TABLE II

BASIC PRODUCTS[a,b]

Fraction	B. p., °C.	$n^{20}\mathrm{D}$	Wt., g.	Amine	B. p., °C.	$n^{20}\mathrm{D}$
1[c]	35-38	1.3831	2.9	Isopropyl	34	1.3770 at 15.4
2	38-45	1.3863	0.5	*n*-Propyl	48.7	1.3900 at 17
3[d]	45-62	1.3870	0.5	*t*-Butyl	45	1.3794 at 18
4[d]	62-65	1.3943	0.4	*s*-Butyl	63	1.3950 at 17
5[d]	65-77	1.3985	0.3	Isobutyl	68	1.3988 at 17
6[e]	77-82	1.4029	2.2	*n*-Butyl	78	1.4008 at 20
7	82-90	1.4043	0.4	Diethylcarbinyl	91	....
8	90-92	1.4021	0.2	Methyl-*n*-propylcarbinol	92	....

[a] The gases boiling below 35° were collected in a Dry Ice-trap and weighed 6-8 g. The material was further separated by distillation at 0 and 20°. The lower boiling portion was purified by recrystallization of its hydrochloride and shown by Nessler reagent to contain ammonia. The more soluble hydrochloride portion (presumably methylamine) and the higher boiling fraction (presumably ethylamine) could not, however, be made to give pure derivatives of these bases. [b] From the aqueous residue treatment with solid sodium hydroxide gave triethylacetamide (1 g.), m. p. 108.4-110°, which did not depress the melting point of an authentic sample. [c] Fraction 1 with diethyl oxalate gave N,N'-di-*n*-propyloxamide, m. p. 160°, which did not depress the melting point (160.5-161.5°) of an authentic sample. No evidence for the presence of isopropylamine (corresponding N,N'-diisopropyloxamide, m. p. 212°[12]) was observed. [d] These cuts were too impure to permit further identification. [e] Fraction 6 with diethyl oxalate gave N,N'-di-*n*-butyloxamide, m. p. 150-151°, which did not depress the melting point (150.5-151.0°) of an authentic sample. Analysis of this derivative showed N, 14.13% (calcd. 14.00%) and the free amine itself had a neutralization equivalent 75.2 (calcd.) 73.

Attempts to Rearrange Various Relatives. (a) Triethylcarbinol.—On warming with concentrated sulfuric acid at 50° for twenty minutes triethylcarbinol gave only polymeric products. In another experiment triethylcarbinol (58 g.) and sodium azide (50 g.) were gradually added to a mixture of concentrated sulfuric acid (310 g.) and chloroform (200 ml.) at the boiling point of the chloroform. Reaction occurred but isolation of the neutral products showed only diethyl ketone with no trace of higher homologs.

(b) **3-Ethylpentene-2.**—This olefin (30 g.) in concentrated sulfuric acid (158 ml.) at 0° was treated with a small amount of sodium azide. Reaction began only after warming to 35°. Excess sodium azide was then added and the products isolated as usual. Both basic and neutral products were polymeric. Even in the absence of sodium azide and below 0°, 3-ethylpentene-2 with this quantity of concentrated sulfuric acid formed only polymeric products.

Summary

1. The products of the reaction of triethylacetic acid with sodium azide and concentrated sulfuric acid are a complex mixture of ketones, amines and other products.

2. The products found can be accounted for by formation and rearrangement of an intermediate carbonium ion.

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(12) Dermer and Hutcheson, *Proc. Oklahoma Acad. Sci.*, **23**, 60-63 (1943); *C. A.*, **38**, 2006 (1944).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA]

Studies in *p*-Cymene. III. Some N,N'-Diarylthioureas*

BY JOSEPH N. LECONTE AND LEON H. CHANCE

This study was made for the purpose of preparing several new N,N'-diarylthioureas to be used in the anticipated preparation of substituted quinolines by the method of Dziewonski and Moszew.[1]

N,N'-Di-2-*p*-cymylthiourea was made by standard procedure from 2-amino-*p*-cymene, then split with concentrated hydrochloric acid to form 2-*p*-cymyl isothiocyanate and 2-amino-*p*-cymene hydrochloride. There was no evidence of the formation of a substituted guanidine. The isothiocyanate was extracted directly with ether and, when isolated, was reacted with 2-amino-*p*-cymene to yield the original di-2-*p*-cymylthiourea. This was proved by the method of mixed melting points. Further, the *p*-cymyl isothiocyanate was allowed to react with phenylhydrazine to form phenyl-*p*-cymyl thiosemicarbazide. Analysis indicated that only one mole of the isothiocyanate reacted with one mole of the hydrazine, whereas the work of Otterbacher and Whitmore[2] showed that two moles of phenyl isothiocyanate react with one mole of phenyl hydrazine.

The preparation of N,N'-(*o*-, *m*-, *p*-)tolyl-2-*p*-cymylthioureas from the reaction of the toluidines with 2-*p*-cymyl isothiocyanate gave mixed products and the resulting separation gave poor yields. The mixed products were verified to be not only the desired products, but also di-*p*-cymylthiourea and the ditolylthioureas. This type of interchange has not heretofore been reported. Since the yields were low, it was decided to treat the tolyl isothiocyanates with 2-amino-*p*-cymene. The results were excellent as evidenced in Table I.

Several methods of splitting these thioureas were tried. The most successful method experienced was by using acetic anhydride. Five to six minutes of refluxing yielded the isothiocyanates and free amine bases. Prolonged heating converted the amines first formed to their acet-compounds. As anticipated from the work[3]

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(1) Dziewonski and Moszew, *Roczniki Chem.*, **26**, 428, 925 (1932); **27**, 3937 (1833); **28**, 152 (1934).

(2) Otterbacher and Whitmore, THIS JOURNAL, **51**, 1909 (1929).

(3) Mainzer, *Ber.*, **16**, 2016-2018 (1883).

TABLE I

TOLYL-*p*-CYMYLTHIOUREAS, $C_{18}H_{22}N_2S$

Isomer	M. p., °C.	Sulfur, % Calcd. = 10.75	Cleavage products	Derivatives
Ortho	111–112	10.91	*o*-Tolyl isothiocyanate *p*-Cymyl isothiocyanate 2-Acetamino-*p*-cymene Acetamino-*o*-toluene	Di-*o*-tolylthiourea *o*-Tolyl-*p*-cymylthiourea
Meta	100–101	10.90	*p*-Tolyl isothiocyanate *p*-Cymyl isothiocyanate Acetamino-*p*-toluene	Di-*p*-tolylthiourea *p*-Tolyl-*p*-cymylthiourea
Para	116	10.76	*p*-Cymyl isothiocyanate 2-Acetamino-*p*-cymene	Di-*p*-cymylthiourea

of Mainzer, the molecules cleaved two ways; *e. g.*, the N,N′-2-*p*-cymyl-*o*-tolylthiourea yielded both the 2-*p*-cymyl isothiocyanate and *o*-tolyl isothiocyanate in nearly equal quantities.

Experimental

I. **Preparation of N,N′-Di-2-*p*-cymylthiourea and its Derivatives.**—90.5 g. (0.607 mole) of 2-amino-*p*-cymene, 151 g. (2.0 moles) of carbon disulfide, 120 ml. of absolute alcohol and 5 g. of solid potassium hydroxide were placed in a 500-ml. balloon flask equipped with an efficient reflux condenser, thoroughly agitated and then heated on a water-bath. A soda-lime trap was used to absorb the hydrogen sulfide evolved. The reaction mixture was refluxed for twenty-five hours when the hydrogen sulfide ceased to be evolved. When cooled, the mixture crystallized into a solid mass. This was filtered at the pump, washed with cold ethanol and then recrystallized from this solvent. Several recrystallizations were necessary for purification; m. p. 129–130° (uncorrected); yield, 52.5%. Solubility: (1) 2 g. dissolve in 100 ml. of ethanol at 20°; (2) 5 g. dissolve in 100 ml. of diethyl ether at 20°; (3) difficultly soluble in ligroin.

Anal. Calcd. for $C_{21}H_{22}N_2S$: S, 9.41. Found: S, 9.46.

2-*p*-Cymyl Isothiocyanate.—A mixture of 95 g. of N,N′-di-2-*p*-cymylthiourea and 300 ml. of concentrated hydrochloric acid in a 500-ml. balloon flask attached to a condenser was refluxed for three hours. When cooled, the mixture crystallized into a solid white mass. This solid was broken up and extracted with ether. The white solid residue proved to be 2-amino-*p*-cymene hydrochloride. The ether layer was dried, the ether evaporated and the residual oil distilled under diminished pressure. The main fraction was a colorless oil, darkening on standing, which boiled at 118–122° (3 mm.). The boiling point at atmospheric pressure was 267–268°; refractive index, 1.5973 (20°); yield, 33 g.

Anal. Calcd. for $C_{11}H_{13}NS$: S, 16.75. Found: S, 17.07.

Phenyl-2-*p*-cymylthiosemicarbazide.—A mixture of two grams of *p*-cymyl isothiocyanate, 1 g. of phenylhydrazine and 8 ml. of absolute ethanol in a 50-ml. Erlenmeyer flask was warmed on a water-bath for fifteen minutes, cooled and the white crystals were filtered and recrystallized from ethanol; m. p. 168.5°; yield, 2 g.

Anal. Calcd. for $C_{17}H_{21}N_3S$: S, 10.72. Found: S, 10.66.

Preparation of the N,N′-Tolyl-*p*-cymylthioureas.—The tolyl isothiocyanates (7 mole pts.), 2-amino-*p*-cymene (10 mole pts.) and absolute ethanol (1.1 mole pts.) were mixed in balloon flasks. After the initial reactions had subsided, five mole parts of additional ethanol was added. The resulting solutions were evaporated to half their volumes and cooled, when white crystalline materials separated. These were filtered, washed with cold alcohol and dried. Yields were approximately 50%.

Cleavage of the N,N′-Tolyl-*p*-cymylthioureas.—The substituted thioureas and acetic anhydride were mixed in the mole ratio of one to two, respectively, and refluxed for five minutes, poured into hot water and steam distilled. The oils were extracted with ether, dried and distilled under diminished pressure.

Summary

Several new N,N′-disubstituted thioureas have been prepared and their cleavage products determined.

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