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α, ω-Difunctionalized Poly(p-thiophenylene) Oligomers

1. Synthesis and Properties

G. Daccord and B. Sillion

Institut Français du Pétrole, C.E.D.I., BP no. 3, 69390 Vernaison, France

Summary

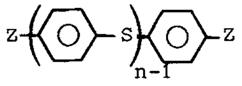
We describe new telechelic poly(p-thiophenylene) monodispersed oligomers and statistical ones. They were obtained by step synthesis and unbalanced condensation. By these ways we obtained oligomers with terminal bromo, cyano, amino, methyl and hydroxyethylester, oxazoline and N-hydroxyethylamide groups.

Introduction

Poly(p-thiophenylene) chains whose properties in the homopolymer state are known (1) have not been used, to our knowledge, to make segmented copolycondensed polymers. The synthesis of nonfunctional oligomers has been described by several authors (14, 15, 22) with the aim of obtaining model molecules.

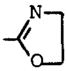
Diamino telechelic oligomers have been described (16) as well as two synthesis of cyano products (10, 23) whose nitrile functions are thus trimerized.

In this paper we describe the synthesis of α,ω- difunctionalized poly(p-thiophenylene) oligomers having the formulas:



with n = 2, 4, 6 (monodispersed products)
n statistical (9 ⩽ n ⩽ 16)

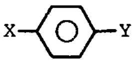
Z being Br (3n), CN (4n), NH_2 (5n), $COOCH_3$ (6n),

$COOCH_2CH_2OH$ (7n),  (8n), $CONHCH_2CH_2OH$ (9n)

Result and Discussion

Products

Most of the products used are not commercial and were synthesized. Products 2b, 2c and 2d were prepared in several steps.



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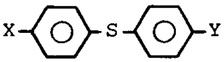

2

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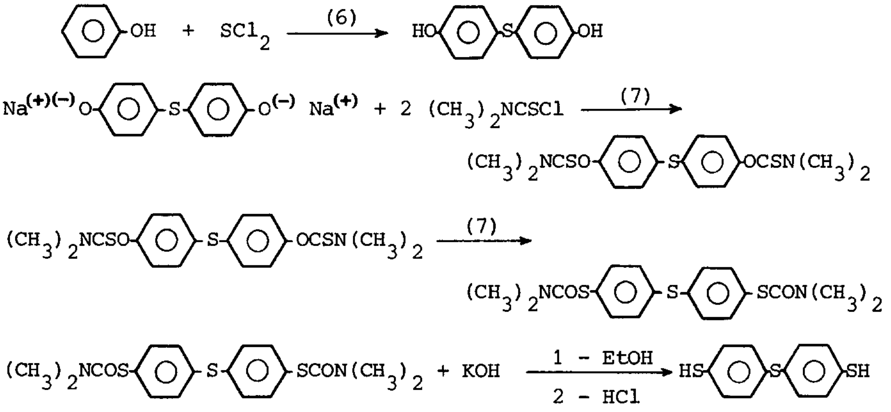
1a X = Br Y = CN
1b X = SH Y = COOH
1c X = SH Y = NH_2

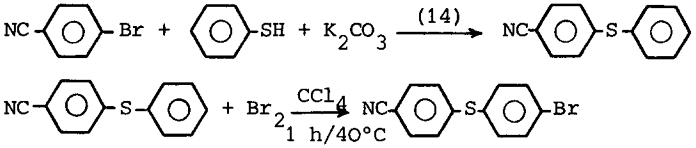
2a X = Y = Br
2b X = Y = SH
2c X = Br Y = CN
2d X = Br Y = $NHCOCH_3$

The bis(p-mercaptophenyl) sulfide 2b was obtained in three different ways:

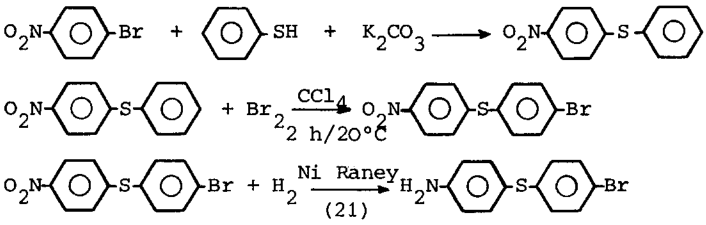
- by chlorosulfonation of diphenylsulfide (3) followed by reduction (4). (Total yield : 5-50%).
- by nucleophilic substitution of the sodium salt of t-butylmercaptan on 2a and reduction of the bisthioether by means of sodium-pyridine (5) (Total yield = 30-40%).
- in a more reproducible way and with a better overall yield (60%) from phenol according to the sequence of the following reactions:

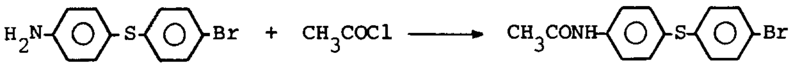


p-bromo-p-cyanodiphenylsulfide 2c is obtained in two steps from 1a (Total yield = 60%).



p-bromo-p'-acetamidodiphenylsulfide 2d is obtained from p-chloronitrobenzene according to the following scheme (Total yield = 59%).



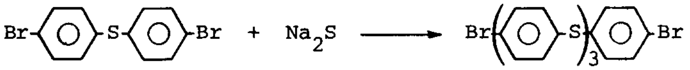


α,ω-difunctionalized oligomers.

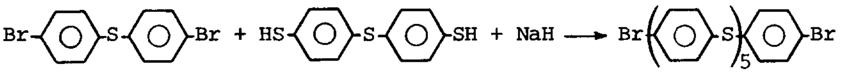
The obtaining of functionalized products whose reactive functions are alcohols, esters or amines compelled us to prepare intermediate dibromo and dicyano oligomers. All the synthesized products are collected in Table 1.

Synthesis of α,ω-dibromo oligomers.

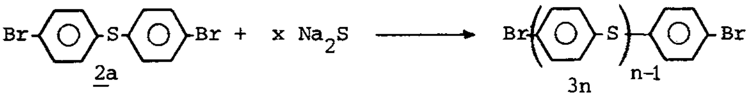
Oligomers 3n (n = 4,6 and statistical) were obtained by unbalanced polycondensation between 2a in excess and sodium sulfide or 2b. Owing to their poor solubility and difficulty of purification, we can thus obtain only the first term arising from the duplication of the monomer (Eqs 1a and 1b) with sufficient purity to consider it to be monodispersed.



2a in excess (150%) 3_4 (Equ. 1a)



2a in excess (150%) 2b 3_6 (Equ. 1b)



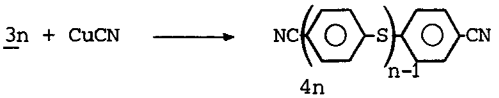
2a 3n (Equ. 1c)

$0{,}7 \leq x \leq 1{,}1$

The monodispersed products were purified by successive crystallizations until a constant melting point. Statistical oligomers (Eq. 1c) were contineously extracted to keep out the lowest one. Their number mean weight was determined by titrating terminal bromines by X-ray fluorescence on solid-state samples (precision 5%). Products with mean weight situated between 900 and 1800 were prepared in this way.

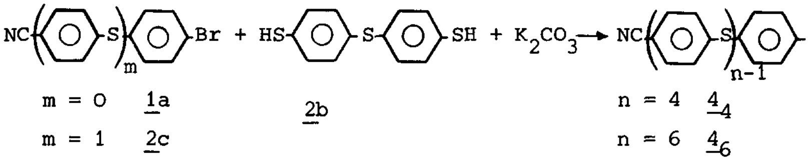
Synthesis of α,ω-dicyano oligomers.

The products were obtained by the action of an excess of cuprous cyanide on dibromo products 3 (10), in an aprotic dipolar solvent with a high boiling point, mainly N,N-dimethylbenzamide (substitution yield = 95% for the statistical oligomers).



4n (Equ. 2a)

Meanwhile in the case of compounds 4_4 and 4_6 the yield is higher when the cyano-bromo products 1a and 2c are condensed with the bismercaptan 2b. This reaction is selective and gives only the aromatic nucleophilic substitution on the bromine bound carbon (14).

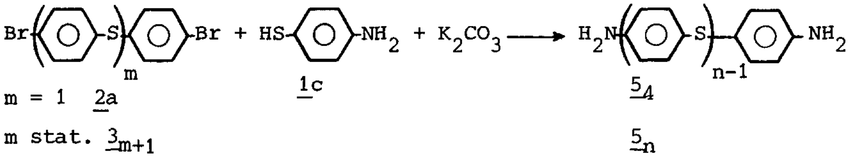


(Equ. 2b)

Product 4_6 is difficult to purify but a pure sample was obtained by high pressure liquid chromatography so as to confirm its structure.

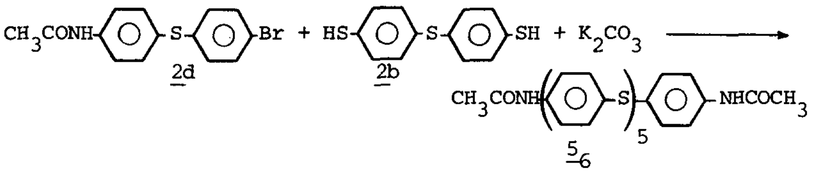
Synthesis of α,ω -diamino oligomers.

A patent (16) describes the action of p-hydroxyaniline on dibromotelechelic poly(p-thiophenylene) chains. We used p-mercaptoaniline to synthesize products 5_4 and 5_n (substitution yield = 90-93% for statistical products).



(Eq.3a)

Products 5_6 was obtained as a diacetamide derivative according to the reaction

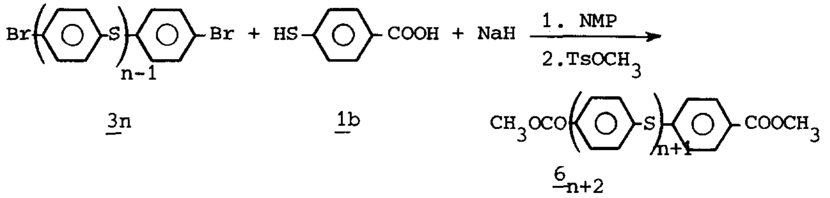


(Eq. 3b)

Owing to its poor solubility, it can be purified only by extraction with pyridine.

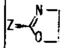
Synthesis of α,ω-diester oligomers.

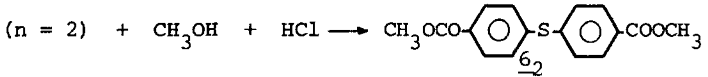
The reaction of the sodium salt of p-mercaptobenzoic acid 1b with a dibromo oligomer 3n followed by an esterification step, either directly by means of methyl iodide or methyl tosylate (12) or in one more step by the bis(acid chloride), gives oligomers with two more phenylene units than the bromo product:



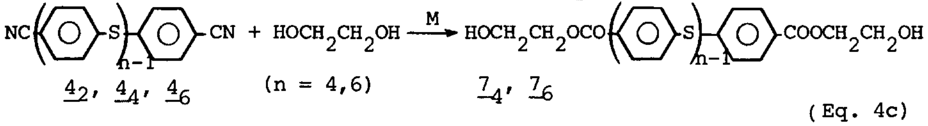
(Eq. 4a)

Since yield is mediocre, in particular for the shortest oligomers (6_4 and 6_6), we used the alcoholysis of nitrile in an acidic medium (26) or in the presence of a metal catalyst ($Cu(OAc)_2$, $Ti(OBu)_4$ (13)), according to the solubility of the products, to synthesize products 6_2, 7_4 and 7_6.

Products		Eq. synth	Yield (%)	Mp (crystallizat. solvent	Anal	C	H	N	O	S	B_r	Mass spectra	IR(cm^{-1}) / RMN (ppm/TMS)
Z= Br	n= 4 $\underline{3}_{4}$	1a	40	170-2 (toluene)	th exp th exp						20,62 20,0±0,5 12,0±0,5	$M^{\cdot +}$ = 558	3050-1470-1390-1080-1065-1005-820 805-720
	n= 6 $\underline{3}_{6}$	1b	75	210 (")								$M^{\cdot +}$ = 774	3060-1390-1080-1005-815
	$\bar{n}$=11,3 $\underline{3}_{11,3}$	1c	86	260-275									3060-1470-1385-1090-1010-820
Z= CN	n= 2 $\underline{4}_{2}$	2a	85	136 (AcOH)	th exp th exp th exp th exp	71,19 71,31 69,03 68,2 68,23 67,7	3,39 3,62 3,54 3,3 3,62 3,50	11,86 11,62 6,19 6,0 4,19 4,03	0,5	13,56 13,34 21,24 20,7 23,96 23,0	< 0,05	$M^{\cdot +}$ = 236	2220-2230 / 7,7-7,2 (m)
	n= 4 $\underline{4}_{4}$	2b	90	205 (AcOH)								$M^{\cdot +}$ = 452	2220
	n= 6 $\underline{4}_{6}$	2b	60	(ØCl)								$M^{\cdot +}$ = 668	2220
	$\bar{n}$=11,3 $\underline{4}_{11,3}$	2a	97	235-245									2220
Z= NH_2	n= 4 $\underline{5}_{4}$	3a	95	132 ($CHCl_3$)	th exp th exp th exp	66,67 65,90 65,57 64,98	4,63 4,56 4,37 4,28	6,48 6,33 3,82 3,60	4,37 4,36	22,22 21,33 21,86 23,05	0,9±0,1		3440-3340-1280
	$\bar{n}$=13,3 $\underline{5}_{13,3}$	3a	91	230-245									3440-3360-1280
Z= NHAc	n= 6 $\underline{5}_{6}$	3b	20									$M^{\cdot +}$ = 732	3300-3180-1660-1595
Z= $COOCH_3$	n= 2 $\underline{6}_{2}$	4b	95	127 (EtOH)	th exp th exp th exp th exp th exp th exp	64,84 65,39 66,5 65,68 64,12 61,94 62,13 63,45 62,5	4,28 4,09 5,0 4,00 3,98 4,68 4,72 4,31 4,15	0,7 0,35 0,3 0,17	12,34 8,72 7,2 6,74 11,63 16,85 16,76 12,07	18,54 21,80 16,9 23,58 19,92 15,59 15,62 20,16 18,6	0,3		1725-1230/3,85 (s-6H) 7,1-8 (8H)
	n= 4 $\underline{6}_{4}$	4a	5-10	200 ($CHCl_3$)								$M^{\cdot +}$ = 518	1725-1715/3,83 (s-6H) 7,1-8 (16H)
	n= 6 $\underline{6}_{6}$	4a	20	190-200 (xylene)									1730/3,85(s-6H) 7,25-7,5(20H) 7,8-7,9 (6H)
	n= 8 $\underline{6}_{8}$	4a	30	190-200 (DMF)									1730
	$\bar{n}$=13,3 $\underline{6}_{13,3}$	4a	90	230-240									1715
Z= COO\/OH	n= 4 $\underline{7}_{4}$	4c	80	198 (AcOH)									3420-1715-1700/3,7-4,7 (8H) 7,3-8,1 (16H)
	n= 6 $\underline{7}_{6}$	4c	80	190-200									3430-1715
Z= 	n= 2 $\underline{8}_{2}$	5	90	173 (EtOH)	th exp th exp th exp	66,67 66,7 66,64 65,6 66,64 65,8	4,94 5,1 4,47 4,5 4,26 4,10	8,64 8,5 5,18 5,25 3,70 3,45	9,88 9,7 5,92 6,4 4,23	9,88 9,8 17,79 17,6 21,17 19,4			1640-1260/3,4-4,7 (m 8H) 7,2-8,0 (m 8H)
	n= 4 $\underline{8}_{4}$	5	95	220 (Ø Cl)									1640-1260/3,8-4,7 (m 8H) 7,1-8,0 (m 16H)
	n= 6 $\underline{8}_{6}$	5	80	220-230									1645-1255
Z= CONH\/OH	n= 2 $\underline{9}_{2}$	6	95	219 (EtOH)	th exp th exp th exp th exp	59,98 59,68 62,48 62,7 53,61 63,3	5,59 5,55 4,89 5,2 4,58 4,70	7,77 7,47 4,86 6,3 3,53 4,82	17,76 17,29 11,10 8,4 8,07	8,89 8,85 16,68 15,5 20,21 18,5	< 0,05		3400-3240-1630-1620-1560-1545/ 3,8 (8H)-4,6 (2H)-7,2-7,9(8H)-8,4(2H)
	n= 4 $\underline{9}_{4}$	6	95	264 (pyridine)								$M^{\cdot +}-2H_2O$= 540	3420-3320-1640
	n= 6 $\underline{9}_{6}$	6	90	225-235									3430-3320-1635
	$\bar{n}$=11,3 $\underline{9}_{11,3}$	6	95	255-265									3420-1645



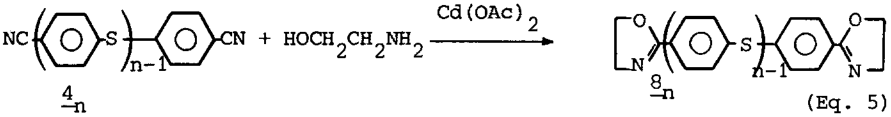
(Eq. 4b)



(Eq. 4c)

Synthesis of α,ω-bis(1,3-oxazoline-2-yl) oligomers.

The reaction of ethanolamine on a nitrile in the presence of a cadmium salt as catalyst (11) gives the corresponding oxazoline with excellent yields:

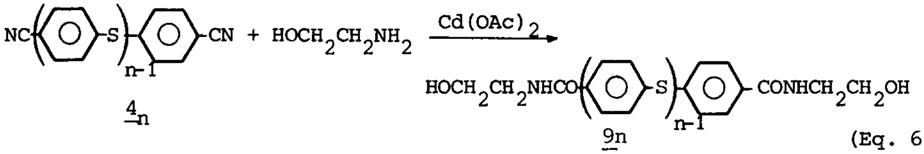


(Eq. 5)

This reaction was used for the synthesis of soluble oligomers (n = 2, 4 and 6).

Synthesis of α,ω-dialcohol oligomers.

These alcohols are the basic hydrolysis products of the corresponding oxazolines. They are prepared by refluxing nitrile in ethanolamine in the presence of a cadmium salt. Statistical oligomers 4, although insoluble, react quantitatively in these conditions, with the reaction being stopped when all the nitrile functions detected by means of their IR band at 2220 cm^{-1} have desappeared.



(Eq. 6)

Experimental

The products were characterized by means of their IR spectra (Perkin-Elmer 377 instrument), RMN spectra (Perkin-Elmer R 24 spectrometer), mass spectra and elemental analysis.

Dipolar aprotic solvents (N,N-dimethylformamide (DMF), N-methylpyrolidone (NMP), N,N-dimethylbenzamide (DMB)) were distilled twice form phosphoric anhydrid, with the DMB being prepared according to (20).

p-bromobenzonitrile. It was prepared from p-bromoaniline according to (22) and crystallized from hexane. Yield = 60%. Mp = 114°C.

p-mercaptobenzoic acid. It was prepared from p-aminobenzoic acid according to (14) and purified by esterification (CH_3OH-HCl), distillation (Bp_2 = 85°C) and saponification (KOH-H_2O). After filtration and drying, the product was obtained with an overall yield of 58%. Mp = 220°C.

p-mercaptoaniline. It was prepared by reduction of p-chloronitrobenzene according to (18) and distillated (Bp_1 = 85°C). Yield = 50%.

bis(p-bromophenyl) sulfide. It was prepared by bromination of diphenylsulfide according to (2, 19) and crystallized from ethanol. Yield = 85 %. Mp = 113°C.

bis(p-mercaptophenyl) sulfide. The first three steps of the synthesis are described (6, 7). The last step is carried out by refluxing, for 1 hour, 39.2 g (0.1 mole) of bis(p-N,N-dimethylthiocarbamatephenyl) sulfide with 28.5 g (0.5 mole) of potash in 200 ml of ethanol. The solution was neutralized with hydrochloric acid, and the product was filtered. After crystallization from ethanol, we obtained $\underline{2}$b with a yield of 60%. Mp = 117°C.

p-cyanodiphenylsulfide. Prepared according to (14). The product was crystallized from a hexane-ethanol blend (90/10). Yield = 95%. Mp = 30°C.

p-bromo-p'-cyanodiphenylsulfide. The product was crystallized from a hexane-ethanol blend (40/60). Yield = 66%. Mp = 98.5°C.

p-nitrodiphenylsulfide. It was prepared in the same way as p-cyanodiphenylsulfide, starting from p-bromo-nitrobenzene. Yield = 90%. $Bp_{0.2}$ = 145°C.

p-bromo-p'-nitrodiphenylsulfide. The product was crystallized from ethanol. Yield = 82%. Mp = 92°C.

p-bromo-p'-amino-diphenylsulfide. The product was crystallized from a pentane-ether blend (50/50). Yield = 95%. Mp = 74°C.

p-bromo-p'acetamidodiphenylsulfide. To a solution of 28 g (0.1 mole) of p-bromo-p'-aminodiphenylsulfide in 200 ml of ether and 14 ml (0.1 mole) of triethylamine, we added 7.2 ml (0.1 mole) of acetyl chloride. After 1 hour at room temperature, the solid product was filtered, washed with water and crystallized from ethanol. Yield = 94%. Mp = 168.5°C.

α,ω-dibromo oligomers. The operating mode is close to the one described for the synthesis of the polymer (24):
Product $\underline{3}_{11.3}$ (Eq. 1c), $\underline{3}_4$ (Eq. 1a) and $\underline{3}_6$ (Eq. 1b):

A blend of 108 g (0.45 mole) of sodium sulfide and 600 ml of NMP was dehydrated by heating at 200°C under a stream of nitrogen. 172 g (0.5 mole) of bis(p-bromophenyl)sulfide were then added, and the temperature was maintained for 3 hours at 200°C. After cooling, the solution was poured into 1.5 l of water. The solid was filtered, washed with water and methanol and then continuously extracted in a Kumagawa instrument with chloroform for 24 hours. The yield was 70 g of product containing 11% of bromine, which is a mean weight of $\overline{M}$ = 1454.

α,ω-dicyano oligomers.
Product $\underline{4}_{11.3}$ (Eq. 2a): 20 g of dibromo oligomer $\underline{3}_{11.3}$ and 10 g of cuprous cyanide were heated in 85 g of DMB for 4 hours at 235°C. After cooling, the excess of cuprous cyanide was destroyed with a hydrochloric solution of ferric chloride according to (10) or (25). The product was filtered, washed with water and methanol and continuously extracted with methanol during 24 hours.

Product $\underline{4}_4$ (Eq. 2b) and $\underline{4}_6$: 38.4 g (0.105 mole) of p-bromobenzonitrile, 25 g (0.1 mole) of bis(p-mercaptophenyl)sulfide and 14.3 g (0.105 mole) of potassium carbonate wera heated in 250 ml of DMF for 3 hours at 120°C in an inert atmosphere. The solvent was vacuum distilled, the solid was washed with water and crystallized.

α,ω-diamino oligomers.
Product $\underline{5}_{13.3}$ (Eq. 3a), $\underline{5}_4$ and $\underline{5}_6$ (Eq. 3b): 20 g of dibromo oligomer $\underline{3}_{11.3}$, 6.5 g of p-mercapto-aniline and 3.6 g of potassium carbonate were heated in

100 g of DMB for 4 hours at 220°C in an inert atmosphere. After cooling, the solution was poured into 400 ml of water. The solid was filtered, washe with methanol and continuously extracted with methanol during 24 hours.

α,ω-diester oligomers.

Product $\underline{6}_{13.3}$ (Eq. 4a): 20 g of dibromo oligomer $\underline{3}_{11.3}$ and 9.3 g of p-mercaptobenzoic acid salified by 2.9 g of sodium hydride were heated in 200 ml of NMP for 3 hours at 200°C. The solution was cooled to 120°C, and 11 g of methyl tosylate were added. After 12 hours, the reaction was stopped. The working up is the same as the one for product $\underline{5}_{13.3}$.

Product $\underline{6}_2$ (Eq. 4b), $\underline{7}_4$ and $\underline{7}_6$ (Eq. c): Bis(p-cyanophenyl)sulfide was alcoholized with methanol according to (26) and with ethylene glycol (13).

α,ω-bis(N-(2-hydroxyethyl) amide) oligomers.

Products $\underline{9}_2$, $\underline{9}_4$, $\underline{9}_6$, $\underline{9}_{11.3}$ (Eq. 6): 10 g of nitrile $\underline{4}_n$ were refluxed in 30 ml of ethanolamine for 2 hours in the presence of 500 mg of cadmium acetate. After cooling, the solution was poured into 100 ml of water. Products $\underline{9}_2$ and $\underline{9}_4$ were crystallized and $\underline{9}_{11.3}$ was continuously extracted with methanol for 24 hours.

References

1. JONES, R.V. and HILL H.W.: Adv. Chem. Ser. 140, 174-85 (1975).
2. BOURGEOIS, E.D. and ABRAHAM A.: Rec. Trav. Chim. Pays-Bas 30, 407 (1911).
3. BOURGEOIS, E.D. and PETERMANN K.: Rec. Trav. Chim. Pays-Bas 22, 349 (190 and U.S.S.R. patent 706 409, Central Patents Index Section A C33, p. 51 (1980).
4. MARVEL, C.S. and CESAR P.D.: J. Am. Chem. Soc. 72 1033 (1950).
5. HUGHES, G.K. and THOMPSON E.O.P.: J. Proc. Roy Soc. N.S. Wales 83, 269 (1949).
6. ARIYAN, Z.S. and WILES L.A.: J. Chem. Soc. 3876, (1962).
7. NEWMAN, M.S. and KARNES H.A.: J. Org. Chem. 31, 3980 (1966).
8. Org. Synth. 35, 57 (1955).
9. Org. Synth., Coll. vol. II, 580 (1957).
10. U.S.S.R. patent 532 609 (1976) (CA 86 17308e)
11. WITTE, H. and SEELIGER W.: Angew. Chem. 84, 343 (1972).
12. SHAW, J.E., KUNERTH P.S. and SHERRY J.J.: Tet. Lett. 9, 689 (1972).
13. ROBINSON, B.: J. Chem. Soc. 3417 (1963) ; NORTON R.V., Tet. Lett., 16, 4643-46, (1972).
14. HADDAD, I., SHAUN HURLEY and MARVEL C.S.: J. Pol. Sci. Chem. Ed. 11, 2793 (1973).
15. MONTAUDO, C., BRUNO G., MARAVIGNA P., FINOCCHIARO and CENTINO G.: J. Pol. Chem. Ed. 11, 65 (1973).
16. U.S.S.R. patent 676 597 (1979) (CA 91 158341a).
17. Org. Synth., Coll. vol. I, 514-516 (1956).
18. GILMAN, H. and GAINER G.C., J. Am. Chem. Soc., 71 1747-1749 (1949).
19. TOUSSAINT, J.: Bull. Soc. Chem. Belg., 54, 319-339 (1945).
20. U.S.S.R. patent 525 717, Central Patent Index, Section A Y37, p. 52 (1977).
21. GILMAN, H. and SMITH BROADLENT H.: J. Am. Chem. Soc., 69, 2053-2057 (1947).
22. CAMPBELL, J.R.: J. Org. Chem., 29, 1830-1833 (1964).
23. U.S. patent 3 987 016 (1976).
24. French patent applications 76 16014, 76 16016, 76 16017.
25. FRIEDMAN, L. and SHECKTER H.: J. Org. Chem., 26, 2522-2524, Method A (1961).
26. MARCH, J. Advanced Organic Chemistry, 2nd Ed., p. 813-814, Mc Graw-Hill (1977).

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