ent. The cloudy, orange-yellow solution was cooled to 0° and filtered. In this way there was obtained 0.3 g. of bis-(2,4-dinitrophenyl) disulfide as a yellow powder (structure shown by identity of its infrared spectrum with that of an authentic sample). The filtrate was extracted with ether, and the ether layer dried over anhydrous sodium sulfate. Evaporation of the solvent yielded 0.24 g. of a brownish acidic solid that could not be identified positively. No evidence for the presence of 2,4-dinitrobenzenesulfenic acid was obtained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXIX. The Reaction of α,α-Dimethylallyl Chloride and γ,γ-Dimethylallyl Chloride with Thiourea and Substituted Thioureas[1]

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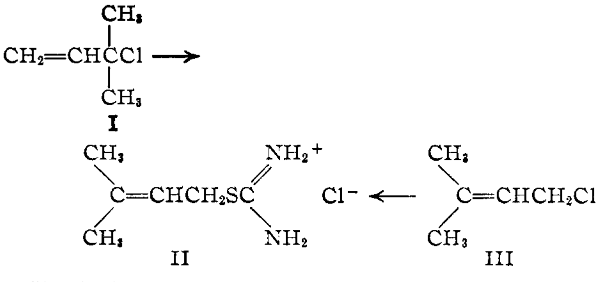
The reactions of α,α-dimethylallyl chloride and γ,γ-dimethylallyl chloride with thiourea in acetone both follow second-order kinetics. The tertiary allylic chloride undergoes an abnormal SN2′ displacement while the primary chloride undergoes a normal SN2 displacement. The same product γ,γ-dimethylallylisothiouronium chloride, was obtained in both cases. *sym*-Diphenylthiourea behaved similarly, but fully substituted thioureas did not undergo reaction with either the primary or the tertiary allylic chloride.

Introduction

Two mechanisms of bimolecular nucleophilic substitution are available to allylic compounds, the normal displacement, SN2, and the abnormal displacement SN2′. Several examples of the latter process are known and have been reviewed recently in detail.[2] For example, it has been shown by de la Mare[3] that nucleophilic attack on α,α-dimethylallyl chloride (I) by thiophenolate ion yielded only the product due to an abnormal SN2′ displacement. Allylic halides are known[4] to react with thiourea to form thiouronium halide salts which can be hydrolyzed to thiols by aqueous alkali. The purpose of the present work was to examine the reaction of pentenylallylic chlorides with various thioureas.

Results

When α,α-dimethylallyl chloride (I) was treated with thiourea in acetone at 25° an abnormal SN2′ displacement resulted and γ,γ-dimethylallylisothiouronium chloride (II) was obtained in 80% yield. This salt was also the sole product from the reaction of γ,γ-dimethylallyl chloride (III) with thiourea, and after ozonization and suitable decomposition of the resulting ozonide it afforded acetone in high yield.



$$CH_2{=}CHC(CH_3)_2Cl \longrightarrow (CH_3)_2C{=}CHCH_2SC(NH_2)_2^+\ Cl^- \longleftarrow (CH_3)_2C{=}CHCH_2Cl$$

Similarly, treatment of α,α-dimethylallyl chloride (I) with N,N′-diphenylthiourea (IV) gave only the abnormal product γ,γ-dimethylallyl-N,N′-diphenylisothiouronium chloride (V) which was also isolated from the reaction of the primary chloride III with IV. No reaction was detected between N,N′-dibutylethylenethiourea and α,α-dimethylallyl chloride (I). In order to lower the activation energy the primary chloride III was substituted for I, but still no reaction was observed. Similarly, neither N,N,N′,N′-tetramethylthiourea (VI) nor N,N′-dibenzoylthiocarbanilide (VII) would react with γ,γ-dimethylallyl chloride (III) in acetone.

A kinetic study of the reaction of the primary and tertiary allylic halides I and III with thiourea, followed by alcoholic base titration of the acidic components present, indicated both reactions to be second order. Rate constants were calculated from the integrated form of the usual second-order rate expression,[5] as given in equation 1.

$$k_2 = \frac{2.303}{t(b - a)} \log \frac{(b - x)\,a}{(a - x)\,b} \qquad (1)$$

Where x is the amount of allylic halide reacted in moles/l., b is the initial concentration of thiourea in moles/l., a is the initial concentration of allylic halide in moles/l. and t is the time, in minutes, elapsed from zero time. The rate was followed by titration with alcoholic sodium methoxide of the acidic isothiouronium salts formed. Rate constants are listed in Table I.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF α,α-DIMETHYLALLYL CHLORIDE AND γ,γ-DIMETHYLALLYL CHLORIDE WITH THIOUREA IN ACETONE

Isomer	RCl[a]	Thiourea[a]	Temp., °C.	k_2[b]
Tertiary	0.03341	0.06595	44.96	$1.54 \pm 0.03 \times 10^{-3}$
Tertiary	.00341	.06595	74.70	$1.93 \pm .18 \times 10^{-2}$
Primary	.01995	.07030	44.96	$3.18 \pm .15 \times 10^{-2}$
Primary	.01995	.07030	74.70	$2.01 \pm .17 \times 10^{-1}$

[a] Units of concentration are moles/l. [b] Units of k_2 are (mole/l.)$^{-1}$ (min.)$^{-1}$.

As the second-order rate constants are known at two different temperatures, it is now possible to calculate the experimental energy of activation, E^{ss},

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[1] This work was supported in part by a grant from the National Science Foundation.

[2] R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

[3] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3555 (1953).

[4] A. Luttringhaus, H. B. Konig and B. Bottcher, *Ann.*, **560**, 201 (1947).

[5] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

by the use of the data of Table I and equation 2, which is derived by consideration of the transition state theory.[5]

$$E^{ss} = \frac{2.303RT_1T_2}{T_2 - T_1}\log\frac{k_2}{k_1} \qquad (2)$$

Where k_1 and k_2 are the second-order rate constants at temperatures T_1 and T_2.

Table II

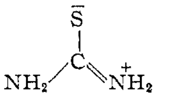
Isomer	k_2/k_1	E^{ss}, kcal./mole
Tertiary	12.532	18.68
Primary	6.321	13.68

Discussion

In considering the factors that lead to the occurrence of the abnormal nucleophilic displacement (SN2′) in the reaction of α,α-dimethylallyl chloride (I) with thiourea, the steric and electronic effects of the two methyl groups are all-important. While the inductive effect of these two substituents might be expected to inhibit somewhat the attack by a nucleophilic reagent at the double bond, it would nevertheless facilitate the concerted removal of the chloride ion. However, probably more important is the fact that a normal nucleophilic attack (SN2) at the α-carbon atom would encounter considerable steric hindrance due to the two methyl groups. Conversely, this steric hindrance is probably of great significance in precluding the occurrence of an abnormal nucleophilic displacement at the γ-carbon atom in the case of the primary allylic halide (III).

As second-order kinetics apply to both these reactions, then on this account the possibility of a slow isomerization of the tertiary chloride to its primary isomer, followed by a rapid reaction of the latter with thiourea, may be discounted as this would not have obeyed the second-order rate law. Also no rapid isomerization of the tertiary to the primary allylic halide could have occurred; otherwise, the observed rates of reaction of both isomers with thiourea would have been identical.

Resonance possibilities with thiourea, resulting from shifts of the unshared electron pair of nitrogen toward sulfur, would lead to a sulfide-ion type structure which accounts for the observed nucleophilicity



However, in the case of tetramethylthiourea (VI) the methyl groups may create steric inhibition of this resonance preventing transmission of this electron shift into the π-electron cloud of the C=S bond and accounting for the failure of such fully substituted thioureas to undergo reaction with the two allylic chlorides.

Experimental

Commercial Materials.—Braun C.P. acetone was dried over, and distilled from, calcium chloride, b.p. 56.6°. N,N′-Dibenzoylthiocarbanilide, N,N′-diphenylthiourea and N,N,-N′,N′-tetramethylthiourea were used after one recrystallization and N,N′-dibutylethylenethiourea after distillation. Eastman Kodak Co. thiourea had m.p. 180–181°. α,α-Dimethylallyl chloride, n^{20}_D 1.4190, and γ,γ-dimethylallyl chloride, n^{20}_D 1.4505, had been prepared in these laboratories.

Reaction of Thiourea and α,α-Dimethylallyl Chloride.—In a 125-ml. glass-stoppered erlenmeyer flask were placed 50 ml. of C.P. acetone and 2.54 g. (0.03 mole) of thiourea. The vessel was shaken until all the thiourea had dissolved. To the milky solution was added 4.08 g. (0.039 mole) of α,α-dimethylallyl chloride. The mixture was shaken thoroughly and the stoppered flask placed in a 25° thermostat. After three days a precipitate and a small amount of oil had formed. The excess acetone and oil were decanted off, the precipitate was washed with dry ether, filtered and dried to yield 4.63 g. (80%) of γ,γ-dimethylallylisothiouronium chloride, m.p. 128–129°. Its picrate had m.p. 176–176.5°.

Reaction of Thiourea and γ,γ-Dimethylallyl Chloride.—An identical procedure to that described above was employed and γ,γ-dimethylallylisothiouronium chloride was obtained in 82% yield, m.p. 129–129.5°.

Reaction of N,N′-Diphenylthiourea and α,α-Dimethylallyl Chloride.—In a 100-ml. flask, to which a reflux condenser had been attached, was placed 50 ml. of C.P. acetone and 7.53 g. (0.033 mole) of N,N′-diphenylthiourea. The mixture was refluxed until the thiourea had dissolved and then 4.08 g. (0.04 mole) of α,α-dimethylallyl chloride was added and the refluxing was continued for 48 hours. The reaction mixture was cooled and the resulting precipitate filtered and recrystallized from isopropyl alcohol, m.p. 132–133°. This was not depressed on admixture with a sample of γ,γ-dimethylallyl-N,N′-diphenylisothiouronium chloride.

Anal. Calcd. for $C_{18}H_{21}N_2AS$: C, 64.98; H, 6.36. Found: C, 64.96; H, 6.39.

Reaction of N,N′-Diphenylthiourea and γ,γ-Dimethylallyl Chloride.—An identical procedure to that described immediately above was employed and afforded γ,γ-dimethylallyl-N,N′-diphenylisothiouronium chloride, m.p. 132–134° in high yield.

Reaction of N,N,N′,N′-Tetramethylthiourea and γ,γ-Dimethylallyl Chloride.—Using the procedure described above a quantitative recovery of the unreacted thiourea resulted on working up the reaction product.

Kinetic Methods.—In a typical rate run 0.502 g. (0.06595 mole) of thiourea was added to about 90 ml. of C.P. acetone in a 100-ml. volumetric flask. The flask was shaken until all the thiourea had dissolved. The vessel and its contents were equilibrated in a 44.86° thermostat and 0.3475 g. (0.03341 mole) of α,α-dimethylallyl chloride was added and the solution was brought up to the mark with acetone that had previously been heated to the same temperature. After thorough shaking, ampoules containing 5.3 ml. of the solution were sealed off and placed in the 44.86° bath. At certain intervals, an ampoule was removed from the bath, cooled and transferred into chilled acetone (20 ml.) and immediately titrated to a *p*H of 7 with methanolic sodium methoxide solution using brom thymol blue as the indicator.

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