SYNTHESIS OF THIOPHENE-NAPHTHALENE ANALOGS OF CHALCONE

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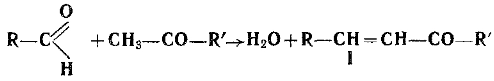
A number of thiophene and nitrothiophene analogs of chalcone containing a naphthalene ring have been obtained by crotonic condensation.

The present paper gives information on the preparation of a number of analogs of chalcone I by the crotonic condensation of α-thiophenealdehyde, α-nitro-α'-thiophenealdehyde, α-naphthaldehyde, and β-naphthaldehyde with α-acetothienone, α-nitro-α'-acetothienone, α-acetylnaphthalene, and β-acetylnaphthalene in an alkaline [1] or acid [2] medium



$$R-C\overset{O}{\underset{H}{\lt}} + CH_3-CO-R' \rightarrow H_2O + R-\underset{I}{CH}=CH-CO-R'$$

The compounds I that we synthesized (see table) consist of solid, predominantly yellow substances crystallizing well (with the exception of 1). They all possess characteristic halochromic properties, forming halochromic solutions with concentrated sulfuric acid with colorations from orange-red to violet.

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R—CH=CH—CO—R′

No.	R	R′	T. Mp, °C	Empirical formula	S, %		Yield, %
					found	calculated	
1	α-Thienyl	α-Naphthyl	61—63*	$C_{17}H_{12}OS$	12.36; 12.15	12.13	83
2	α-Nitro-α'-thienyl	α-Naphthyl	156—158**	$C_{17}H_{11}NO_3S$	10.21; 10.62	10.37	43
3	α-Thienyl	β-Naphthyl	96—97**	$C_{17}H_{12}OS$	12.08; 12.32	12.13	67
4	α-Nitro-α'-thienyl	β-Naphthyl	198—199 (from benzene)	$C_{17}H_{11}NO_3S$	10.43; 10.53	10.37	39
5	α-Naphthyl	α-Thienyl	115—116*	$C_{17}H_{12}OS$	12.22; 12.28	12.13	80
6	α-Naphthyl	α-Nitro-α'-thienyl	179—180**	$C_{17}H_{11}NO_3S$	10.35; 10.69	10.37	76
7	β-Naphthyl	α-Thienyl	155—156*	$C_{17}H_{12}OS$	12.18; 11.96	12.13	95
8	β-Naphthyl	α-Nitro-α'-thienyl	196—197 (from acetic acid)	$C_{17}H_{11}NO_3S$	10.63; 10.71	10.37	70

* Recrystallized from aqueous ethanol.

** Recrystallized from propanol.

REACTIONS EXPANDING THE AZIRIDINE RING

I. Reaction of N-Phenylethyleneimine with Carbon Dioxide and Its Sulfur Analogs

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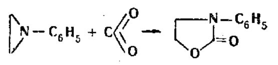
N-Phenylethyleneimine reacts with carbon dioxide to form 3-phenyl-2-oxazolidone. Carbon disulfide and carbon oxysulfide give poly(ethylene dithiocarbanilate) and poly(S-ethylene thiocarbanilate) which, on thermal decomposition, form 3-phenyl thiazolidine-2-thione and 3-phenyl-1,3-thiazolid-2-one.

The reaction of oxiranes and thiiranes with carbon disulfide and its sulfur analogs takes place with the expansion of the three-membered rings [1]. The analogous reactions of aziridines have been studied little.

Thus, at room temperature carbon dioxide caused the vigorous polymerization of ethyleneimine [2]. With ethyleneimine and its C-derivatives, carbon disulfide forms the corresponding thiothiazolidones [3]. With carbon monoxide, carbon oxysulfide, and carbon disulfide, ethyleneimine forms thermoplastic resins [4].

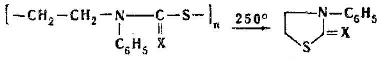
We have studied the reaction of N-phenylethyleneimine (I) with carbon dioxide, carbon oxysulfide, and carbon disulfide. Carbon dioxide does not react with I in the absence of a catalyst. In the presence of the tetraethylammonium bromide (TEAB) catalyst at 95° C, equimolecular amounts of the reactants give a high yield of 3-phenyl-2-oxazolidone (II)



I II

The reaction of carbon oxysulfide with I in the presence of TEAB or triethylamine at 95° C did not lead to the formation of the expected 3-phenyl-1, 3-thiazolid-2-one, but gave a peculiar copolymer of phenylethyleneimine with carbon oxysulfide in a molecular ratio of 1:1 which was insoluble in the majority of organic solvents with the exception of the cresols and dimethylformamide. The IR spectrum had a strong absorption band characteristic for the carbonyl group (1670 cm^{-1}), and therefore structure III may be assumed for the copolymer obtained. An analogous polymer, poly(S-ethylene thiocarbanilate), obtained by Japanese workers [5] by heating 3-phenyl-1, 3-oxazolidine-2-thione at 140–160° C or by treating it at room temperature with boron trifluoride etherate or ferric chloride, decomposes at 300–320° C with the formation of 3-phenylthiazolid-2-one.

On being heated under similar conditions, the copolymer that we had isolated also formed 3-phenylthiazolid-2-one (V), which confirms the formula III.

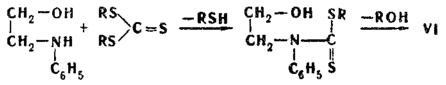


III, IV V, VI

III, V X = O; IV, VI X = S

The reaction of I with carbon disulfide at 95° C in the presence of TEAB or triethylamine forms a copolymer together with 3-phenylthiazolidine-2-thione (VI). The copolymer obtained had the structure of poly(ethylene dithiocarbanilate) (IV) since its thermal decomposition gave VI.

We also obtained 3-phenylthiazolidine-2-thione (VI) by the transesterification of diethyl trithiocarbonate with β-hydroxyethylaniline.



EXPERIMENTAL

The N-phenylethyleneimine (I) was obtained by the dehydrochlorination of β-chloroethylaniline by analogy with the work of Heine and Kapur [6].

3-Phenyl-2-oxazolidone (II). A mixture of 2.0 g (0.017 mole) of I, 0.75 g (0.017 mole) of solid CO_2, and 0.02 g of TEAB was heated in a tube at 95° C for 10 hr. This gave 2.2 g (80%) of II, mp 120° C (ethanol) (mp 122° C [7]).

Reaction of I with carbon oxysulfide. A mixture of 1.4 g (0.012 mole) of I, 0.7 g (0.012 mole) of carbon oxysulfide, and 0.02 g of TEAB was heated in a tube at 95° C for 40 hr. The contents of the tube were treated with ether, to give 0.7 g (33.3%) of the copolymer III, mp 195° C $[\eta]^{40}$ 0.25 (o-cresol). It was reprecipitated from dimethylformamide in methanol. Found, %: C 60.19; 60.22; H 4.95; 5.12; N 7.65, 7.71; S 17.79; 17.82. Calculated for $[C_9H_9NOS]_x$, %: C 60.33; H 5.04; N 7.81; S 17.87.

Pyrolysis of III. 0.25 g of II was heated in an evacuated tube at 250° C for 30 min. This gave 0.11 g (44%) of 3-phenyl-2-thiazolidone (IV), mp 76° C (ethanol) (mp 75.5° C [8]), and 0.07 g of the initial polymer was recovered.

3-Phenyl-2-thiazolidinethione (VI). a) A mixture of 2.0 g (0.017 mole) of I, 1.28 g (0.016 mole) of CS_2, and 0.02 g of TEAB was heated in a tube at 95° C for 10 hr. The contents of the tube were treated with cold ether, and from this was isolated 0.5 g (25%) of unchanged I. The residue was extracted with 50 ml of hot ethanol and 0.20 g (8.9% of the I that had reacted) of VI was isolated, mp 128° C (ethanol) (mp 128° C [9]). Found, %: C 55.12; 55.58; H 4.65; 4.60; N 7.19, 7.28; S 32.68, 32.95; mol. wt. 194. Calculated for $C_9H_9NS_2$, %: C 55.38; H 4.61; N 7.23; S 43.77; mol. wt. 195.

The residue consisted of the copolymer IV, 1.8 g (73.5%) on the I that had reacted), decomp. p. 200–210° C, $[\eta]^{40}$ 0.24 (o-cresol). Found, %: C 55.51, 55.40; H 4.78, 4.67; N 7.19, 7.25; S 32.00, 32.30. Calculated for $(C_9H_9NS_2)_x$, %: C 55.38; H 4.61; N 7.23; S 32.77%.

b) **Pyrolysis of IV.** 1.0 g of IV was heated in an evacuated tube at 250° C for 30 min, yielding 0.65 g (65%) of VI, mp 128° C (ethanol), which gave no depression with an authentic sample.

c) A mixture of 36.4 g (0.27 mole) of β-hydroxyethylaniline, 44.1 g (0.26 mole) of diethyl trithiocarbonate, and 0.2 g of sodium in 100 ml of xylene was heated at a bath temperature of 130–170° C for 3 hr. Ethyl mercaptan was evolved. The residue was distilled in vacuum and a fraction boiling at 185–210° C (2–3 mm), which crystallized, was collected. The yield of VI with mp 128° C (ethanol) was 10.5 g (20.0%).

The IR spectrum was identical with that of the product obtained in the reaction of I with CS_2.

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