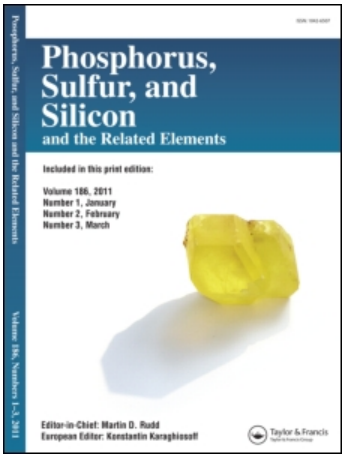

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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS (IV) PYROLYSIS OF 2-ARYLIMINO-3-ARYL-5-BENZYLIDENETHIAZOLIDIN-4-ONE

A. M. Gaber[a]; A. M. Kamal El-Dean[a]; A. A. Atalla[b]
[a] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt [b] Chemistry Department, Faculty of Science, Al-Azher University, Assiut, Egypt

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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS (IV)† PYROLYSIS OF 2-ARYLIMINO-3-ARYL-5-BENZYLIDENETHIAZOLIDIN-4-ONE

A. M. GABER,‡ A. M. KAMAL EL-DEAN‡ and A. A. ATALLA§
‡*Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt; and*
§*Chemistry Department, Faculty of Science, Al-Azher University, Assiut, Egypt*

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Thermal rearrangement of 2-arylimino-3-aryl-5-benzylidene-thiazolidin-4-ones (I–IV) by reflux in air at 250°C has been thoroughly investigated. The isolated products are H_2S, CO, CO_2, ammonia, water, arylamines, aryl isothiocyanates, benzothiophenes, arylnitriles, arylurea derivatives, arylthiourea derivatives, 2-arylquinolines, benzimidazole derivatives and polystyrene. With compound III, in addition to the previous products benzaldehyde, bibenzyl, stilbene, bibenzylamine, benzylcyanamide and 2,3,4,5-tetraphenylthiophene were obtained. Free radical mechanisms involving homolysis of C—S and C—N bonds have been suggested to account for the identified products.

Key words: Molecular rearrangement; pyrolysis; 2-arylimino-3-aryl-5-benzylidenethiazolidin-4-ones.

INTRODUCTION

Thiazolidine-4-ones possess hypnotic, anesthetic, antifungal,[1] and other biological activity as a streptomyces-antibiotic exhibiting in vitro antitubercular activity.[2]

5-Arylidene-3-phenyl-2-phenylimino-4-thiazolidinones are reported to give fast colours when dyed on wool.[3] Several 3-aryl substituted 5-arylidene-2-phenylimino-4-thiazolidinones are useful ultraviolet filtering agents.[4] Furthermore, 5-arylidene derivatives of 4-thiazolidinones have been found to possess great bactericidal and fungicidal activity.[5]

Recently, we have recorded[6,7,8] the thermal rearrangement of these biologically active compounds aimed to clarify the behaviour of these compounds when subjected to the high temperature and moreover to get a clue for the behaviour of such compounds when subjected to photolysis. This prompted us to reinvestigate such reactions in an effort to gain further information about more generalized pyrolytic mechanisms.

RESULTS AND DISCUSSION

In continuation of our recent studies on the pyrolysis of organic compounds containing heteroatoms, pyrolysis of 2-phenylimino-3-phenyl-5-benzylidenethiazolidin-4-one(I) and 2-*p*-tolylimino-3-*p*-tolyl-5-benzylidenethiazolidin-4-one(II) at 250°C for

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10 h give rise to the products shown in Table I. The formation of these products from I can be assumed to follow the series of reactions shown in Scheme 1 which implies the preliminary homolysis (C—S) bond (route a) forming biradical (Ia, IIa) which undergoes fragmentation under the same conditions into the radical pairs (i) and (ii). The latter may undergo decarbonylation followed by intramolecular cyclization to afford benzothiophene,[9] whereas the former may abstract hydrogen followed by cyclization to give 1-phenylbenzimidazole.[10]

On the other hand, Scheme 1 also includes (C—N) bond homolysis (route b) to give the biradical (Ib, IIb) which may abstract hydrogen and subsequently decompose into cinnamoyl radicals and the biradical (iii). The biradical (iii) may abstract hydrogen followed by fragmentation under the same conditions forming arylamines and aryl isothiocyanate. The latter may couple with arylamines to form arylthiocarbanilides.[11]

The formation of 2-phenylquinoline and 2-*p*-tolylquinoline may take place through coupling of the cinnamoyl radical with the anilino radical forming cinnamanilide which tautomerizes to the enol form and then eliminates water with a 1,2-phenyl shift forming 2-arylquinolines.[5]

Furthermore, route (c) gives rise to biradical (Ic, IIc) which may abstract hydrogen and subsequently decompose giving a styryl radical, aryl isothiocyanate and aryl isocyanate. The styryl radical may undergo polymerization forming polystyrene, whereas aryl isocyanate react with arylamines to form arylcarbanilides[12] or react with water from the medium of the reaction giving arylamines and carbon dioxide[13] as shown in Scheme 1.

Analogous results were also obtained in the case of thermal rearrangement of 2-benzylimino-3-benzyl-5-benzylidenethiazolidin-4-one (III) under the same conditions, which gives rise to ammonia, CO, H_2S, water, benzaldehyde, bibenzyl, stilbene, benzothiophene, benzyl isothiocyanate, benzylamine, bibenzylamine, benzylcyanamide, phenylacetonitrile, 2-benzylquinoline, 2,3,4,5-tetraphenylthiophene and polystyrene as shown in Scheme 2.

The formation of benzaldehyde, bibenzyl, stilbene and tetraphenylthiophene can be assumed to proceed through the homolysis of the (C—S) bond (route a) via biradicals (IIIa) forming benzylcyanamide and benzyl radicals which can be considered to be the precursor of benzaldehyde, bibenzyl, and stilbene through processes of oxidation; dimerization followed by dehydrogenation respectively.[14]

A possible pathway for the formation of tetraphenylthiophene is interaction of stilbene with sulphur readily available in the reaction medium as reported earlier.[15]

The formation of benzyl isothiocyanate, 2-benzylquinoline, phenylacetonitrile, benzylamine, bibenzylamine and polystyrene can be suggested to proceed through the homolysis of (C—N) and (C—S) bonds via biradicals (IIIb) and (IIIc), respectively. Such products can be interpreted as shown previously in Scheme 1. The results are summarized in Table I.

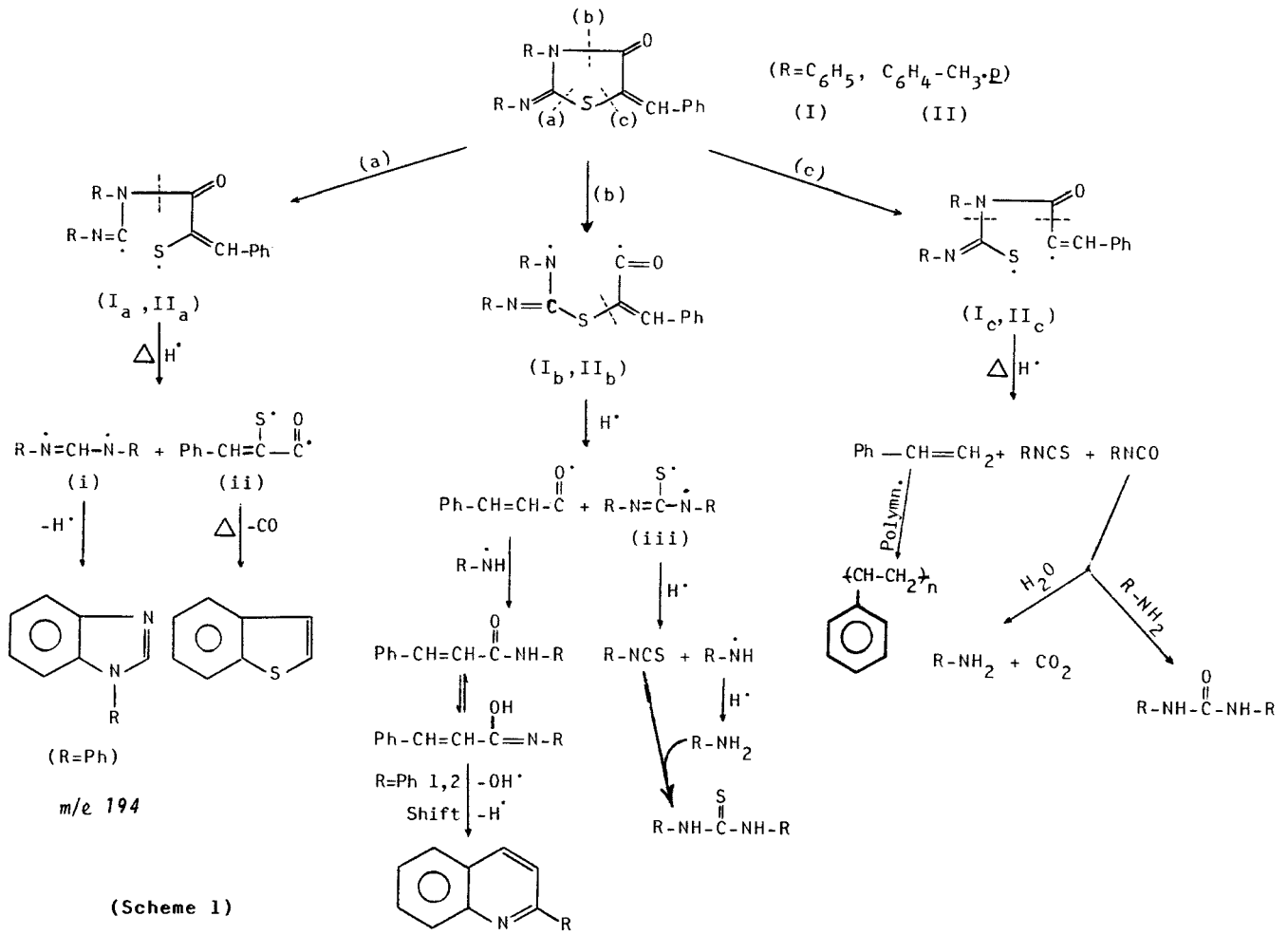
Similarly, thermal rearrangement of 2-*p*-methoxyphenylimino-3-*p*-methoxyphenyl-5-benzylidenethiazolidin-4-one (IV) under the same conditions gives CO, CO_2, H_2S, water, *p*-anisidine, anisole, *p*-methoxybenzonitrile, *p*-methoxyphenyl isothiocyanate, benzothiophene, N,N-di-*p*-methoxyphenylurea, N,N-di-*p*-methoxyphenylthiourea, 6-methoxybenzimidazole, 2-*p*-methoxyphenylquinoline and polystyrene as in Scheme 3.

TABLE I

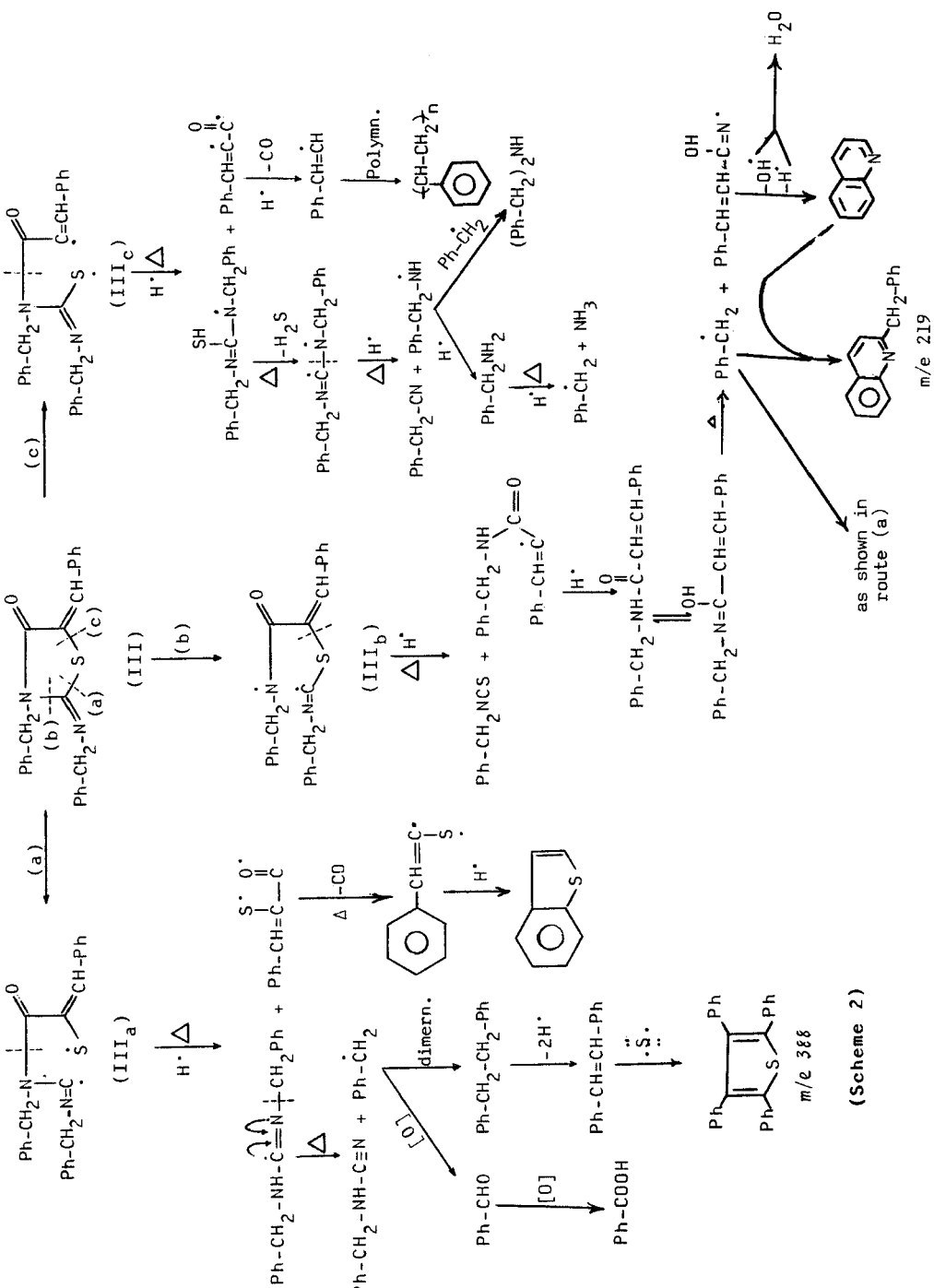
Pyrolysis products of thiazolidin-4-one derivatives (I–IV) in gram (% yield).

Products in g (%)	I	II	III	IV
CO	evolved	evolved	evolved	evolved
CO_2	evolved	evolved		evolved
H_2S	—	—	evolved	evolved
Water	drops	drops	drops	drops
Ammonia	—	—	evolved	—
Benzaldehyde[a]	—	—	1.8(12)	—
Bibenzyl[b]	—	—	1.5(10)	—
Stilbene[c]	—	—	1.3(8.9)	—
Benzylcyanamide[d]	—	—	0.8(5.3)	—
Bibenzylamine[e]	—	—	1.0(6.7)	—
Anisole[f]	—	—	—	1.8(12)
Benzothiophene[g]	1.6(10.7)	1.8(12)	1.1(7.3)	1.4(9.3)
Amine derivatives	1.5[h](10)	2.2[i](14.7)	1.5[j](10)	1.5[k](10)
Thiourea derivatives	2.0[l](13.3)	2.6[m](17.3)	—	1.8[n](12)
Urea derivatives	1.6[o](10.7)	2.0[p](13.3)	—	1.6[q](10.7)
Benzimidazole derivatives	1.8[r](12)	—	—	1.1[s](7.3)
Isothiocyanate derivatives	2.1[t](14)	2.5[u](16.7)	1.2[v](8)	1.4[w](9.3)
Nitrile derivatives	—	—	0.6[x](4)	0.5[y](3.3)
Quinoline derivatives	1.2[z](8)	—	1.0*(6.7)	1.1**(7.3)
2,3,4,5-tetraphenylthiophene***	—	—	1.2(8)	—
Residue and polystyrene****	1.6(10.7)	1.8(12)	0.9(6)	1.2(8)

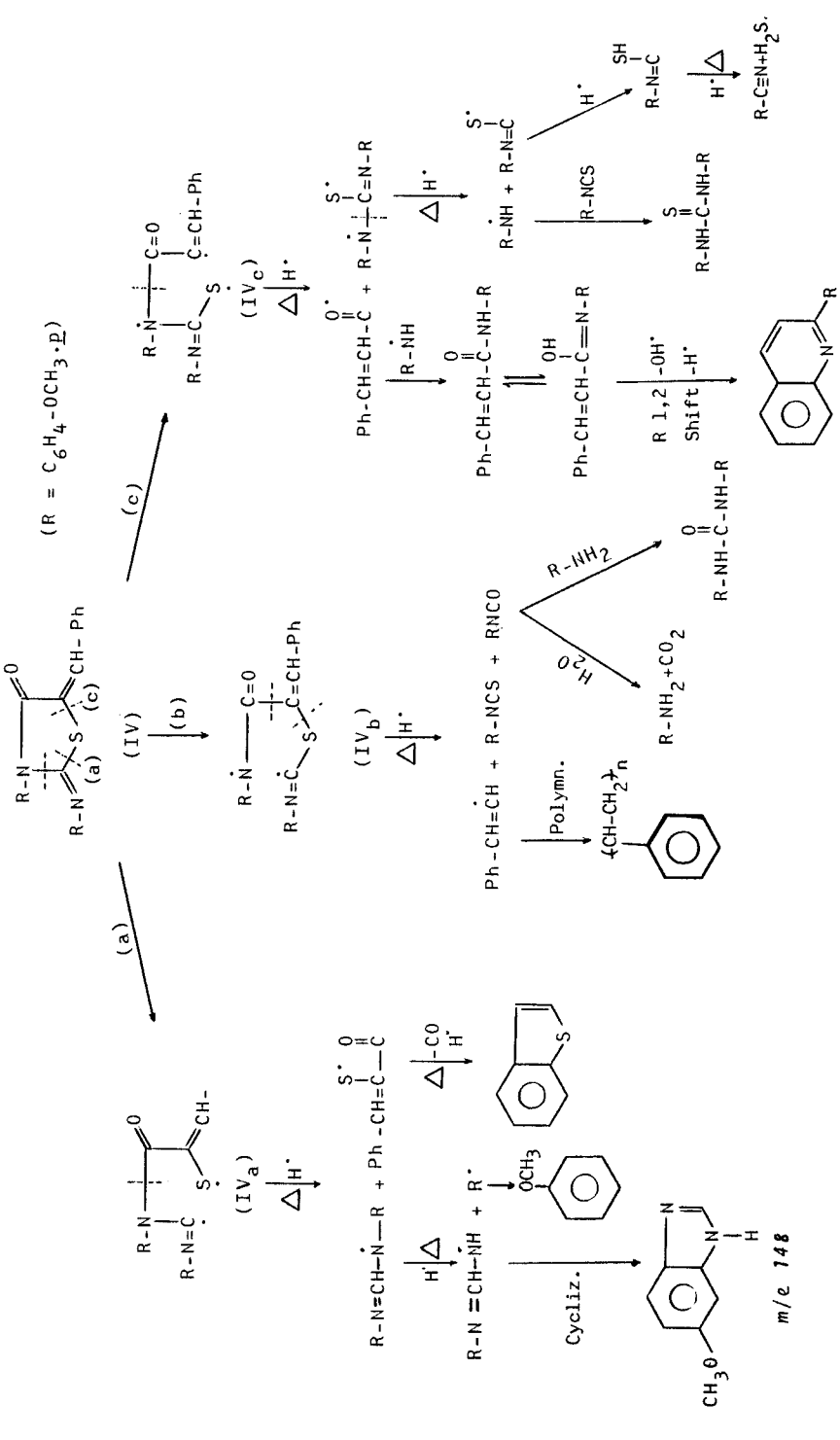
[a] b.p. 75–85°C/10 mm.Hg.; 2,4-dinitrophenylhydrazone, mm.p. 230–5°C.
[b] Mixture mp 50–2°C, 4,4′-dinitroderivative mm.p. 180°C.
[c] Mixture mp 120–4°C.
[d] Sample[19]: mp 45–7°C; crystallized from ether mm.p. 45°C.
[e] Sample[20]: pale yellow oil, b.p. 300°C; n_D^{20}: 1.5743; hydrochloride mm.p. 250–6°C.
[f] b.p. 150°C; n_D^{20}: 1.5120, lit. n_D^{20}: 1.5160.
[g] b.p. 221–222°C; mp 29–32°C; mm.p. 30°C.
[h] Aniline; b.p. 180–5°C; n_D^{20}: 1.5615 and acetyl derivative mm.p. 110–3°C.
[i] *p*-Toluidine; mp 45–7°C; mp and mm.p. 45°C; benzoyl derivative mm.p. 140–5°C.
[j] Benzylamine; b.p. 184–5°C; n_D^{20}: 1.5211, lit. n_D^{20}: 1.5424.
[k] *p*-Anisidine; b.p. 240–3°C; m.p. 60–2°C; mp and mm.p. 57–60°C.
[l] Thiocarbanilide[21]: sample mp. 150–5°C; crystallized from ethanol mm.p. 154–7°C.
[m] N,N-Di-*p*-tolylthiourea[22]: sample mp. 178–180°C.
[n] N,N-Di-*p*-methoxyphenylthiourea[23]: sample mp. 132–135°C; crystallized from ethanol mm.p. 136°C.
[o] Carbanilide[24]; sample mp. 242–245°C; crystallized from ethanol mm.p. 245°C.
[p] N,N-Di-*p*-tolylurea[25]: sample mp. 258–260°C.
[q] N,N-Di-*p*-methoxyphenylurea[26]: sample mp 232–4°C; crystallized from ligroin mm.p. 235°C.
[r] *p*N-Phenylbenzimidazole[27]: sample mp. 95–7°C; crystallized from ligroin mm.p. 96–8°C.
[s] 6-Methoxybenzimidazole[28]: sample mp 124–6°C; picrate derivatives, mp and mm.p. 191–3°C.
[t] Phenyl isothiocyanate, b.p. 110–5°C/10 mm.Hg.; n_D^{20}: 1.6287.
[u] *p*-Tolyl isothiocyanate; b.p. 240–5°C; mp 25–30°C; n_D^{20}: 1.6225.
[v] Benzyl isothiocyanate[29]: sample colourless oil b.p. 140–5°C/17 mm.Hg; n_D^{20}: 1.6202.
[w] *p*-Methoxyphenyl isothiocyanate[30]: sample colourless oil b.p. 275–7°C; n_D^{20}: 1.6416.
[x] Phenylacetonitrile; b.p. 230–5°C; n_D^{20}: 1.5011.
[y] *p*-Methoxybenzonitrile[31]: sample mp 58–60°C; crystallized from H_2O mm.p. 60–2°C; b.p. 250–6°C.
[z] 2-Phenylquinoline[32]: sample mp 84–6°C; picrate derivatives mp and mm.p. 185–7°C.
* 2-Benzylquinoline[33]: sample pale yellow oil, b.p. 230–5°C/19 mm.Hg.; picrate derivatives mp and mm.p. 155–7°C.
** 2-(4-Methoxyphenyl)quinoline[34]: sample mp 124–6°C; crystallized from ethanol mp and mm.p. 125°C.
*** 2,3,4,5-Tetraphenylthiophene[15]: sample mp 188°C (lit[15] and mp 185°C; crystallized from pet. ether (60–80°C)-benzene mixture (1:1) mp and mm.p. 185–8°C; calcd. for S%: 8.26%, found S:8.71%.
****Polystyrene is separated as pellets and T_g 100°C. T_m 237–240°C; n_D^{20}: 1.5603, lit. n_D^{20}: 1.5916.



(Scheme 1)



(Scheme 2)



(Scheme 3)

The formation of these identified products were assumed to take place with the same mechanism suggested previously in Scheme 1. The results are given in Table I.

EXPERIMENTAL

All melting points were measured with a Gallenkamp apparatus and are uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrophotometer, Model Sp.200G. Thin-layer chromatography was carried out on glass plates covered with silica gel (25–40 mesh), eluting with acetone/pet. ether (60–80°C) (2:8 v/v), gas-liquid chromatography was carried out on a Perkin-Elmer Model Sigma 3B (thermal conductivity). Columns used are 4 ft (1 ft = 0.3048 m) × 4 mm, packed with 30% SE 30 on Chromosorb W (35–80 mesh), or 10% SE on Celite (60–80 mesh) at 200°C, using nitrogen as a carrier gas. Mass spectra were determined on a Dupont 21-492B mass spectrometer at 70 eV.

Standard methods were used for the following[16]: 2-Phenylimino-3-phenyl-5-benzylidenethiazolidin-4-one (I), m.p. 210–5°C; 2-*p*-tolylimino-3-*p*-tolyl-5-benzylidenethiazolidin-4-one (II), m.p. 190–4°C; 2-benzylimino-3-benzyl-5-benzylidinethiazolidin-4-one (III), m.p. 180–5°C; 2-*p*-methoxyphenylimino-3-*p*-methoxyphenyl-5-benzylidinethiazolidin-4-one (IV), m.p. 192–5°C.

General procedure for thermal rearrangement of 2-arylimino-3-aryl-5-benzylidenethiazolidin-4-ones: Thiazolidine-4-one derivatives (15 g) were refluxed in air at 250°C for 10 hrs. The gases evolved were detected by standard chemical means: CO detected by platinum chloride,[17] CO_2 detected by lime water or baryta solution, NH_3 detected by Nessler's reagent and H_2S detected by lead acetate. The pyrolysate was separated into its constituents by fractional distillation under reduced pressure and the remaining oil was separated into its constituents by means of column chromatography over silica gel using gradient elution techniques.[18] The separated products were identified by physical constants: bp's, mp's, tlc, glc, IR, or MS as compared with authentic samples.

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