

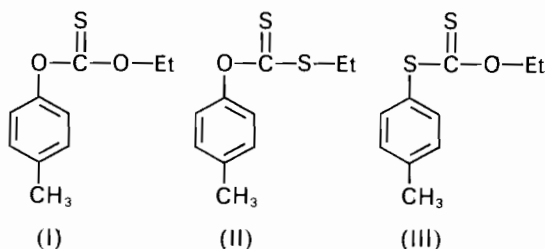
Behaviour of ethyl *p*-methylphenylthion and dithiocarbonates at elevated temperature

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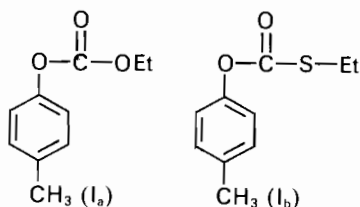
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ABSTRACT

Ethyl *p*-methylphenylthioncarbonate (I), S-ethyl-O-*p*-methylphenyldithiocarbonate (II) and O-ethyl-S-*p*-methylphenyldithiocarbonate (III) were heated in the condensed phase at 170°C for 6 hr.



Identification by n.m.r., i.r. spectroscopy and g.l.c. of the reaction products revealed that the yield from compound (I) is a mixture (1:2:2) of ethyl *p*-methylphenylcarbonate (I_a) and S-ethyl *p*-methylphenylthiolcarbonate (I_b). The overall yield of I_a and I_b was 69% and 30% respectively.



The composition of the reaction product was further checked by alkaline hydrolysis which resulted in the formation of *p*-cresol, EtOH and EtSH in case of compound (I), *p*-cresol and EtSH for compound (II), *p*-thiocresol and EtSH for compound (III) and no *p*-thiocresol was detected in case of compounds (I) and (II).

INTRODUCTION

Salomaa (1959) reported that heating O- α -fenchyl-O-methylthioncarbonate at 200–230°C yielded fenchene, carbon oxysulphide and methanol. In addition, O- α -fenchyl-S-methylthiocarbonate was also obtained.

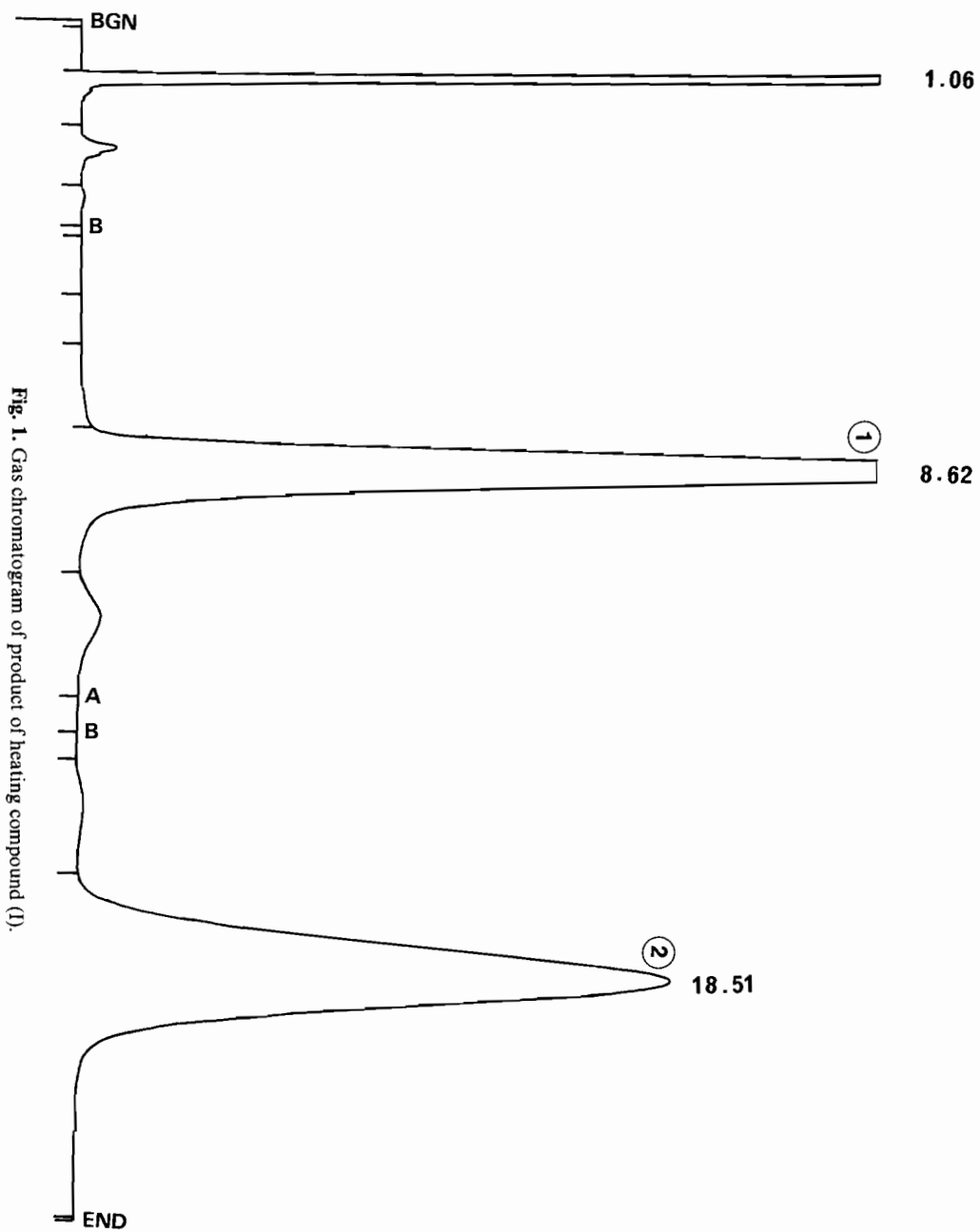


Fig. 1. Gas chromatogram of product of heating compound (I).

Thiocarbonate rearrangement was observed in diaryl and alkylaryl system by Schonberg *et al.* (1930), as a result of prolonged heating at low temperature of these compounds in the condensed phase. The rate of rearrangement of diaryl thioncarbonate was shown by Kazimi *et al.* (1955) to be increased by electron-withdrawing substituents in the migrating group, and to have a negative entropy of activation by Power & Tarbell (1956). A transition state was postulated involving nucleophilic displacement of the oxygen atom adjacent to the aromatic ring by sulphur by Schonberg *et al.* (1930). Kwart & Evans (1966) showed that the yield of the rearrangement product could be increased by heating the thioncarbonate at high temperature in the vapour phase for shorter periods of time.

In the present study we report that the n.m.r., i.r. and gas liquid chromatography investigations of the product obtained by heating compound (I) at 170°C for 6 hr show that the product is a mixture of compounds (I_a) and (I_b). The percentages of these two compounds in the mixture was also determined using g.l.c. and n.m.r. Both techniques gave the same ratio, (I_a):(I_b) = 1:2.2.

RESULTS AND DISCUSSION

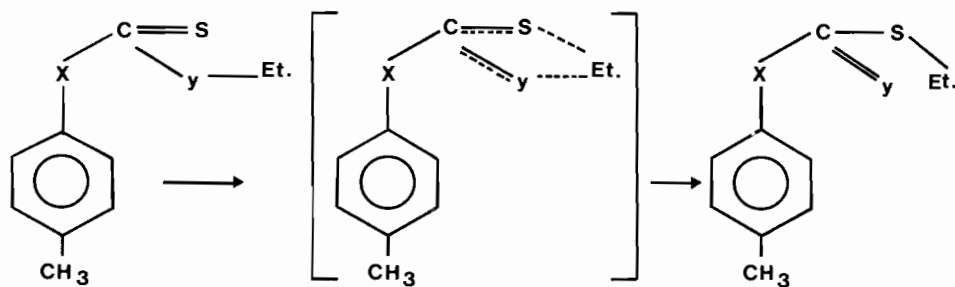
Gas chromatographic analysis revealed that the product of heating compound (I) contains two components (Fig. 1). The identities of peaks (1) and (2) in the chromatogram were established from separate and independent retention time measurements on authentic samples of ethyl-*p*-methylphenylcarbonate and *S*-ethyl-*O*-*p*-methylphenylthiolcarbonate, respectively.

The area under peak (1) is 56.2, and that under peak (2) is 122.8, while the concentrations corresponding to peak (1) and peak (2) in the mixture are, respectively, 20.4 and 44.5, which indicates that the ratio of I_a:I_b = 1:2.2.

Analysis by n.m.r. (Fig. 2) confirmed that the reaction product is a mixture of two components, for which a quartet group at 4.2 ppm indicates methylene protons for compound (I_a) and another quartet at 2.9 ppm corresponds to methylene protons for compound (I_b), with an integration ratio of I_a:I_b = 1:2.2.

The i.r. spectrum of the product (Fig. 3) shows two carbonyl groups at 1765 cm⁻¹ and 1725 cm⁻¹ corresponding to the carbonyl groups of compounds (I_a) and (I_b), respectively. When this product was subjected to alkaline hydrolysis it gave *p*-cresol, EtSH and EtOH.

It is clear from the observations reported above that a rearrangement process of thioncarbonate to thiolcarbonate (Scheme 1) took place leading to the formation of (I_b).



Scheme 1 ($x = 0, y = 0$)

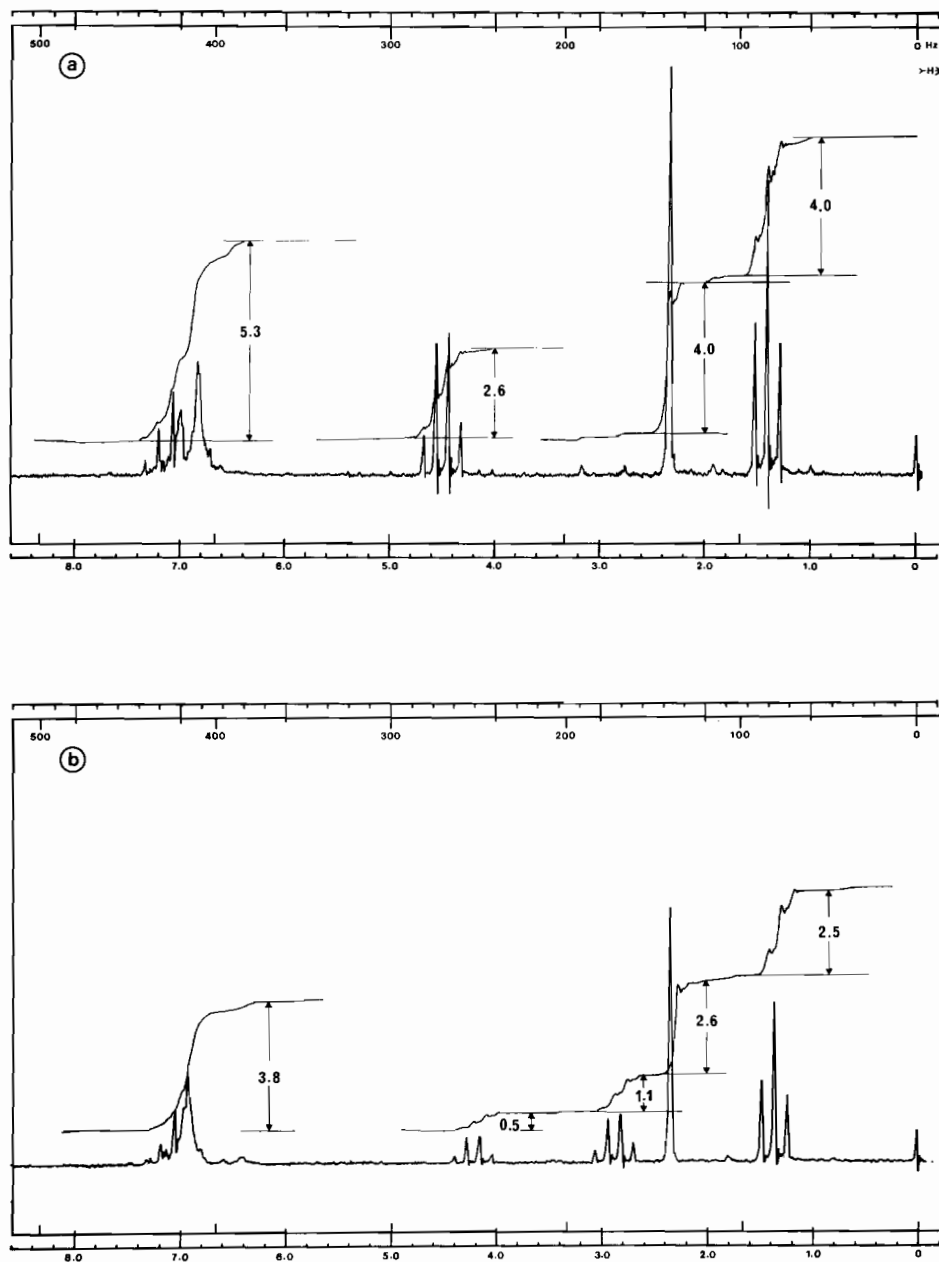


Fig. 2. n.m.r. spectrum of (a) compound (I), (b) product of heating compound (I).

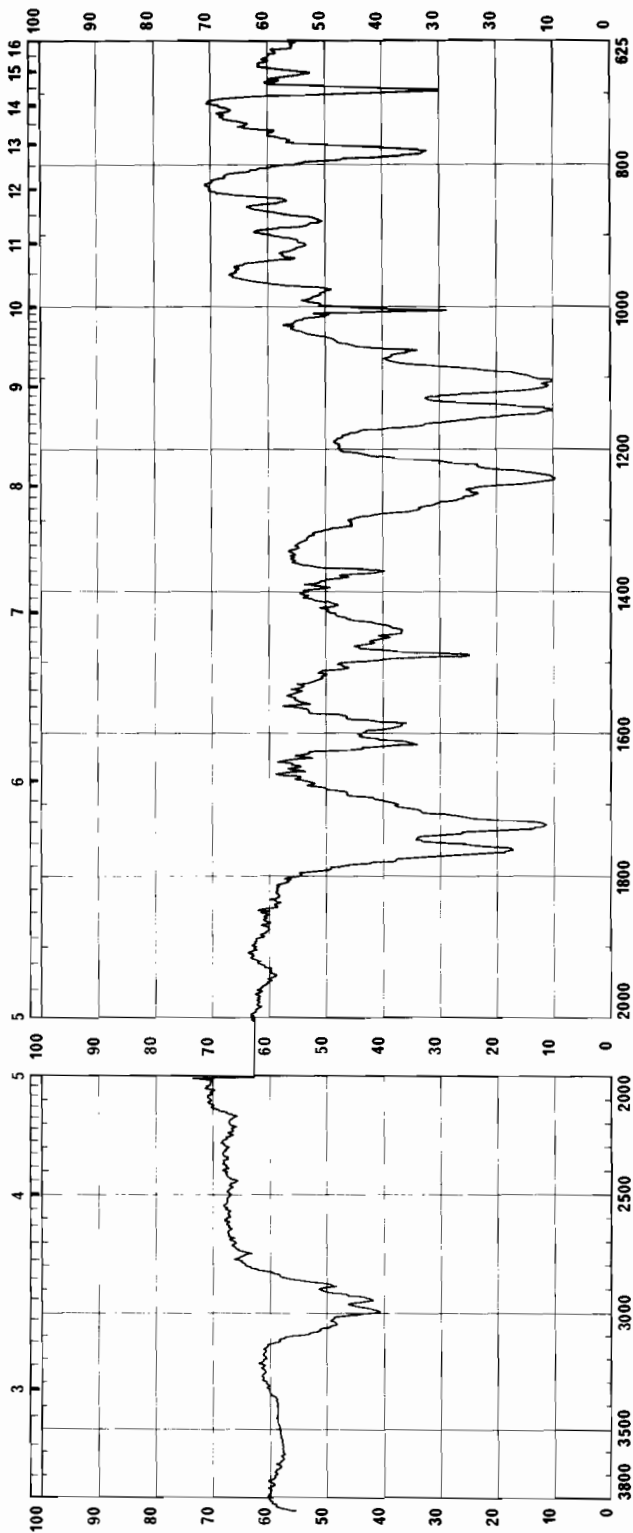


Fig. 3. i.r. spectrum of the product of heating compound (I).

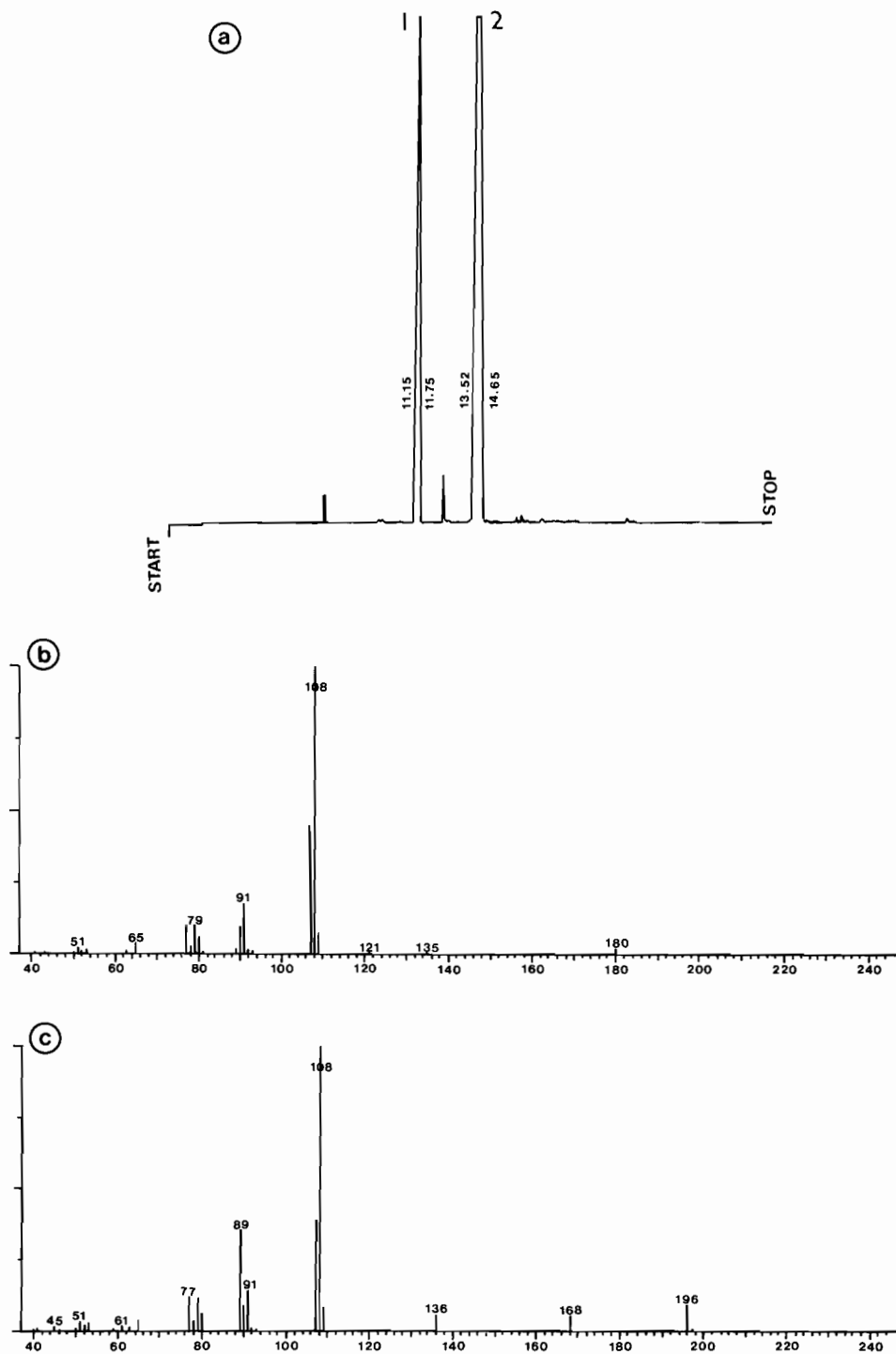


Fig. 4. (a) Gas chromatogram/mass spectroscopy of product of heating compound (I), (b) Mass spectrum of peak (1), (c) Mass spectrum of peak (2).

p-methyl aryl ethylcarbonate:

It was prepared according to the procedure of Tsou & Seligman (1954). Ethylchloroformate (0.1 mole) was added dropwise to a solution of 0.1 mole *p*-cresol in dry pyridine at 0°C. The crude ester after normal work up was then fractionally distilled to give the ester; b.p. 195°C.

p-methyl aryl-S-ethylthiocarbonate:

One tenth mole of *p*-methyl phenyl chloroformate which had been prepared from the reaction of *p*-cresol with phosgene in dry pyridine according to the procedure reported by Hamilton & Sly (1925) was added dropwise to a solution of 0.1 mole of ethane thiol in 0.1 mole dry pyridine at 0°C. Normal work up gave the crude ester which had been fractionally distilled at reduced pressure; b.p. 50°C/0.07 mm Hg.

p-methyl-S-ethyl phenyldithiocarbonate:

Twenty-one g KOH (pellets) and 72 cm³ *p*-cresol were refluxed for 2 hr, 22 cm³ of CS₂ were added, the resultant potassium xanthate was then refluxed with 25 cm³ of ethylbromide. After normal work up, the crude product was fractionally distilled to give compound (II); b.p. 50°C/0.08 mm Hg.

p-methyl ethyl-S-phenyldithiocarbonate:

It was prepared according to the procedure reported above for compound (I), using *p*-thiocresol instead of *p*-cresol which gives compound (III); b.p. 60°C/0.13 mm Hg.

Rearrangement of thion and dithiocarbonates:

Eight cm³ of compound (I), (II) and (III) in three separate dry test tubes (without solvent) were immersed in an oil bath at 170°C for 6 hr.

Hydrolysis of the product of heating thion and dithiocarbonates:

Solutions of 6 cm³ of the product of heating (I), (II) and (III) in 20 cm³ dichloromethane were refluxed separately on a water bath with 6 cm³ of 25% sodium hydroxide for 30 min. The reaction mixture was concentrated, the residue was fractionally distilled and identified by spectroscopic means. EtSH gave a characteristic smell.

g.l.c. analysis:

Reaction products were chromatographed using Perkin Elmer Sigma 115 Gas Chromatograph, 9 ft (274 cm) glass column, liquid crystal 43% BMBT (N,N-bis(*p*-methoxybenzibidine)- $\alpha,\bar{\alpha}$ -bi-*p*-tolylidene) 57% BEBT (N,N-bis(*p*-ethoxybenzibidine)- $\alpha,\bar{\alpha}$ -bi-*p*-tolylidene), oven temperature 120°C, nitrogen as carrier gas with a flow rate of 30 cm³/min, injection temperature 180°C, flame ionization detector, zone at 170°C.

g.c./m.s. analysis:

This was carried out using Riber Mag g.c./m.s., fused silica capillary column SE-30, 25 m, I.D. 0.25 mm, temperature 70–220°C at 110/min, helium as carrier gas with a flow rate of 2 cm³/min, split ratio of 1/20.

Spectroscopic analysis:

i.r. spectra were recorded using a Unicam SP1000 spectrophotometer. ¹H-n.m.r. spectra in CDCl₃ were recorded on a Varian T-60A spectrometer using TMS as external standard.

ACKNOWLEDGEMENT

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سلوك أيثيل باراميثيل ثيون وثنائي ثيو الكربونات في درجات الحرارة المرتفعة

نورية العوضي و آدم درويش
قسم الكيمياء بجامعة الكويت

خلاصة

تم تسخين مركبات ايثيل باراميثيل فينيل ثيو كربونات (١) ، (٢) ، (٣) عند ١٧٠°م لمدة ست ساعات ، وعند تحليل نواتج التسخين بواسطة أجهزة الطيف المختلفة بالاضافة إلى استخدام جهاز التحليل الكروماتوجرافي ، وجد أن ناتج تسخين ايثيل باراميثيل ثيون كربونات هو ايثيل باراميثيل فينيل كربونات (أ) و س - ايثيل باراميثيل فينيل ثيو كربونات (ب) .