

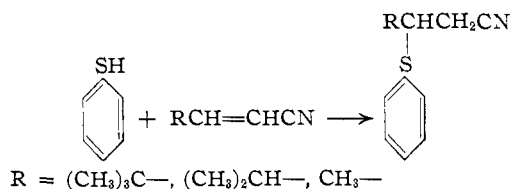
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Cyanoalkylation: The Addition of Thiophenol to  $\beta$ -AlkylacrylonitrilesBY ROBERT M. ROSS<sup>1</sup>

Although cyanoethylation has been the subject<sup>2</sup> of considerable work within recent years, no systematic study has been reported anent the relationship of acceptor structure to the reactivity of the conjugate system in alkylated acrylonitriles. Consequently, it became the purpose of this research to investigate the cyanoalkylations of an active hydrogen component by substituted acrylonitriles, wherein alkyl groups were located in the  $\beta$ -position.

The addition of compounds which contain labile hydrogen atoms to acrylonitrile<sup>2</sup> proceeds readily with the formation of excellent yields of adducts. However, substituted acrylonitriles almost invariably react less readily than acrylonitrile with nearly all active hydrogen components. Among the nitriles which have been described in reactions of this type are  $\alpha$ -methylacrylonitrile,<sup>2</sup> crotonitrile,<sup>3</sup> cinnamitrile<sup>4</sup> and 1-cyano-1,3-butadiene.<sup>5</sup> Although the behavior of various addenda with such alkylacrylonitriles has been investigated, thiophenol has seen little or no use in this capacity. Furthermore, since thiophenol has shown especial reactivity<sup>6</sup> in cyanoethylation, it was decided to determine whether  $\beta$ -alkylacrylonitriles would again present difficulties of decreased reactivity even with thiophenol.

Thiophenol was added in the conjugate manner to the following unsaturated nitriles:  $\beta$ -*t*-butylacrylonitrile,  $\beta$ -isopropylacrylonitrile and  $\beta$ -methylacrylonitrile. Triton B<sup>7</sup> was employed as a cat-



alyst, and the reactions were carried out under constant conditions in each of the cyanoalkylations. The poorest yield of adduct was obtained from  $\beta$ -*t*-butylacrylonitrile and thiophenol (21%), whereas crotonitrile afforded the best yield (54%) of the  $\beta$ -phenylmercapto addition compound. It should be noted that these yields are not nearly as satisfactory as those reported<sup>8</sup> for the

reaction between thiophenol and acrylonitrile. Apparently, even with the extraordinarily active thiophenol,  $\beta$ -alkylacrylonitriles do not possess the high order of reactivity which is characteristic of acrylonitrile in the presence of a Triton B catalyst.

A further study of the thiophenol reaction, however, has brought to light a catalyst which affords high yields even with the alkylated acrylonitriles. It has been found that a mixture of Triton B and piperidine produced  $\beta$ -alkyl- $\beta$ -phenylmercapto-propionitriles in yields which varied from 87 to 93% of the theoretical value. No significant difference in yields was apparent whether the acceptor molecule was  $\beta$ -*t*-butylacrylonitrile,  $\beta$ -isopropylacrylonitrile or crotonitrile. Reaction conditions for this series of experiments were identical to those employed previously with the Triton B catalyst. Possibly, the mixture of piperidine and Triton B counteracted any adverse equilibrium conditions present when Triton B was the sole catalyst.

A series of similar cyanoalkylations were carried out using piperidine alone as a catalyst. The yields of adducts thus prepared corresponded closely to those obtained with a mixture of piperidine and Triton B; in every instance, however, the yields were slightly less than in the case of the mixed catalyst. Whether or not the diminution of yield was significant is debatable.

All of the adducts were characterized by micro and infrared analyses of the substituted phenylmercapto-propionitriles, hydrogen peroxide oxidation of the adducts to the corresponding sulfonyl derivatives, and microanalyses of the sulfones thus obtained. On the basis of precedent, the addition was assumed to take place in the normal 1,4-manner, since the reactions were not carried out under the influence of peroxides.

It is believed that the true catalyst responsible for the increased yields in those cyanoalkylations carried out with the piperidine and Triton B or piperidine catalysts is a salt or complex of thiophenol and piperidine. This phase of the work is to be investigated further.

Experimental<sup>8</sup>

**$\beta$ -Alkylacrylonitriles.**—New methods for the preparation of  $\beta$ -*t*-butylacrylonitrile and  $\beta$ -isopropylacrylonitrile have been described elsewhere.<sup>9</sup> Crotonitrile was prepared by a modification of the method described by Dollfus,<sup>10</sup> which involved acetic anhydride dehydration of crotonaloxime.<sup>11</sup>

(8) The author is indebted to Emily Davis, Ruth Kopel and Jane Wood for all microanalyses reported, and to Elizabeth M. Petersen for the infrared data.

(9) Ross and Burnett, *THIS JOURNAL*, **71**, 3562 (1949).

(10) Dollfus, *Ber.*, **25**, 1920 (1892).

(11) The author is indebted to Mary Louise Burnett for preparing the crotonitrile used in this work.

(1) A portion of this investigation was carried out during the period in which the author was the du Pont Postdoctoral Fellow at the University of Illinois; the author is indebted to the du Pont Company for the opportunities made available during this time.

(2) Bruson, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. V (in press).

(3) Bruylants, *Bull. soc. chim. Belg.*, **31**, 225 (1922).

(4) Borsche, *Ber.*, **42**, 4496 (1909).

(5) Charlsh, Davies and Rose, *J. Chem. Soc.*, 227 (1948).

(6) Hurd and Gershbein, *THIS JOURNAL*, **69**, 2328 (1947).

(7) Triton B is a 35% aqueous solution of trimethylbenzylammonium hydroxide which may be procured from Rohm and Haas.

TABLE I  
 $\beta$ -ALKYL- $\beta$ -PHENYLMERCAPTOPROPIONITRILES AND  $\beta$ -ALKYL- $\beta$ -PHENYLSULFONYLPROPIONITRILES

$\beta$ -Alkyl substituent, g.	Method and % yield	$\beta$ -Alkyl- $\beta$ -phenylmercaptopropionitriles, RCH(SC <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> CN				$\beta$ -Alkyl- $\beta$ -phenylsulfonylpropionitriles, RCH(SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CN							
		B. p., °C. <sup>a</sup> adduct	<i>n</i> <sub>D</sub> <sup>20</sup> <sup>e</sup>	Analyses, %		M. p., °C. <sup>a</sup> oxida- tion product	Yield, %	Analyses, %		Found H			
				Calcd. C	Calcd. H	Found C	Found H		Calcd. C	Calcd. H	Found C	Found H	
<i>t</i> -Butyl 2.20	A 93	108 (0.5 mm.) <sup>d</sup>	1.5546	71.18	7.81	71.06	7.72	97.3-98	52 <sup>b</sup>	62.12	6.82	62.34	6.86
	B 77												
	C 21 <sup>f</sup>												
Isopropyl 1.90	A 87	110 (0.38 mm.) <sup>d</sup>	1.5535	70.20	7.37	70.15	7.38	79.7-80.5	75 <sup>c</sup>	60.73	6.37	60.90	6.35
	B 85												
	C 32												
Methyl 1.34	A 89	114 (0.9 mm.)	1.5581	67.75	6.26	68.01	6.45	92.5-93.5	73	57.39	5.33	57.56	5.42
	B 85												
	C 54												

<sup>a</sup> All boiling points and melting points are uncorrected. <sup>b</sup> *t*-Butyl- $\beta$ -phenylsulfonylpropionamide was obtained as a white solid (10% yield) from the fractional crystallization, m. p. 182.2-183.2°. Anal. Calcd. for C<sub>13</sub>H<sub>19</sub>NO<sub>3</sub>S: C, 57.96; H, 7.11. Found: C, 57.86; H, 7.30. <sup>c</sup> A small amount (19%) of crude  $\beta$ -isopropyl- $\beta$ -phenylsulfonylpropionamide was isolated from the hydrogen peroxide oxidation by fractional crystallization, m. p. 145-154°. Further recrystallizations from hot ethyl acetate did not alter its purity sufficiently so that the product could be analyzed. <sup>d</sup> The infrared absorption spectra for these adducts were in complete agreement with the proposed structure. <sup>e</sup> Constants listed are those observed from a middle cut of constant refractive index. <sup>f</sup> A considerable amount (1.6 g.) of unchanged  $\beta$ -*t*-butylacrylonitrile was recovered during the distillation.

#### Addition of Thiophenol to $\beta$ -Alkylacrylonitriles

**Method A (Triton B and Piperidine Catalyst).**—A mixture of 0.02 mole of  $\beta$ -alkylacrylonitrile and 2.20 g. (0.02 mole) of thiophenol<sup>12</sup> was placed in a 10-ml. flask equipped with a reflux condenser. To the contents of the flask was added 5 drops of dry, freshly distilled piperidine. A white precipitate, believed to be the salt of thiophenol and piperidine, formed immediately. After the reaction mixture was allowed to stand for forty-five minutes, 5 drops of Triton B and 2.5 ml. of peroxide-free dioxane<sup>13</sup> were added. The homogeneous contents of the flask were refluxed for twenty-four hours at an oil-bath temperature of 112°. At the end of this time, the source of heat was removed and the amber-colored solution was allowed to stand overnight at room temperature.

The dioxane was removed by distillation under atmospheric pressure, and the residue was extracted with 10 ml. of benzene. The benzene solution was scrubbed successively with 10-ml. portions of water, 5% aqueous sodium hydroxide solution, and finally with water. This procedure was found to be effective in removing any unreacted thiophenol. The benzene extract was dried over anhydrous magnesium sulfate, and the excess benzene removed by distillation. A distillation done under reduced pressure yielded the adduct as a slightly yellow, viscous oil. Redistillation of several combined runs was effected in order to obtain an analytical sample. A middle fraction of colorless  $\beta$ -alkyl- $\beta$ -phenylmercaptopropionitrile of constant refractive index was obtained.

**Method B (Piperidine Catalyst).**—Other than the omission of Triton B as a catalyst component, the amounts of reactants and the procedure utilized remained the same as that described under Method A.

**Method C (Triton B Catalyst).**—The conditions for this method were the same as for Method A with the exception that Triton B alone was employed as the catalyst.

(12) "Organic Syntheses," Coll. Vol. I, second edition, 1946, p. 504.

(13) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., second edition, 1941, p. 368.

**$\beta$ -Alkyl- $\beta$ -phenylsulfonylpropionitriles.**—A mixture of 1.0 g. of the  $\beta$ -alkyl- $\beta$ -phenylmercaptopropionitrile and 1.8 ml. of glacial acetic acid was placed in a test-tube and 2.0 g. of 30% hydrogen peroxide was added. The resulting mixture was stoppered, shaken occasionally, and allowed to stand for eight days at room temperature. At the end of two days, shaking was no longer necessary since solution had been effected.

A total of 6 ml. of water was added to the contents of the tube which usually contained some white crystals of oxidation product. These crystals had separated during the eight-day period of standing. Complete crystallization was effected after the tube and contents were chilled at 0° for several hours. The white, crystalline material was removed by filtration, washed with water, and dried in air. The product thus obtained was found to be a mixture of a  $\beta$ -alkyl- $\beta$ -phenylsulfonylpropionitrile and a  $\beta$ -alkyl- $\beta$ -phenylsulfonylpropionamide. Six fractional crystallizations using the mixed solvent pair, ethyl acetate and *n*-hexane, were effective in separating the nitrile from the amide. All the amides were found to be less soluble in this solvent pair; thus, the nitrile was isolated in a satisfactory state for elementary analysis by concentrating to dryness the mother liquors from each recrystallization and subjecting the residue to further crystallizations.

#### Summary

The addition of thiophenol to some *beta*-alkylated acrylonitriles has been studied. It has been found that a catalyst which consists of piperidine and Triton B causes the reaction to proceed with the formation of excellent yields of  $\beta$ -alkyl- $\beta$ -phenylmercaptoacrylonitriles. Piperidine was also effective in affording high yields, but the use of Triton B as the sole catalyst gave significantly smaller amounts of adduct.

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