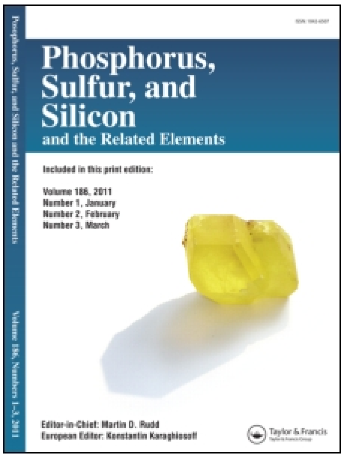

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MOLECULAR REARRANGEMENTS OF SULPHUR COMPOUNDS (II)† PYROLYSIS OF SOME SUBSTITUTED THIAZOLIDINONES

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MOLECULAR REARRANGEMENTS OF SULPHUR COMPOUNDS (II)† PYROLYSIS OF SOME SUBSTITUTED THIAZOLIDINONES

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Thermal rearrangement of 2,3-diarylthiazolidine-4-one (I and II) provided H_2S, H_2O benzene and its alkyl derivatives, thioglycolic acid, aromatic primary amine, benzonitrile, biaryl, tetraphenylthiophene, indole derivatives, benzil, acetophenone derivatives and benzthiazole derivatives. A suitable mechanism has been suggested which explains the obtained products.

Key words: Thermolysis; 2,3-diarylthiazolidine-4-one; tetraphenylthiophene and 2-phenylbenzthiazole derivatives.

INTRODUCTION

Thiazole derivatives exhibit a variety of pharmacological activities. Quantitative decomposition of N-(4-chlorophenyl) rhodanine to the corresponding isothiocyanate under physiological conditions led van der Kerk[1] to propose that antimicrobial action of such compounds is due to the in situ formation of isothiocyanates. Accordingly a number of rhodanines were screened for antimicrobial activity.[2]

Recently, we have recorded the termal rearrangement of some substituted rhodanines to give products of great significance. The presence of a thio group in the thiazoline compounds is expected to increase their fungicidal activity.[3]

RESULTS AND DISCUSSION

In continuation of our recent studies on the pyrolysis of organic compounds we studied now the pyrolysis of 2,3-diarylthiazolidine-4-one at Ca. 250°C for 10 hours which gives rise to products as shown in Table I. The formation of these products can be assumed to follw the series of reactions shown in Scheme I which implies the preliminary homolytic fission of (C—S) bond (route a) to give biradical (IIIa) which rearranges to thiobenzoyl and arylaminoacetyl (IVa) radical pairs. The for-

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TABLE I

Pyrolysis products of 2,3-diphenyl thiazolidine-4-one (I) and 2-phenyl-3-*p*-tolyl-thiazolidine-4-one (II)

Products	Expt. No. I	Expt. No. II
H_2S	evolved	evolved
H_2O	traces	traces
Benzene	0.05(0.25)	—
Toluene	—	0.02(0.1)
Aniline[a]	2.5(12.5)	—
p-Toluidine[b]	—	0.03(0.15)
Acetanilide[c]	0.05(0.25)	—
4-Methylacetanilide[d]	—	2.01(1.5)
Thioglycolic[e] acid	1.5(7.5)	—
Benzonitrile[f]	1.2(6)	—
Biphenyl[g]	0.8(4)	—
4,4′-Bitolyl[h]	—	0.2(1)
Benzil[i]	—	1.1(5.5)
Acetophenone[j]	0.05(0.25)	—
4-Methylacetophenone[k]	—	0.08(0.4)
Indole[l]	1.1(5.5)	—
5-Methyl indole[m]	—	0.8(0.4)
p-Aminoacetophenone[n]	—	0.04(0.2)
2-phenylbenzthiazole[o]	1.8(9)	—
2-phenyl-6-methylbenzthiazole[p]	—	1.6(8)
Residue	2.9(14.5)	3.8(19)

Expt. (I) reflux of 2,3 diphenylthiazolidine-4-one in air; (II) reflux of 2-phenyl-3-*p*-tolylthiazolidine-4-one in air.

[a] b.p. 80–85°C/13 mm.Hg, n_D^{20}: 1.5836, acetyl derivative m.p. and mixture m.p. 113–114°C.

[b] m.p. 45–47°C, its I.R. spectrum coincident with that of an authentic sample.

[c] m.p. 113–115°C, its I.R. spectrum coincident with that of an authentic sample.

[d] 150°C, its I.R. spectrum coincident with that of an authentic sample.

[e] b.p. 96°C/5 mm.Hg.n_D^{20}: 1.5030, its I.R spectrum coincident with that of an authentic sample.

[f] b.p. 72°C/13 mm.Hg, n_D^{20}: 1.5280.

[g] m.p. 70°C, 4,4′-dinitro derivative m.p. and mixture m.p. 234°C.

[h] m.p. 121–122, its I.R. spectrum coincident with that of an authentic sample.

[i] m.p. 94–95°C.

[j] 85°C/13 mm.Hg, n_D^{20} 1.5325, D.N.P derivative m.p. and mixture m.p. 250°C.

[k] m.p. 28°C.

[l] m.p. 52°C, its I.R. spectrum coincident with that of an authentic sample.

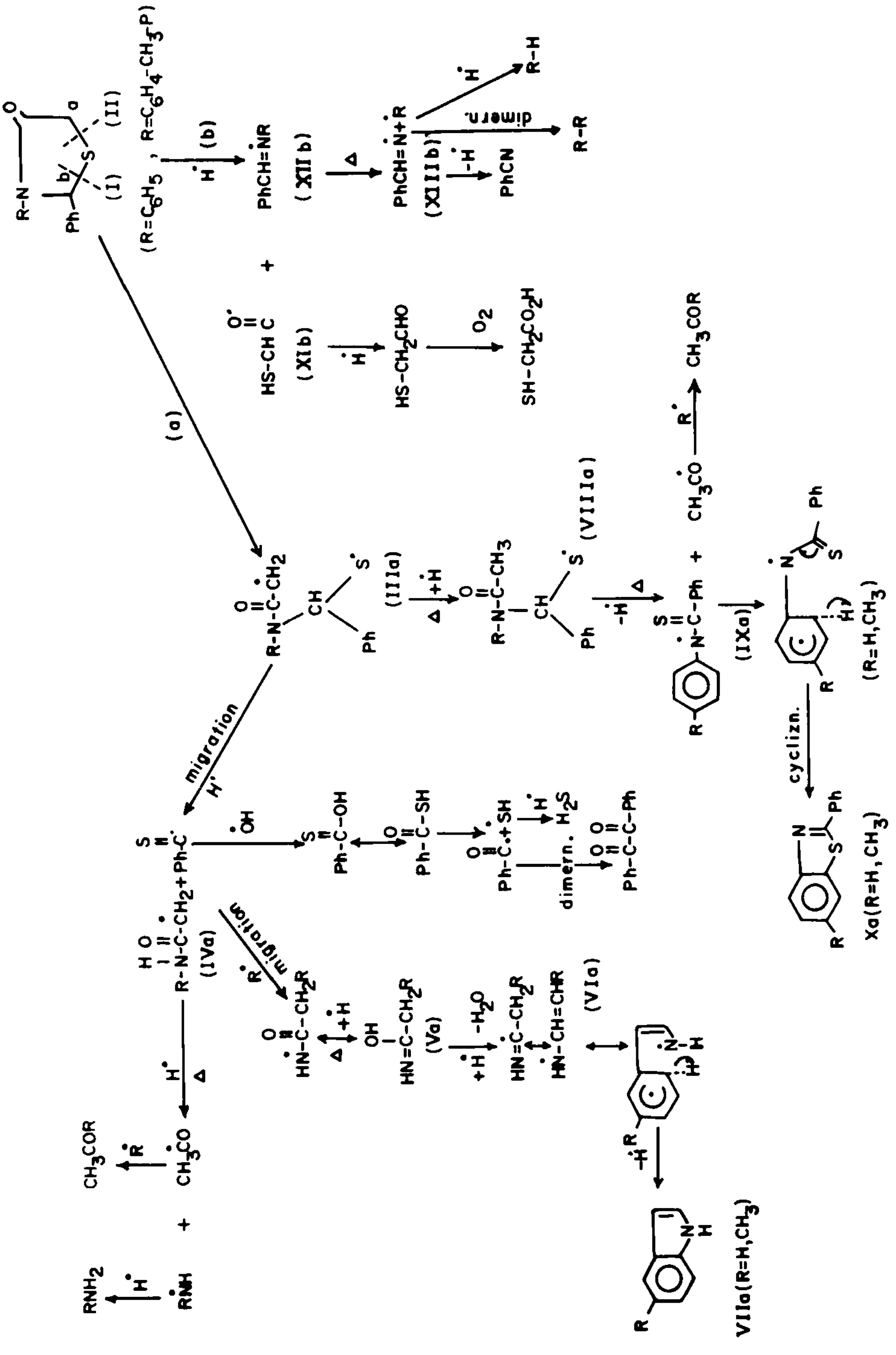
[m] m.p. 60°C, picrate derivative m.p. and mixture m.p. 151°C.

[n] m.p. 105–107°C, its I.R. spectrum coincident with that of an authentic sample.

[o] m.p. 112–113°C, its I.R. spectrum coincident with that of an authentic sample.

[p] m.p. 122–123°C, its I.R. spectrum coincident with that of an authentic sample.

mer couples with hydroxyl radical from the medium of the reaction forming thiobenzoic acid which rearranges to benzoylthiol which fragments into benzoyl radicals and hydrogen sulphide.[4] The benzoyl radical abstracts hydrogen to give benzal-


(I) (R=C6H5 , R=C6H4-CH3-P) (II)
(a)
(b)
PhCH=NR
(XIIb)
PhCH=N+R
(XIIIb)
PhCN
R-H
R-R
dimern.
HS-CH C=O
(XIb)
HS-CH2CHO
SH-CH2CO2H
(IIIa)
(VIIIa)
(IXa)
CH3CO
CH3COR
(R=H,CH3)
cyclizn.
Xa(R=H,CH3)
migration
(IVa)
Ph-C-OH
Ph-C-SH
Ph-C.+SH
H2S
dimern.
Ph-C-C-Ph
(Va)
(VIa)
VIIa(R=H,CH3)
RNH2
CH3COR

Scheme (1)

dehyde or dimerizes forming benzil, whereas the latter (IVa) undergoes R migration and then tautomerizes to radical (Va). This abstracts hydrogen and loses H_2O forming species (VIa) which through intramolecular cyclization gives indole[5] or 5-methylindole (VIIa); or (IVa) abstracts hydrogen to give anilide derivatives which subsequently decompose into anilino and acetyl radical pairs.[6,7] Acetyl radical couple with aryl radical in the reaction medium forming acetophenone or 4-methylacetophenone but anilino radicals may abstract hydrogen forming aniline or *p*-toluidine.

On the other hand, the biradical (IIIa) may abstract hydrogen to give the radical (VIIIa) which rearranges to thioanilide (IXa) and acetyl radicals. The former thermally undergoes intramolecular cyclization forming 2-phenylbenzthiazole or 2-phenyl-5-methyl-benzthiazole (Xa) as reported earlier.[8]

Another competing pathway for pyrolysis of 2,3-diarylthiazolidine 4-one (I and II) is the homolysis of C—S bond (route b) leading to the formation of thioloacetyl radical (XIb) and benzalamine (XIIb). The thioloacetyl radical may abstract hydrogen giving thioglycolic aldehyde which undergoes oxidation to give thioglycolic acid. The benzalamine which subsequently decompose under the same conditions forming benzaliminyl (XIIIb) and aryl radical pairs. The former may lose hydrogen to afford benzonitrile but the aryl radicals may abstract hydrogen giving benzene, toluene or undergoes dimerization forming biphenyl or 4,4-bitolyl.

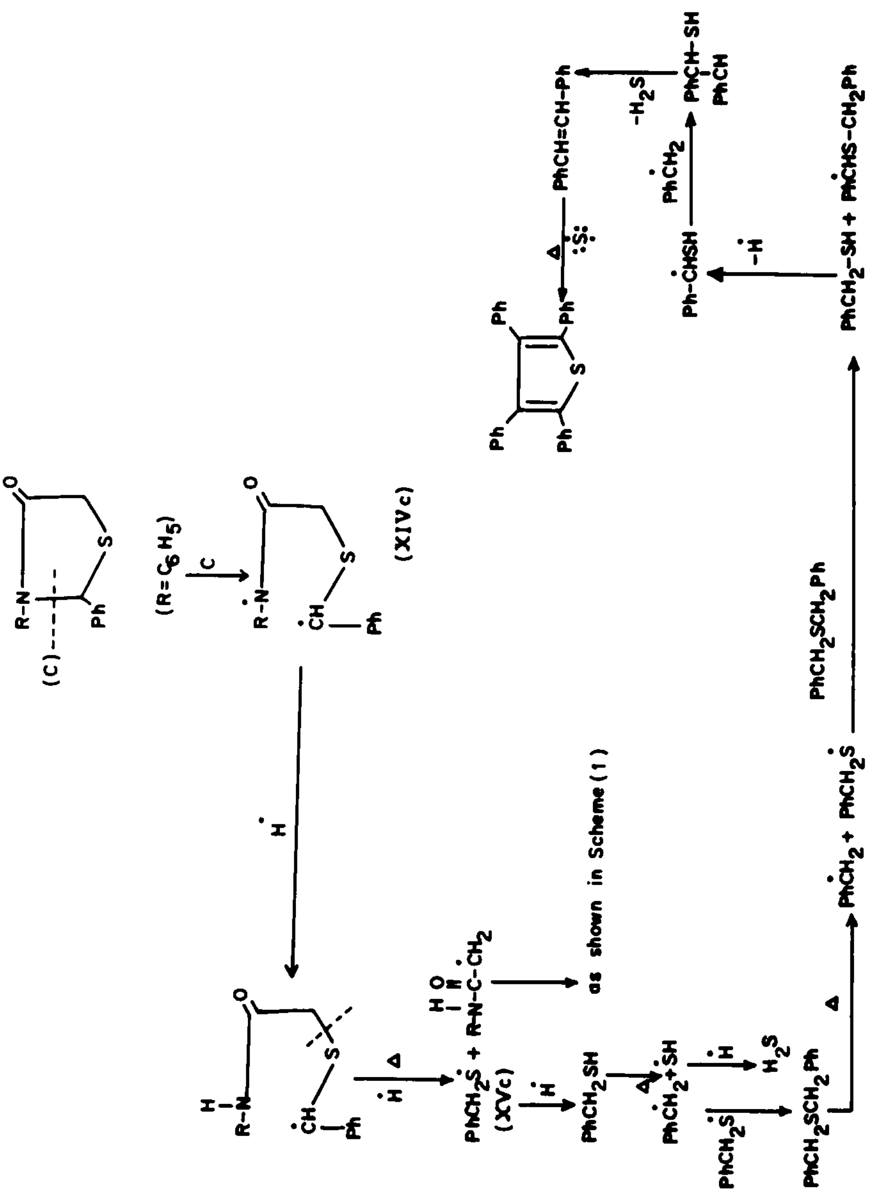
Futhermore, another competing pathway for pyrolysis of 2,3-diphenylthiazolidine-4-one (I) is the homolysis of C—N bond as shown in Scheme II forming the biradical (XIVc) which may abstract hydrogen followed by decomposition under the same conditions into benzyl thiyl (XVc) and arylaminoacetyl radical pairs. The latter is the precursor of indole derivatives, primary aromatic amine and acetophenone derivatives as shown previously (c.f. Scheme 1). The formation of 2,3,4,5-tetraphenylthiophene can be suggested to take place through the interaction of dibenzyl sulphide with stilbene or interaction of sulphur with stilbene.[9,14] However, the former mechanism was excluded on basis of the instability of dibenzyl sulphide under the present reaction conditions meanwhile sulphur suggested to be formed previously appears as H_2S.

EXPERIMENTAL

Melting points were measured with a Gallenkamp apparatus and are uncorrected. Thin-layer chromatography was carried out on glass plates covered with silicagel (25 × 40 mesh) and eluted with acetone-pet-ether (60–80 C) (2–8 v/v).

Gas-liquid chromatography was carried out on Perkin-Elmer Sigma 3B. Columns used were 4 ft. × 4 mm packed with 30% SE 30 on chromosorb w (35–80 mesh), or 10% SE on Celit (60–80 mesh) using nitrogen as carrier gas. 2,3-Diphenyl-thiazolidin-4-one was prepared by a standard method[10] by warming equimolar amounts of thioglycolic acid and benzalaniline in absolute ether for 2 hours, yield 60%, m.p. 131°C. 2-Phenyl-3-*p*-tolylthiazolidine-4-one was prepared by the same procudure,[10] m.p. 143°C.

Thermolysis of 2,3-diphenylthiazolidine-4-one and 2-phenyl-3-p-tolylthiazolidine-4-one. General procedure: 20 g of thiazolidinone derivatives was heated at ca 250°C for 10 hours. The gases evolved were detected by standard chemical means (H_2S detected by lead acetate and CO detected by platinum chloride). The pyrolysate was subjected to vacuum distillation and the remaining oil was separated into its constituents by means of column chromatography over silicagel using a gradient elution technique. The separated products were identified by physical constants, bp, mp, T.L.C., G.L.C., I.R. as compared with authentic samples. the results are listed in Table I.


(C)
R-N
O
S
Ph
(R=C$_6$H$_5$)
C
R-N
·CH
(XIVc)
H·
H-N
R
Δ
PhCH$_2$S· + R-N-C-CH$_2$
(XVc)
as shown in Scheme (1)
PhCH$_2$SH
PhCH$_2$ + SH
H$_2$S
PhCH$_2$S·
PhCH$_2$SCH$_2$Ph
PhCH$_2$· + PhCH$_2$S·
PhCH$_2$-SH + PhCHS-CH$_2$Ph
-H·
Ph-CHSH
PhCH$_2$·
PhCH-SH
PhCH
-H$_2$S
PhCH=CH-Ph
:S:

Scheme (2)

Preparation of Reference compounds:

2-Phenylbenzthiazole m.p. 112–113°C, recrystallized from ethanol. Lit[7] m.p. 113.

2-Phenyl-6-methylbenzthiazole m.p. 122–123°C recrystallized from ethanol. Lit[11] m.p. 123°C.

5-Methyl indole m.p. 58°C, recrystallized from water, its picrate m.p. 151°C, recrystallized from hot H_2O, Lit[12] m.p. 58°C.

4,4-Bitolyl m.p. 121–122°C, recrystallized from ether. Lit[13] m.p. 122°C.

Acetyl-p-toluidine m.p. 145–147°C recrystallized from ethanol.

Tetraphenylthiophene[14,15] m.p. 184°C. Lit[15] m.p. 184°C.

4-Methylacetophenone m.p. 28°C.

Carbanilide m.p. 242°C, recrystallized from glacial acetic acid or ethyl acetate.

REFERENCES

1. Van Der Kerk, G. J. M., Mededel Van de Landbouwhog School OPZSStat. *Staat Gent.*, **21**, 305 (1956).
2. T. Z. Solnai, *Arzneim-Forsch.*, **19**, 558 (1969).
3. M. K. Rout, G. N. Mahapatra, *J. Am. Chem. Soc.*, **77**, 2427 (1955).
4. E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron*, **21,** 2685 (1965).
5. M. Z. A. Badr, M. M. Aly, S. A. Mahgoub, A. M. Fahmy and A. A. Atalla, *Bull. Chem. Soc. Jpn.* **61**, 1779 (1988).
6. J. F. J. Dippy and J. H. Wood, *J. Chem. Soc.* 2719 (1949).
7. D. N. Kursanov, *J. Gen. Chem. U.S.S.R.*, **13**, 286 (1943).
8. Jacobsen, *Ber.*, **19**, 1070 (1886).
9. A. A. Abdel-Wahab and A.E. Abdel Rahman, *Indian J. of Chemistry*, **20B**, 636 (1981).
10. H. Erlenmeyer and V. Oberlin, *Helv. Chim. Acta*, **30**, 1329-1335 (1947).
11. L. Gattermann, *Ber.*, **22**, 1065 (1889).
12. J. Raschen, *Liebs. Ann.*, **239**, 226 (1887).
13. F. Ullmann, Meyer, *Liebs. Ann.*, **332**, 44 (1903).
14. A. E. Abd El-Rahman, and A. A. Abd El-Wahab, *Indian J. of Chemistry*, **18B**, 402 (1979).
15. E. Bergman, *J. Chem. Soc.*, 505 (1936).