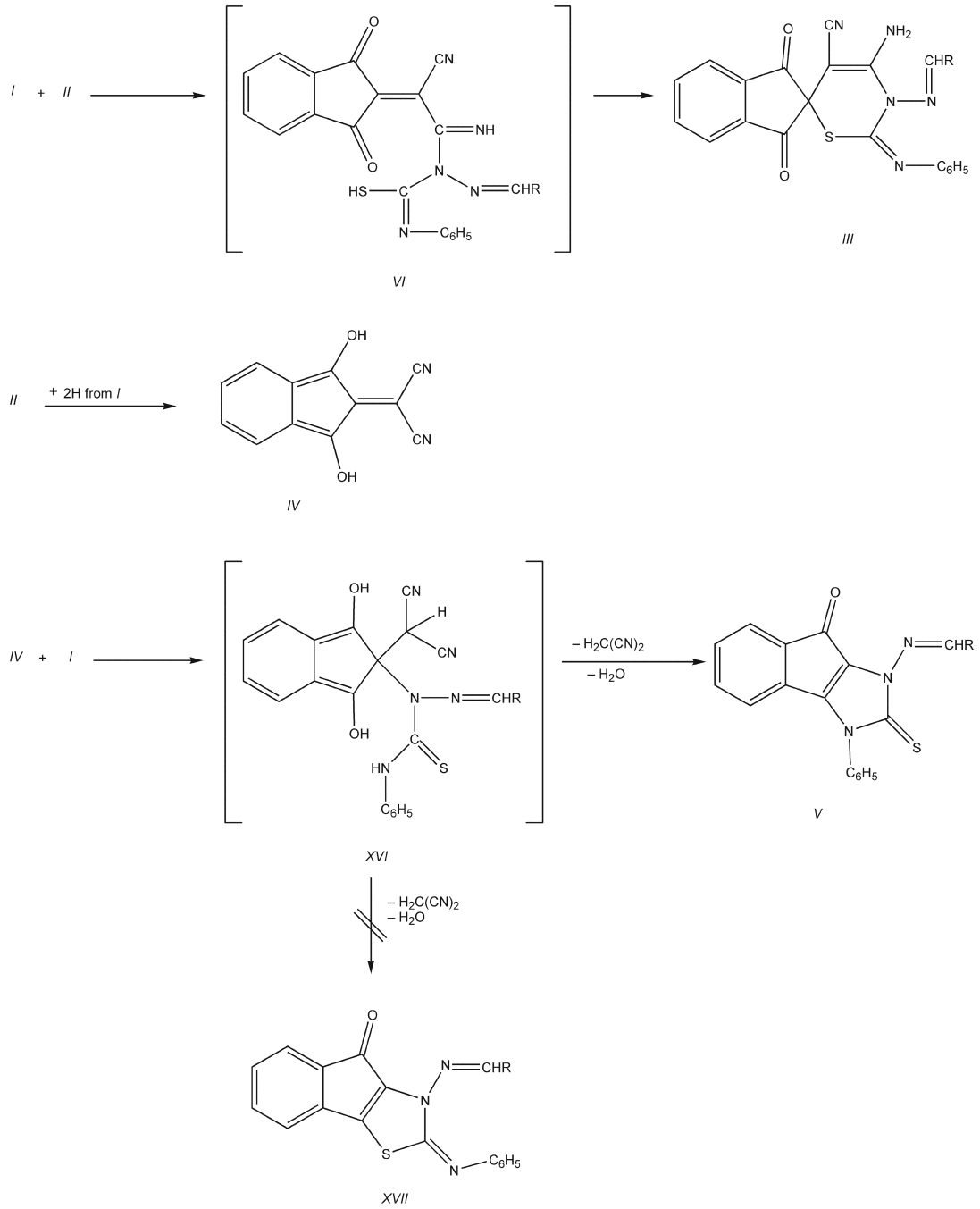

Fig. 6. The mechanism of formation products *III* and *V*.

Table 1. Spectral data of newly prepared compounds *Ia–Ie*, *IIIa–IIIe*, and *Va–Vd*

Compound	Spectral data
Ib	IR, $\tilde{\nu}$/cm^{-1}: 983, 1362 (C═S, C—N), 1594, 1619 (Ar-C═C), 2983 (Ali-CH), 3123 (Ar-CH), 3236, 3315 (NH′s) ^{1}H NMR ($CDCl_3$), δ: 3.90 (s, 3H, OCH_3), 6.90–7.10 (m, 3H, Ar-H and CH═CH), 7.14–7.17 (m, 2H, Ar-H), 7.32–7.35 (m, 3H, Ar-H), 7.58–7.60 (m, 3H, Ar-H), 8.00 (d, 1H, J = 9.4 Hz, CH═N), 9.95 (br, 1H, NH) ^{13}C NMR ($CDCl_3$), δ: 55.5 (OCH_3), 110.6, 120.7, 124.1, 124.8, 124.9, 125.8, 127.8, 128.0, 130.4 (Ar-CH), 134.4, 138.1 (Ar-C), 145.8 (CH═N), 156.4 (Ar-C—O), 175.2 (C═S) MS, m/z (I_r/%): 311 (100) (M^+), 280 (11), 135 (36), 91 (28), 77 (21)
Ic	IR, $\tilde{\nu}$/cm^{-1}: 983, 1324 (C═S, C—N), 1595, 1644 (Ar-C═C), 2988 (Ali-CH), 3142, 3292 (NH′s) ^{1}H NMR ($CDCl_3$), δ: 0.85 (t, 3H, J = 6.7 Hz, CH_3), 1.45 (m, 2H, CH_2), 2.20–2.24 (m, 2H, CH_2), 6.22 (d, 2H, J = 15.9 Hz, CH═CH), 7.15–7.17 (m, 1H, Ar-H), 7.30–7.33 (m, 2H, Ar-H), 7.60–7.63 (m, 2H, Ar-H), 7.85 (d, 1H, J = 9.4 Hz, CH═N), 9.85 (br, 1H, NH) ^{13}C NMR ($CDCl_3$), δ: 13.5 (CH_3), 21.3 (CH_2), 34.4 (CH_2), 124.8, 124.9, 127.2, 127.9 (Ar-CH), 138.9 (Ar-C), 143.6 (Ar-CH), 145.2 (CH═N), 175.4 (C═S) MS, m/z (I_r/%): 247 (100) (M^+), 151 (76), 135 (64), 110 (51), 91 (48), 77 (41)
Id	^{1}H NMR ($CDCl_3$), δ: 1.85 (d, 3H, J = 6.6 Hz, CH_3), 6.23–6.25 (m, 2H, CH═CH), 7.15–7.17 (m, 1H, Ar-H), 7.35–7.38 (m, 2H, Ar-H), 7.55 (m, 2H, Ar-H), 7.82 (d, 1H, J = 9.3 Hz, CH═N), 9.80 (br, 1H, NH) ^{13}C NMR ($CDCl_3$), δ: 18.5 (CH_3), 125.9, 127.7, 128.0, 128.4 (Ar-CH), 138.9 (Ar-C), 141.2 (Ar-CH), 145.2 (CH═N), 175.3 (C═S) MS, m/z (I_r/%): 219 (12) (M^+), 192 (14), 151 (18), 135 (12), 77 (15), 41 (100)
Ie	IR, $\tilde{\nu}$/cm^{-1}: 981, 1379 (C═S, C—N), 1599 (Ar-C═C), 2998 (Ali-CH), 3064 (Ar-CH), 3151, 3301 (NH′s) ^{1}H NMR ($CDCl_3$), δ: 1.12 (d, 6H, J = 6.5 Hz, 2 × CH_3), 2.55–2.57 (m, 1H, CH), 7.15–7.18 (m, 1H, Ar-H), 7.33–7.35 (m, 2H, Ar-H), 7.50–7.52 (m, 1H, Ar-H), 7.60–7.63 (m, 2H, Ar-H and CH═N), 9.70 (br, 1H, NH) ^{13}C NMR ($CDCl_3$), δ: 19.5, 19.9 (CH_3), 30.7 (CH), 125.3, 128.5, 129.4 (Ar-CH), 138.9 (Ar-C), 152.4, (CH═N), 176.6 (C═S) MS, m/z (I_r/%): 221 (14) (M^+), 178 (28), 151 (11), 135 (12), 91 (21), 77 (26), 43 (100)
IIIa	IR, $\tilde{\nu}$/cm^{-1}: 1590, 1610 (Ar-C═C), 1650 (C═N), 1725 (CO), 2210 (C≡N), 3290–3360 (NH_2) ^{1}H NMR ($CDCl_3$), δ: 6.51 (br, 2H, NH_2), 6.60–6.85 (m, 2H, CH═CH), 7.14–7.35 (m, 8H, Ar-H), 7.80–7.84 (m, 7H, Ar-H and CH═N) ^{13}C NMR ($CDCl_3$), δ: 53.7 (C-5′), 57.6 (spiro-C-2,6′), 118.8 (C≡N), 124.9, 126.2, 127.2, 127.5, 128.8, 129.0, 129.1, 129.3, 129.8, 135.6, 136.1 (Ar-CH), 140.6, 142.0 (Ar-C), 143.7 (CH═N), 158.0 (C-2′), 168.4 (C-4′), 192.2 (C═O) MS, m/z (I_r/%): 489 (8) (M^+), 447 (12), 354 (10), 210 (22), 206 (48), 188 (7), 135 (76), 129 (100), 104 (33), 91 (42), 77 (51), 66 (15)
IIIb	IR, $\tilde{\nu}$/cm^{-1}: 1610 (Ar-C═C), 1655 (C═N), 1730 (C═O), 2215 (C≡N), 3300–3350 (NH_2) ^{1}H NMR ($CDCl_3$), δ: 3.85 (s, 3H, OCH_3), 6.55 (br, 2H, NH_2), 6.88–6.95 (m, 2H, CH═CH), 7.10–7.15 (m, 2H, Ar-H), 7.22–7.38 (m, 5H, Ar-H), 7.40–7.53 (m, 4H, Ar-H), 7.90 (m, 2H, Ar-H), 8.00 (d, 1H, J = 9.4 Hz, CH═N) ^{13}C NMR ($CDCl_3$), δ: 54.3 (C-5′), 54.4 (OCH_3), 57.7 (spiro-C-2,6′), 110.0 (Ar-CH), 119.5 (C≡N), 123.9, 125.8, 125.9, 126.8, 126.9, 127.2, 128.6, 128.7, 129.3, 130.8 (Ar-CH), 134.5, 134.7, 135.7 (Ar-C), 142.9 (CH═N), 158.6 (C-2′), 159.1 (Ar-C—OCH_3), 167.9 (C-4′), 192.5 (C═O) MS, m/z (I_r/%): 519 (11) (M^+), 504 (9), 332 (26), 318 (14), 261 (29), 218 (7), 145 (22), 135 (64), 104 (45), 77 (100), 66 (46)
IIIc	IR, $\tilde{\nu}$/cm^{-1}: 1600 (Ar-C═C), 1645 (C═N), 1725 (C═O), 2220 (C≡N), 3310–3340 (NH_2) ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3H, J = 6.7 Hz, CH_3), 1.40 (m, 2H, CH_2), 2.18 (m, 2H, CH_2), 6.23 (m, 2H, CH=CH), 6.72 (NH_2), 7.22–7.30 (m, 2H, Ar-H), 7.32–7.46 (m, 2H, Ar-H), 7.48–7.56 (m, 2H, Ar-H), 7.59–7.75 (m, 2H, Ar-H), 7.93 (d, 1H, J = 9.3 Hz, CH═N) ^{13}C NMR ($CDCl_3$), δ: 12.7 (CH_3), 20.7 (CH_2), 33.9 (CH_2), 52.6 (C-5′), 56.6 (spiro-C-2,6′), 119.5 (C≡N), 124.1, 126.7, 128.5, 128.8, 130.8, 131.3 (Ar-CH), 133.5, 134.6 (Ar-C), 144.1 (Ar-CH), 146.4 (CH═N), 158.2 (C-2′), 167.4 (C-4′), 191.7 (C═O) MS, m/z (I_r/%): 455 (21) (M^+), 413 (41), 370 (46), 245 (53), 210 (41), 154 (12), 135 (100), 91 (78), 77 (74), 66 (39)
IIId	IR, $\tilde{\nu}$/cm^{-1}: 1610 (Ar-C═C), 1645 (C═N), 1720 (C═O), 2210 (C≡N), 3310–3350 (NH_2) ^{1}H NMR ($CDCl_3$), δ: 1.80 (d, 3H, J = 6.5 Hz, CH_3), 6.26 (m, 2H, CH═CH), 6.50 (br, 2H, NH_2), 7.20–7.55 (m, 5H, Ar-H), 7.60–7.76 (m, 4H, Ar-H), 7.84 (d, 1H, J = 9.3 Hz, CH═N) ^{13}C NMR ($CDCl_3$), δ: 17.6 (CH_3), 53.1 (C-5′), 57.1 (spiro-C-2,6′), 119.2 (C≡N), 124.7, 127.5, 128.1, 128.6, 128.7, 130.8 (Ar-CH), 134.5, 135.5 (Ar-C), 138.8 (Ar-CH), 143.8 (CH═N), 157.3 (C-2′), 168.2 (C-4′), 191.6 (C═O) MS, m/z (I_r/%): 427 (9) (M^+), 371 (18), 329 (34), 292 (21), 217 (72), 210 (91), 135 (100), 126 (8), 104 (72), 77 (68), 66 (31)
IIIe	IR, $\tilde{\nu}$/cm^{-1}: 1595, 1610 (Ar-C═C), 1655 (C═N), 1730 (C═O), 2215 (C≡N), 3290–3370 (NH_2) ^{1}H NMR ($CDCl_3$), δ: 1.14 (d, 6H, J = 6.5 Hz, 2 × CH_3), 2.48 (m, 1H, CH), 6.61 (br, 2H, NH_2), 7.20–7.76 (m, 9H, Ar-H), 7.83 (d, 1H, J = 9.3 Hz, CH═N) ^{13}C NMR ($CDCl_3$), δ: 19.9 (CH_3), 29.5 (CH), 52.9 (C-5′), 56.8 (spiro-C-2,6′), 119.2 (C≡N), 126.7, 127.3, 128.0, 128.3, 130.1 (Ar-CH), 134.7, 135.9 (Ar-C), 152.76 (CH═N), 157.3 (C-2′), 167.9 (C-4′), 192.6 (C═O) MS, m/z (I_r/%): 429 (8) (M^+), 363 (14), 333 (12), 292 (21), 279 (19), 220 (65), 179 (51), 150 (46), 135 (31), 128 (6), 104 (100), 77 (46), 66 (21)

Table 1. (continued)

Compound	Spectral data
Va	IR, $\tilde{\nu}$/cm^{-1}: 995, 1360 (C═S, C—N), 1590, 1610 (Ar-C═C), 1685 (C═O) ^{1}H NMR ($CDCl_3$), δ: 6.80 (m, 2H, CH═CH), 6.90–7.10 (m, 3H, Ar-H), 7.16–7.76 (m, 11H, Ar-H), 7.98 (d, 1H, J = 9.4 Hz, CH═N) ^{13}C NMR ($CDCl_3$), δ: 117.8 (C-8a), 119.8, 125.0, 126.2, 126.6, 127.0, 127.4, 127.6, 127.9, 128.3, 128.8, 129.2, 130.5 (Ar-CH), 132.0 (C-3a), 132.2, 134.4, 135.0, 136.5 (Ar-C), 140.7 (CH═N), 181.2 (C═S), 188.9 (C═O) MS, m/z (I_r/%): 407 (100) (M^+), 303 (22), 272 (9), 263 (47), 135 (52), 104 (34), 91 (67), 77 (45)
Vb	IR, $\tilde{\nu}$/cm^{-1}: 1010, 1355 (C═S, C—N), 1585, 1615 (Ar-C═C), 1690 (C═O) ^{1}H NMR ($CDCl_3$), δ: 3.85 (s, 3H, OCH_3), 6.80–6.90 (m, 3H, CH═CH and Ar-H), 7.00–7.40 (m, 6H, Ar-H), 7.50–7.65 (m, 6H, Ar-H), 8.00 (d, 1H, J = 9.3 Hz, CH═N) ^{13}C NMR ($CDCl_3$), δ: 55.5 (OCH_3), 110.6 (C-8a), 111.0, 122.9, 125.0, 125.3, 126.0, 126.5, 127.4, 128.1, 128.9, 129.8, 130.0, 130.2, 131.5 (Ar-CH), 132.5 (C-3a), 133.2, 135.4, 135.7, 137.6 (Ar-C), 146.2 (CH═N), 157.6 (Ar-C—O), 182.3 (C═S), 189.1 (C═O) MS, m/z (I_r/%): 437 (11) (M^+), 391 (51), 302 (6), 271 (100), 210 (391), 135 (26), 104 (52), 91 (44), 77 (67)
Vc	IR, $\tilde{\nu}$/cm^{-1}: 1000, 1345 (C═S, C—N), 1600, 1605 (Ar-C═C), 1690 (C═O) ^{1}H NMR ($CDCl_3$), δ: = 0.90 (t, 3H, J = 6.7 Hz, CH_3), 1.40 (m, 2H, CH_2), 2.15 (m, 2H, CH_2), 6.10 (dd, 2H, J = 15.8 Hz, CH═CH), 6.95 (m, 2H, Ar-H), 7.15–7.40 (m, 5H, Ar-H), 7.50–7.63 (m, 2H, Ar-H), 7.80 (d, 1H, J = 9.4 Hz, CH═N) ^{13}C NMR ($CDCl_3$), δ: 12.6 (CH_3), 20.8 (CH_2), 33.9 (CH_2), 119.7 (C-8a), 124.9, 125.3, 127.1, 127.2, 128.6, 128.9, 130.5, 131.5 (Ar-CH), 132.2 (C-3a), 132.7, 134.4, 136.6 (Ar-C), 144.1 (Ar-CH), 148.6 (CH═N), 181.2 (C═S), 188.9 (C═O) MS, m/z (I_r/%): 373 (37) (M^+), 330 (100), 277 (18), 264 (22), 238 (6), 135 (26), 91 (32), 77 (27)
Vd	IR, $\tilde{\nu}$/cm^{-1}: 985, 1360 (C═S, C—N), 1580, 1600 (Ar-C═C), 1695 (C═O) ^{1}H NMR ($CDCl_3$), δ: 1.30 (d, 6H, J = 6.4 Hz, 2 × CH_3), 2.50 (m, 1H, CH), 7.00 (m, 5H, Ar-H), 7.30–7.65 (m, 5H, Ar-H and CH═N) ^{13}C NMR ($CDCl_3$), δ: 22.0 (CH_3), 29.9 (CH), 122.4 (C-8a), 126.2, 127.1, 127.9, 128.5, 128.8, 129.0, 129.5 (Ar-CH), 131.5 (C-3a), 135.3, 136.5, 138.1 (A-C), 153.3 (CH═N), 181.1 (C═S), 189.2 (C═O) MS, m/z (I_r/%): 347 (9) (M^+), 304 (11), 219 (100), 204 (32), 149 (63), 135 (29), 91 (24), 77 (34)

Table 2. Characterisation data of newly prepared compounds *Ib–Ie*, *IIIa–IIId*, and *Va–Vd*

Compound[a]	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
			C	H	N	S	%	°C
Ib	$C_{17}H_{17}N_3OS$	311.40	65.57	5.50	13.49	10.30	89	190
			65.65	5.41	13.60	10.17		
Ic	$C_{13}H_{17}N_3S$	247.36	63.12	6.93	16.99	12.96	81	152
			62.97	7.07	17.14	12.79		
Ie	$C_{11}H_{15}N_3S$	221.10	59.69	6.83	18.99	14.49	77	144
			59.82	6.74	19.22	14.34		
IIIa	$C_{28}H_{19}N_5O_2S$	489.55	68.70	3.91	14.31	6.55	53	300
			68.86	4.07	14.19	6.73		
IIIb	$C_{29}H_{21}N_5O_3S$	519.57	67.04	4.07	13.48	6.17	46	315
			66.87	3.93	13.65	6.04		
IIIc	$C_{25}H_{21}N_5O_2S$	455.53	65.92	4.65	15.37	7.04	49	290
			66.14	4.49	15.51	6.88		
IIId	$C_{23}H_{17}N_5O_2S$	427.48	64.62	4.01	16.38	7.50	47	274
			64.78	3.93	16.22	7.66		
IIIe	$C_{23}H_{19}N_5O_2S$	429.49	64.32	4.46	16.31	7.47	41	280
			64.51	4.43	16.52	7.32		
Va	$C_{25}H_{17}N_3OS$	407.49	73.69	4.21	10.31	7.87	28	238
			73.87	4.32	10.13	7.98		
Vb	$C_{26}H_{19}N_3O_2S$	437.51	71.38	4.38	9.60	7.33	29	260
			71.16	4.47	9.76	7.15		
Vc	$C_{22}H_{19}N_3OS$	373.47	70.75	5.13	11.25	8.59	31	220
			70.94	4.98	11.42	8.73		
Vd	$C_{20}H_{17}N_3OS$	347.43	69.14	4.93	12.09	9.23	28	205
			68.91	5.02	11.93	9.39		

a) Physical-chemical data of compounds *Ia* and *Id* are in accordance with literature (Shah & Trivedi, 1963; Grammaticakis, 1950, 1953).

206, 188, 135, 129, 104, 91, 77, and 66. Only the structure of *IIIa–IIIe*, however, accommodates all the spectral data listed above.

The results of combustion analysis and spectroscopic data suggested the presence of thioxoindenoimidazolone derivatives *Va–Vd* as one of the products from the reaction between *Ia–Ie* and *II*. The molecular formula $C_{22}H_{19}N_3OS$ for *Vc* was confirmed by the mass spectrum which exhibited the molecular ion at $m/z = 373$ (37 %) and the fragmentation pattern at $m/z = 373$, 330, 277, 264, 238, 135, 91, 77. The IR spectrum showed absorption at 1690 cm^{-1} (C═O), and 1345 cm^{-1} as well as 1000 cm^{-1} due to strong vibrational coupling of the C═S and C—N entities. The ^{1}H NMR spectrum of *Vc* displayed one doublet at δ 7.80 for one proton (CH═N) and a doublet of doublets at δ 6.10 due to (CH═CH), in addition to the aromatic protons. The signals around δ 124.9 and δ 144.1 (Ar–CH), δ 148.6 (CH═N), δ 181.2 (C═S), and δ 188.9 (C═O) in the salient features of the NMR spectra are in line with the structures assigned to *V*.

The alternative possible isomeric structures *XVII* which were excluded on the basis of the lowest field signals in the ^{13}C NMR spectra (*Va*, δ 181.2; *Vb*, δ 182.3; *Vc*, δ 181.2; and *Vd*, δ 181.1) clearly show a thiourea C═S group (Hassan & Shehatta, 2007; Hassan & Döpp, 2006) and not an isothiourea carbon as in *XVII*.

In addition, 1,3-dihydroxy-2*H*-inden-2-ylidenepropanedinitrile (*IV*) was formed in yields varying from 8 % to 12 %. Compound *IV* was demonstrated by comparing its melting point, IR, and ^{1}H NMR with an authentic sample (Junek et al., 1977).

A rationale for the formation of products *III–V* is depicted in Fig. 6. Nucleophilic attack of N-2 of *Ia–Ie* on one of the cyano groups of *II*, followed by intramolecular attack of SH group on C-2 of the indanedione skeleton of *VI* leads to spiro dioxo(indene-2,6′-[1,3]thiazine derivatives (*IIIa–IIIe*). Starting material *II* is partially reduced to *IV*. Alkenylidene-hydrazinecarbothioamides *I* could serve as reducing agents. Nucleophilic attack of N-2 in *Ia–Ie* on C═C of *IV* with the elimination of a molecule of malononitrile and another of H_2O from adduct *XVI* gives rise to *Va–Vd*. The alternative option, namely intra-nucleophilic attack by the thione sulphur atom on C-3 of *XVI*, is not observed.

On the other hand, the semi-micropreparative scale reaction of *IV* with *Ia* in ethyl acetate under reflux yielded compound *Va*, as established from the comparison of the IR spectrum and melting point with those of the authentic sample.

Conclusions

Alkenylidene-hydrazinecarbothioamides are multidentate nucleophiles allowing for various modes of heterocyclisation with 2-(dicyanomethylidene)indan-1,3-dione, (*II*) providing several electrophilic sites. Thus, thiaheterocycles S—C—N + C≡N or N—(CS)—N + C_2 mode of cyclisation are favoured. Both spiroanellated 1,3-thiazines and fused imidazolines are formed.

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