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

Cyanoalkylation. II. The Addition of Mercaptans to 1-Cyano-1-cyclohexene

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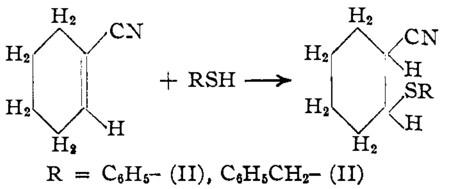
The present communication describes an extension of earlier work[1] performed in this laboratory on conjugate addition. 1-Cyano-1-cyclohexene has now been condensed with benzyl mercaptan and thiophenol.



R = C_6H_5– (II), $C_6H_5CH_2$– (II)

Bruson[2,3] has pointed out that, in reactions involving conjugate addition, methacrylonitrile is a particularly unreactive acceptor, possessing an activity of even lower order than that of crotononitrile. In fact suitable conditions could not be found to effect the addition of aldehydes[3] and ketones to methacrylonitrile. However, certain amines and alcohols participate in the reaction with an α-alkylacrylonitrile, such as methacrylonitrile, but with only mild and varying degrees of success.

In view of our previous experience with cyanoalkylation, however, it was believed that facile addition of mercaptans to an α,β-dialkylacrylonitrile could be realized if a suitable choice of catalyst were made. This belief was validated by the use of 1-cyano-1-cyclohexene as the acceptor. It is recognized that 1-cyano-1-cyclohexene is not a representative example of an α,β-dialkylacrylonitrile, if steric factors are considered. On the other hand, a number of examples of conjugate addition[1,4,5] are known wherein steric hindrance does not assume a significant role.

Thiophenol was caused to react with 1-cyano-1-cyclohexene in the presence of the piperidine salt of thiophenol as catalyst. The addition proceeded equally well in either *t*-butyl alcohol or dioxane as solvent at the reflux temperature. The adduct, 1-cyano-2-phenylmercaptocyclohexane (I), was isolated in yields which varied between 65–70%. Use of a mixed catalyst, consisting of the piperidine–thiophenol salt and Triton B, did not alter the yields appreciably. It is significant, although not surprising in view of previous work,[1] that no adduct was isolated when only Triton B was employed as the catalyst. Actually, a nearly quantitative amount of unchanged starting material was recovered in the experiment.

Conjugate addition to 1-cyano-1-cyclohexene was also realized with benzyl mercaptan as the addendum. In these experiments, 1-cyano-2-benzylmercaptocyclohexane (II) was isolated in yields of about 50%. The adduct was formed under essentially the same conditions as those described for the cyanoalkylation of thiophenol. Again, the catalysts that were employed consisted either of the piperidine salt of the mercaptan or the mixed salt–Triton B catalyst.

The superiority of the piperidine type of catalyst over Triton B in certain cyanoalkylations[1] and cyanoethylations[6] has been noted previously. Thus, the data reported herein are consistent with and analogous to the conjugate additions of thiophenol[1] to β-alkylacrylonitriles. However, the influence that the catalyst has upon cyanoalkylation reactions is still not clear. At least, it is conceivable that the reaction is affected by the relative basicity of the catalyst, and that an optimum *p*H is maintained with the salt catalyst, or possibly a buffer mixture of salt and Triton B.

All the adducts were oxidized to the corresponding sulfones for purposes of characterization. Elemental and infrared analyses[7] of the thio ethers and the sulfones served to substantiate the structures which have been assigned to the adducts. Conjugate addition was presumed to operate in the customary manner.

The infrared absorption spectra of the adducts as well as the corresponding sulfones are illustrated in Fig. 1. The spectra were determined in Nujol mulls and the Nujol bands are apparent at 2934, 2868, 1459 and 1378 cm.$^{-1}$.

Experimental

Addition of Mercaptans to 1-Cyano-1-cyclohexene.—A procedure analogous to that described previously[1] was utilized in this work. In Table I are given the necessary data for carrying out the additions.

Mention is made of an interesting example of *cis–trans* interconversion or isomorphism which was observed during the course of work with 1-cyano-2-phenylmercaptocyclohexane. This adduct was isolated in the form of lustrous, white platelets which melted at 54.9–55.6°, after several recrystallizations from ethanol. Two weeks later, the melting point was redetermined and found to be 60–63°. After several days the melting point was constant at 63–64°. No change in crystalline appearance was manifest during the transition. However, when a portion of the relatively high melting product was recrystallized from the same solvent that was employed previously, its crystalline structure did change to the form of hard needles. Attempts to isolate the low melting product first obtained have been unsuccessful thus far.

Furthermore, a similar experience was encountered with 1-cyano-2-benzylmercaptocyclohexane. Invariably the adduct was obtained as a yellow viscous oil, about half of which slowly crystallized to yield a white solid, m.p. 44°. The residual oil partially crystallized after further standing to yield the same low melting adduct. Rapid conversion of the oil to the crystalline form could not be induced either by seeding the oil or scratching the inner walls of the flask. Complete conversion to the solid necessitated at least a month's time. Crystallization was found to be accelerated, however, by warming the oil in the presence of piperidine.

Oxidation of Thio Ether Adducts to the Corresponding Sulfones.—The oxidation was carried out in 30% hydrogen

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[1] Ross, THIS JOURNAL, **71**, 3458 (1949).

[2] Bruson, "Org. Reactions," Vol. 5, John Wiley & Sons, Inc., New York, N. Y., p. 108.

[3] Bruson, unpublished work.

[4] Fuson and Jackson, THIS JOURNAL, **72**, 1637 (1950).

[5] Kohler and Blanchard, *ibid.*, **57**, 367 (1935).

[6] Gribbins, Miller and O'Leary, U. S. Patent 2,397,960 [*C. A.*, **40**, 3542 (1946)].

[7] The authors are indebted to Miss Elizabeth M. Petersen for the infrared absorption analyses, their interpretation, and the drawing of the absorption curves.

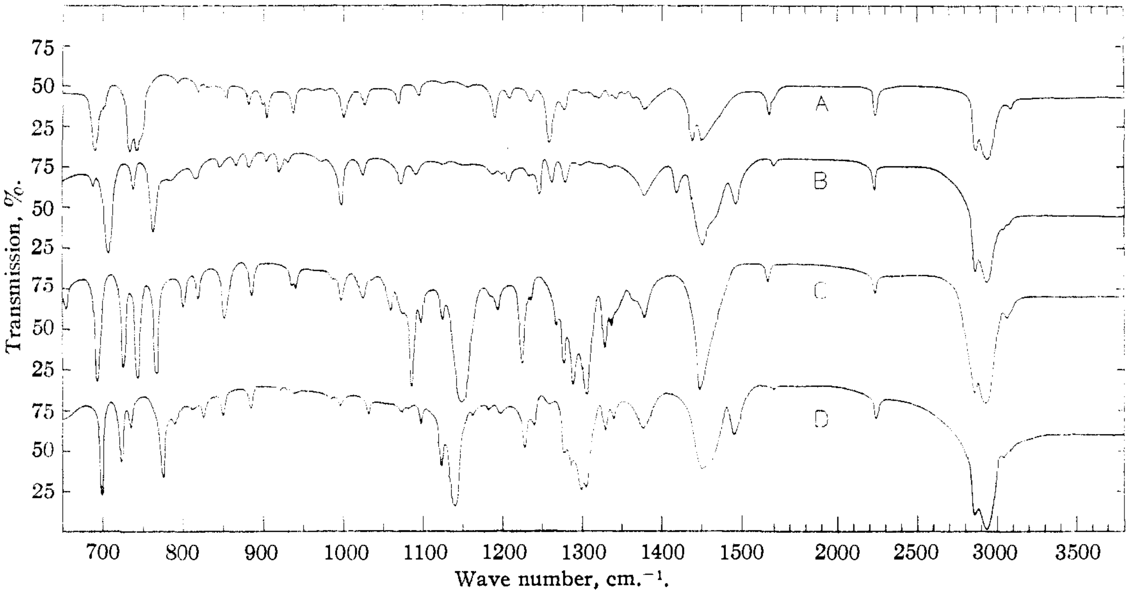

Fig. 1.—Infrared absorption spectra: A, 1-cyano-2-phenylmercaptocyclohexane; B, 1-cyano-2-benzylmercaptocyclohexane; C, 1-cyano-2-phenylsulfonylcyclohexane; D, 1-cyano-2-benzylsulfonylcyclohexane.

TABLE I

ADDUCT FORMATION

Acceptor, 1-cyano-1-cyclohexene,[a] g.			4.28	4.28	4.28	3.00	5.00	10.0
Addendum	Mercaptan		C_6H_5SH			C_6H_5SH	$C_6H_5CH_2SH$	$C_6H_5CH_2SH$
	Grams		4.40	4.40	4.40	3.10	5.80	11.6
Catalyst[b]	Cmpd.		PTS	PTS	PTS	TB	PBS	PBS
	Grams		0.4	0.4	0.8	0.6	0.5	1.0
	Compd.		TB	TB			TB	
	Grams		0.4	0.4			0.5	
Solvent	Compd.		Dioxane		t-C_4H_9OH	Dioxane	t-C_4H_9OH	
	Ml.		10	10	10	7	10	15
Reflux time, hr.			48	24	48	24	48	48
1-Cyano-2-phenyl-(benzyl)-mercaptocyclohexanes	Yield,[g] %		70	66	65	Trace	50.3	49.4
	B. p.	°C.	119–121				133	
		Mm.	0.04[c,e]				0.07	
	M. p.[d]	°C.	63.7–64.1[e,f]				43.5–44.0	
		Cryst.	Ndls.				Prisms	
	C, %	Calcd.	71.84				72.68	
		Found	72.00				72.61	
	H, %	Calcd.	6.96				7.41	
		Found	6.96				7.51	

[a] Dr. George I. Poos generously supplied us with this nitrile for the early investigations; the remainder of nitrile was prepared by the method of Coillier [*Bull. soc. chem. Belg.*, **42** 419 (1933)], physical constants: b. p. 86° (15 mm.) $n^{20}D$ 1.4823. [b] The salt catalysts were generated *in situ* by addition of piperidine to an equimolar amount of mercaptan (above that used as addendum). PTS and PBS are abbreviations for piperidine–thiophenol salt and piperidine–benzyl mercaptan salt, respectively, while TB represents a 35% aqueous solution of trimethylbenzylammonium hydroxide. [c] The adducts were isolated by distillation through a short path assembly. The reported boiling points are those for the crude material and are uncorrected. [d] All melting points reported in Table I were determined on a brass micro melting point apparatus and have been corrected. [e] See experimental for a description of the unusual physical behavior of these adducts. [f] Recrystallized from 95% ethanol. [g] Unchanged 1-cyano-1-cyclohexene was recovered in sufficient quantities to account for the materials balance.

peroxide and glacial acetic acid by a method which was described previously.[1,8]

1-Cyano-2-phenylsulfonylcyclohexane.—This material was obtained in the form of white needles in a yield of 80%, m.p. 140.5–140.8°.[8a] Recrystallization from ethyl acetate afforded an analytical sample.

Anal. Calcd. for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.07. Found: C, 62.74; H, 6.17.

1-Cyano-2-benzylsulfonylcyclohexane.—The sulfone was isolated as flat, white platelets in 95% yield, m.p. 131–131.5°.[8a] Ethyl acetate was employed as the solvent for recrystallization.

Anal. Calcd. for $C_{14}H_{17}NO_2S$: C, 63.85; H, 6.51. Found: C, 63.69; H, 6.43.

Summary

The additions of thiophenol and benzyl mercaptan to 1-cyano-1-cyclohexene have been studied. Adducts were isolated only in those experiments wherein a piperidine–mercaptan salt was used as catalyst.

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RECEIVED JUNE 12, 1950

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

(8a) See footnote *d*, Table I.