Anal. Calcd. for $C_{10}H_{16}N_2O_5$: C, 49.17; H, 6.60; N, 11.47. Found: C, 48.77; H, 6.81; N, 11.30.

The residue from the combined mother liquor, which amounted to 320 mg., was further fractionally crystallized from chloroform. From a slightly soluble portion, 90 mg. more of VI was obtained. An insoluble portion which mainly consisted of the hydrolyzed product (VII) of VI was not purified. The remaining 170 mg. of a very soluble substance was submitted to fractional crystallization from tetrahydrofuran, which yielded 10 mg. of VI and 100 mg. of its diastereoisomer (VI′), m.p. 208–209°, depressed to 185–195° on admixture with the isomer of m.p. 215–216°; ν_{max}^{KBr} 3315, 1734, 1700, 1640, and 1205 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}N_2O_5$: C, 49.17; H, 6.60; N, 11.47. Found: C, 49.28; H, 6.85; N, 11.28.

The total yield of VI was 210 mg. and that of VI′ was 100 mg. Thin layer chromatography of VI and VI′ on silica gel was carried out with ethanol–chloroform (1:1 v./v.) as the solvent. The chromatograms were chlorinated by the action of chlorine gas and detected with starch–iodide reagent as violet spots which appeared near each other.

3-Acetamido-4-hydroxy-1-methyl-2-oxo-5-pyrrolidinecarboxylic Acid (VII).—To a suspension of 200 mg. (0.00082 mole) of VI in 0.5 ml. of ethanol, 0.4 ml. of 2 *N* potassium hydroxide solution was added dropwise with agitation. After leaving the solution for 1 day at room temperature, the reaction mixture was diluted with water to 5 ml. and the solution was passed through a column of 10 ml. of Dowex-50 (X2). The column was washed with water until the washings were neutral. The effluent was collected while it was acid. This solution was evaporated to dryness under reduced pressure, leaving 170 mg. of a white crystalline mass. Recrystallization from acetone yielded 100 mg. (47.9%) of colorless plates, m.p. 203–204° dec.

Anal. Calcd. for $C_8H_{12}N_2O_5 \cdot H_2O$: C, 41.02; H, 6.03; N, 11.96. Found: C, 41.37; H, 5.92; N, 12.04.

The anhydrous substance was a hygroscopic solid.

Anal. Calcd. for $C_8H_{12}N_2O_5$: N, 12.96. Found: N, 12.84.

α-Amino-α′-methylamino-β-hydroxyglutaric Acid (VIII).—A solution of 150 mg. of VII in 5 ml. of 6 *N* hydrochloric acid was refluxed for 4 hr. After cooling, the reaction mixture was evaporated to dryness under reduced pressure, leaving a white crystalline mass. The yield, almost quantitative, amounted to 130 mg. By adding excess ethanol to a saturated solution in water and allowing it to stand in a refrigerator, colorless plates, m.p. 228–230° dec., crystallized slowly. Thin-layer chromatography of the derivative on silica gel was carried out with water saturated with phenol as the solvent. The reddish purple spot appeared near the spot of serine with ninhydrin reagent and the reddish orange positive coloration with the Nessler reagent for hydroxyamino acids. These results indicate that the product is a β-hydroxyamino acid.

Anal. Calcd. for $C_6H_{12}N_2O_5 \cdot H_2O$: C, 34.28; H, 6.71; N, 13.33. Found: C, 34.62; H, 6.29; N, 13.03.

The anhydrous substance is hygroscopic.

Anal. Calcd. for $C_6H_{12}N_2O_5$: N, 14.58. Found: N, 14.70.

Reduction of VIII to Glutaric Acid.—A mixture of 140 mg. of VIII and 5 ml. of hydriodic acid (sp. gr. 1.7) was heated at 200–220° in a sealed tube for 4 hr. After cooling, the reaction mixture was diluted with water to 25 ml. The solution was extracted twice with 50 ml. of ether. The ether layer was shaken with a minimum amount of a saturated solution of sodium thiosulfate to remove the dissolved iodine and then washed several times with a small amount of water until the pH of the last washing was about 3. The ether solution was dried over sodium sulfate and evaporated to dryness; the residue was dissolved in a minimum amount of absolute ether. On addition of petroleum ether (b.p. 40–60°) resinous products separated. The decanted solution was evaporated to dryness and the residue was recrystallized from petroleum ether. The yield of the reduction product, m.p. 97–98°, amounted to 5 mg. The melting point of this derivative was not depressed by admixture with authentic glutaric acid. The infrared spectra (KBr) of the two substances were identical and exhibited characteristic peaks at 1702, 1308, and 1210 cm.$^{-1}$.

Acknowledgment.—The author wishes to thank Mrs. Muneo Hiura for the elemental analyses.

Spectral Solvent Shifts. Substituent Effects

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Received September 30, 1963

A number of workers have observed that polar solvents cause shifts of the ultraviolet absorption maxima of aromatic molecules as compared to nonpolar solvents. This effect has been explained on the basis of various solute–solvent interactions in both the ground state and the excited state. Ungnade,[2] Nagakura and Baba,[3] and Baba and Suzuki[4] have emphasized hydrogen bonding and dipole–dipole interactions of the ground state. Bayliss and McRae[5] have considered the importance of dipole moment transitions of the solute molecule in going from ground to excited state, along with orientations of the solvent cage in the ground state and the excited state. Schubert and coworkers[6] also believe that solvation of ground state and excited states is important. They believe red shifts to be caused by greater solvation of excited states than ground states with a resultant increase in dipole moments of the solute molecule. Blue shifts would be caused by highly solvated ground states which tend to hinder excitation. Ungnade[2] has proposed a similar type of solvation to explain these shifts. McRae,[7] Semba,[8] and others have attempted to relate solvent shifts to dielectric constant and index of refraction. However, some solvents, especially dioxane, do not fit the proposed equations.

The present study is an attempt to relate the solvent shifts of substituted benzenes to known proprerties of the solute molecule, in order to evaluate the importance of hydrogen bonding and polarization effects. We have studied a series of *ortho*-, *meta*-, and *para*-substituted nitrobenzenes and have observed the effect of the substituent on the solvent shifts for the ^1L_a and ^1L_b[9] bands of nitrobenzene (primary and secondary bands of Doub and Vandenbelt),[10] when polar solvents are compared to cyclohexane. The polar solvents chosen on the basis of their proton donor–acceptor properties and dielectric constants were dioxane, a proton acceptor of low dielectric constant (2.209); methanol, a proton donor of high dielectric constant (37.5); and 2-propanol, a proton donor of intermediate dielectric constant (15.7). Of the two alcohols, methanol is the stronger acid[11] and hence the stronger proton donor. Substituent groups were chosen on the basis of their potential hydrogen-bonding properties. For the nitrobenzenes, the ^1L_a and ^1L_b bands were found to be symmetrical about the peak and band shapes did

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[1] In part from the M.S. thesis of J. Olguin.

[2] H. E. Ungnade, *J. Am. Chem. Soc.*, **75**, 432 (1953).

[3] S. Nagakura and H. Baba, *ibid.*, **74**, 5963 (1952).

[4] H. Baba and S. Suzuki, *J. Chem. Phys.*, **35**, 1118 (1961).

[5] N. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[6] (a) W. M. Schubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957); (b) W. M. Schubert, H. Steadley, and J. M. Craven, *ibid.*, **82**, 1353 (1960).

[7] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

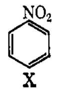
[8] K. Semba, *Bull. Chem. Soc. Japan*, **34**, 722 (1961).

[9] J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

[10] L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

[11] J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).

TABLE I

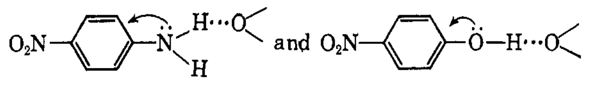
 X	σ_p	Cyclohexane[a]	Dioxane[a]	ΔE, $\frac{\text{kcal.}}{\text{mole}}$	Methanol[a]	ΔE, $\frac{\text{kcal.}}{\text{mole}}$	2-Propanol[a]	ΔE, $\frac{\text{kcal.}}{\text{mole}}$
NH_2	−0.66	324 (4.34)	354 (4.12)	−7.48	370 (4.12)	−10.98	379 (4.29)	−12.81
$N(CH_3)_2$	−0.83	356 (4.36)	382 (4.32)	−5.46	390.5 (4.25)	−7.1	390.0 (4.25)	−7.0
OH	−0.36	287 (4.09)	306 (3.96)	−6.19	313 (3.92)	−8.28	313 (3.92)	−8.28
$NHCOCH_3$	0	300 (3.74)	315 (4.15)	−4.54	314 (4.11)	−4.25	314 (4.21)	−4.25
OCH_3	−0.27	294 (4.09)	305 (4.20)	−3.50	305.5 (3.98)	−3.66	305.0 (4.12)	−3.51
CH_3	−0.17	266 (4.02)	274.5 (3.99)	−3.34	274.5 (4.00)	−3.34	273.5 (4.01)	−2.95
H	0	253 (3.94)	260 (3.95)	−3.04	260.5 (3.89)	−3.26	258 (3.82)	−2.19
Br	+0.23	270.5 (4.15)	276.5 (4.22)	−2.30	275.7 (3.98)	−2.00	274.5 (4.12)	−1.55
COOH	+0.41	253 (3.69)	257 (3.70)	−1.76	263.5 (3.83)	−4.51	259.5 (4.15)	−2.83
COOEt	+0.45	254.5 (4.25)	258.5 (4.33)	−1.74	259 (4.31)	−1.95	258.5 (4.16)	−1.74
HC=O	...	260.5 (4.10)	264 (4.08)	−1.45	265 (4.01)	−1.86	263.5 (4.13)	−1.25

[a] Wave lengths in mμ (log ε).

not vary with solvent except for a slight decrease in intensity in going from cyclohexane to polar solvent. In line with accepted practice the absorption maximum was taken as the band position.[5,6]

The results for the solvent shifts of the ${}^1L_a$ band for a series of *para*-substituted nitrobenzenes (Table I) show a decrease in excitation energy (red shift) in going from cyclohexane to polar solvents. This energy lowering decreases as the electron donor properties of the group *para* to the nitro decrease. Hammett σ-constants were chosen as a measure of the electron donor–acceptor properties of the groups. The values used are those compiled by McDaniel and Brown[12] taken from ionization constants of benzoic acids. A plot of ΔE *vs.* σ_p (Fig. 1 and 2) shows the substituents to fall into two separate groups, those which contain hydrogen attached to nitrogen or oxygen (NH_2, OH, and $NHCOCH_3$), and those which do not [$N(CH_3)_2$, OCH_3, CH_3, Br, and COOEt], the position of the carboxyl group being solvent dependent. Identical correlations were obtained using $\sigma_p{}^+$-constants of Brown and Okamoto.[13]

The red shifts observed for nonproton-donor groups in the case of the *para* isomers are in line with the suggestions of Bayliss and McRae[5] and Schubert[6] that polar solvent molecules are oriented to polar sites on the solute molecule in the ground state. On excitation the solvent molecules are then in a position to solvate more strongly the more polar excited state, thus stabilizing the excited state with respect to the ground state. These shifts are directly related to the ability of the group *para* to the nitro to release electrons in the excited state under the influence of the electron demand of the nitro group, and to become more positive. The ability of the solvent oxygen to solvate this positive site is reflected in the linear relationship of the excitation-energy lowering and σ_p. When substituents are capable of hydrogen bonding with the solvent oxygen, ground state polarization is probably enhanced by forms such as



which would build up electron densities on the substituent atom and assist electron migration toward the NO_2 group on excitation. Solvation of the oxygens of the nitro group in both the ground and excited states by the alcohols must also be considered[8] and may account, in part, for the slightly larger red shifts observed in methanol for nonproton-donor groups. The abnormally large red shift of *p*-nitrobenzoic acid in methanol suggests some hydrogen-bonded form of the excited state involving the protons of both the carboxyl group and the alcohol.

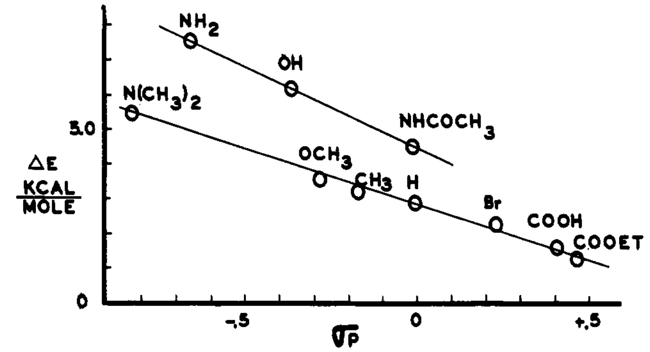


Fig. 1.—Plot of ΔE *vs.* σ_p for dioxane compared to cyclohexane for a series of *para*-substituted nitrobenzenes.

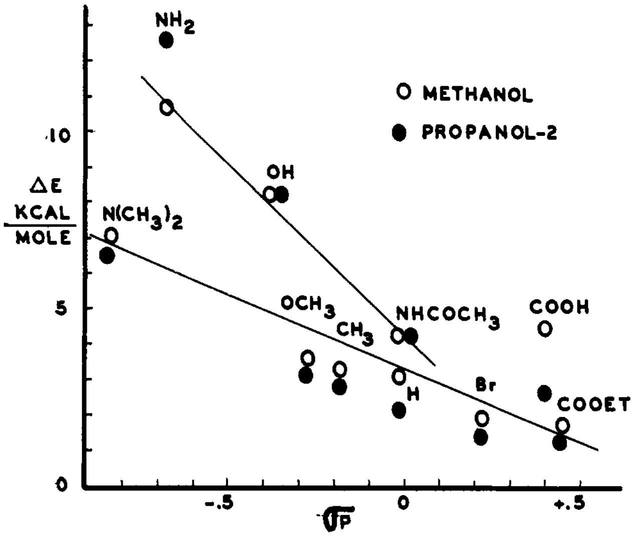


Fig. 2.—Plot of ΔE *vs.* σ_p for methanol and 2-propanol compared to cyclohexane for *para*-substituted nitrobenzenes.

The solvent shifts for the *meta* isomers (Table II) do not show a linear relationship with Hammett's σ_m-constants. However, the results for the ${}^1L_a$ band in dioxane show a high degree of linearity for ΔE values

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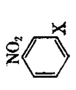
(12) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(13) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

TABLE II

	Cyclohexane			Dioxane				Methanol				2-Propanol			
	σ_I	$^1L_a{}^a$	$^1L_b{}^a$	$^1L_a{}^a$	ΔE	$^1L_b{}^a$	ΔE	$^1L_a{}^a$	ΔE	$^1L_b{}^a$	ΔE	$^1L_a{}^a$	ΔE	$^1L_b{}^a$	ΔE
CH_3	−0.05	257 (3.85)		264.5 (3.91)	−3.16			264 (3.89)	−2.95			263.5 (3.90)	−2.75		
OH	+0.25	260 (4.03)	315 (3.40)	269.5 (3.77)	−3.88	330 (3.32)	−4.13	269.5 (3.77)	−3.88	332 (3.46)	−4.65	269.5 (3.77)	−3.88	334 (3.40)	−5.19
NH_2	+0.10	229 (4.20)	348 (3.38)	234.5 (4.06)	−2.93	370 (3.02)	−4.89	234.5 (4.08)	−2.93	376 (3.06)	−6.12	234.5 (4.07)	−2.93	378 (3.08)	−6.52
$NHCOCH_3$	+0.28	236 (3.94)	316 (2.83)	241.5 (3.92)	−2.76	328 (2.75)	−3.32	242 (4.06)	−3.00	328 (2.74)	−3.32	242 (4.04)	−3.00	330 (2.70)	−3.85
OCH_3	+0.25	263 (3.85)	319.5 (3.32)	269 (3.67)	−2.42	330.5 (3.30)	−2.98	267 (3.48)	−1.62	325 (3.06)	−1.51	267 (3.45)	−1.62	321 (3.05)	−0.42
COOH		250 (3.78)		255 (3.92)	−2.25			257 (3.80)	−3.12			256 (3.86)	−2.68		
COOET	+0.32	250.5 (3.92)		255.5 (3.87)	−2.20			255.5 (3.86)	−2.20			254 (3.93)	−1.60		
Br	+0.45	254.5 (3.77)		259.5 (3.81)	−2.16			258.5 (3.73)	−1.74			259 (3.74)	−1.95		

[a] Wave lengths in mμ (log ε).

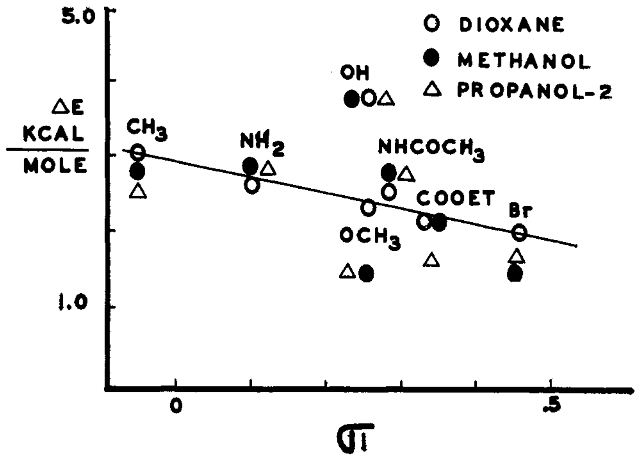
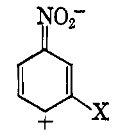


Fig. 3.—Plot of ΔE *vs.* σ_I for dioxane, methanol, and 2-propanol compared to cyclohexane for a series of *meta*-substituted nitrobenzenes.

vs. the inductive σ-constants (σ_I) of Taft[14] (Fig. 3), with only hydroxyl showing an abnormally large red shift due to hydrogen bonding with the solvent. Methanol and 2-propanol give considerable scattering, probably due to solvent–solute interactions, especially in the case of methoxyl, in which hydrogen-bonding forms of this type may be important in ground state solvation.

$$CH_3\text{—}O\cdots H\text{—}O\text{—}R$$

A correlation of ΔE values for dioxane with $\sigma_m{}^+$ gave linear results except for the methyl group which shows a larger electron donor effect on excitation than would be expected from its $\sigma_m{}^+$ value. The two alcohols gave scattered results here also. The linear relationship of the solvent shifts for dioxane with σ_I for the *meta* substituents is in line with the supposition that groups *meta* to one another are not directly conjugated. Therefore, it would be expected that inductive and field effects, of which σ_I is a measure, would be more important at the *meta* position for the ^1L_a band in which excited state forms of this type may be important.



ortho-Substituted nitrobenzenes are more difficult to interpret because of steric and internal hydrogen-bonding effects which can occur at the *ortho* position. The red shifts in dioxane (Table III) are in the order $OCH_3 > NH_2 > CH_3 > OH > NHCOCH_3$. The low values for the hydroxyl and acetamido groups can probably be accounted for by internal hydrogen bonding with the nitro group, thus preventing interaction with the solvent. In methanol, the order $OCH_3 > CH_3 > NH_2 > OH > NHCOCH_3$, in which a blue shift is obtained with *o*-nitroacetanilide, suggests that methanol is bonding with the unshared pair of electrons on the nitrogen of NH_2 and $NHCOCH_3$.

In the case of both the *ortho* and the *meta* isomers, the ^1L_b band, when present, undergoes larger red shifts than the ^1L_a band, and follows the mesomeric order

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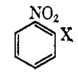
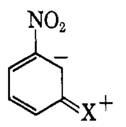
[14] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

TABLE III

	Cyclohexanol		Dioxane				Methanol			
	^1L_a[a]	^1L_b[a]	^1L_a[a]	ΔE	^1L_b[a]	ΔE	^1L_a[a]	ΔE	^1L_b[a]	ΔE
NH_2	270 (3.44)	379 (3.54)	276 (3.27)	−2.31	400 (3.28)	−3.96	275 (3.43)	−1.93	398 (3.44)	−3.60
OCH_3	250 (3.67)	305.5 (3.53)	255.5 (3.75)	−2.47	320 (3.55)	−4.24	257 (3.73)	−3.12	321 (3.50)	−4.53
CH_3	250 (3.84)		254 (3.73)	−1.80			255 (3.69)	−2.24		
OH	273 (4.30)	348 (3.76)	276 (4.25)	−1.14	351 (3.96)	−0.70	274 (4.07)	−0.38	351 (3.80)	−0.70
$NHCCCH_3$	275 (3.90)	354 (3.80)	276 (3.89)	−0.38	355 (3.78)	−0.23	270	+1.92	340 (3.73)	−3.33

[a] Wave lengths in mμ (log ε).

rather than the inductive order as for the ^1L_a band. This may be due to greater solvation of excited state forms such as



in which the charge appears on the bond[9] and would contribute more to the low intensity ^1L_b band.

Experimental

Absorption spectra in the region 220–400 mμ were obtained using a Bausch and Lomb automatic recording ultraviolet spectrophotometer, Model 505, with a constant 5-Å. band width and 1-cm. matched silica cells. The spectra were run in Spectroquality solvents (Matheson Coleman and Bell), using concentrations of 1.1×10^{-5} to 7.2×10^{-5} mole/l. and a scan time of 10 min. For those compounds which could undergo association in cyclohexane (*i.e.*, the nitrobenzoic acids), determinations were carried out at concentrations below which no change in the absorption maxima was observed (usually absorbancy values of 0.2 to 0.3). After each series of determinations the instrument was calibrated against the 253.7- and 313.1-mμ lines of mercury.

The nitrobenzenes were purchased as the highest purity compounds available and in some cases were further purified by recrystallization or distillation until the physical constants agreed with literature values. Each compound was then dried for a period of 3–24 hr. in an Abderhalden apparatus. Those compounds not available commercially (*p*-nitro-N,N-dimethylaniline, ethyl *p*-nitrobenzoate, and ethyl *m*-nitrobenzoate) were synthesized by methods listed in "Organic Syntheses" or "Beilstein."

Acknowledgment.—The work of Mr. Jorge Olguin was supported in part by a National Science Foundation Undergraduate Research Participation grant.

Exchange Reaction of Isocyanic Acid Esters and Isothiocyanic Acid Esters

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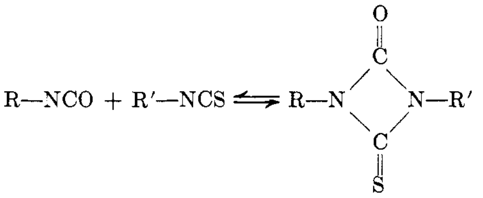
Received February 24, 1964

Isocyanic acid esters and isothiocyanic acid esters have been found[1] to undergo an exchange reaction when simply heated together at temperatures in the range of 190–230°. This exchange reaction has been taken

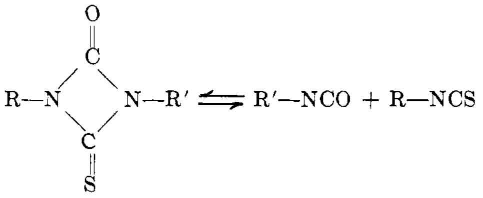
$$R{-}NCO + R'{-}NCS \rightleftharpoons R'{-}NCO + R{-}NCS \qquad (1)$$

advantage of to prepare isocyanates from isothiocyanates. Since isocyanates boil appreciably lower than corresponding isothiocyanates, separation of the desired isocyanates conveniently was achieved by conducting the reaction in the stillpot of a fractionating column. In this manner *n*-hexyl isocyanate was prepared from *n*-hexyl isothiocyanate and *m*-chlorophenyl isocyanate in 61% yield. Allyl isocyanate was obtained in yields of 22.5 and 23% from allyl isothiocyanate and toluene diisocyanate (80% 2,4-; 20% 2,6-) and *o*-chlorophenyl isocyanate, respectively. Similarly, 2-methylallyl isocyanate was obtained in 31% yield from 2-methylallyl isothiocyanate and toluene diisocyanate.

Case proposed that this exchange reaction proceeds through the intermediate formation of uretidinethione ketones.



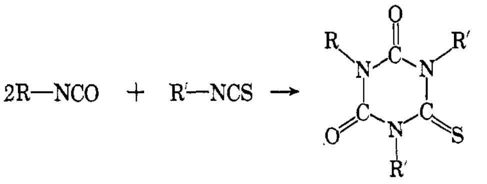
(2)



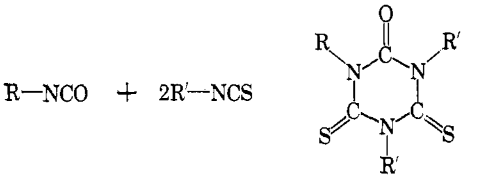
(3)

The marked difference in yield between the allylic isocyanates and the alkyl isocyanates points to competitive reactions. Vinyl polymerization of the allyl groups is not believed to be a significant factor, owing to the nearly identical yields of allyl isocyanate in exchange with toluene diisocyanate and with *m*-chlorophenyl isocyanate, in spite of the markedly different reaction times (2 hr. *vs.* 26.5 hr.).

Trimerization reactions leading to essentially irreversible formation of thio- and dithioisocyanurates are believed to be the major competitive reactions.



(4)



(5)

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[1] L. C. Case, *Nature*, **183**, 675 (1959).