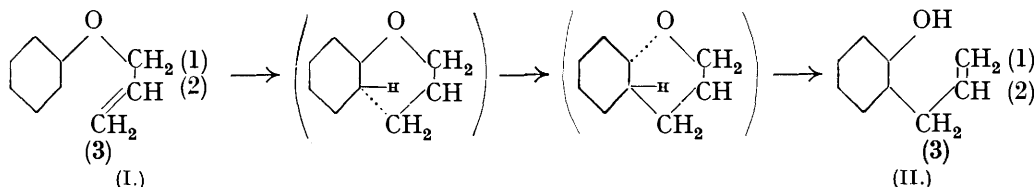


321. The Rearrangement of Thiocyanates into isoThiocyanates.

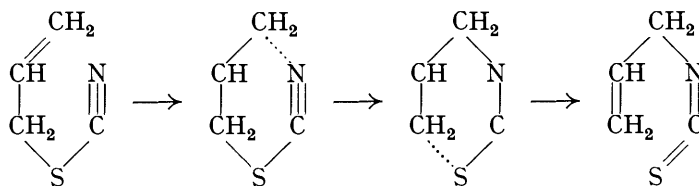
By ERNST BERGMANN.

Most of the typical intramolecular rearrangements are characterised by the fact that the migrating radical suffers no change in constitution during the process; e.g., a *p*-chloro- will never be converted into an *o*- or *m*-chloro-phenyl group. The only exception to this rule is the rearrangement of phenyl allyl ethers (Claisen, *Annalen*, 1919, **418**, 78), (I) \rightarrow (II), and this may be explained as follows: Between the carbon atom (3) of the allylic



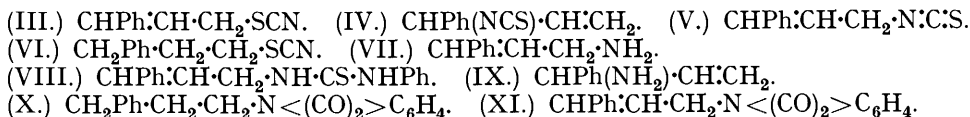
system and the *o*-position of the benzene nucleus a co-ordinate link is formed and becomes strengthened, with consequent loosening of the bond between the nucleus and the oxygen atom. Reorganisation of the molecule may then occur, as shown in the above formulæ (in which the omission of the allylic double bond is intentional).

If the above explanation is valid, the same type of intramolecular rearrangement might be anticipated in all cases of similar allyl compounds; and, indeed, Schlenk and Bergmann ("Lehrbuch der organischen Chemie," 1932, Vol. I, p. 609) have represented the well-known rearrangement of allyl thiocyanate into the *isothiocyante* as follows:



The validity of this hypothesis may be tested by Claisen's device, *viz.*, by using an unsymmetrically substituted allyl radical. Our starting material was *cinnamyl thiocyanate* (III), readily prepared from cinnamyl bromide and potassium thiocyanate. According to the above scheme, its rearrangement should give phenylvinylcarbiny *isothiocyante* (IV), whereas the classical type of rearrangement should lead to *cinnamyl isothiocyante* (V). Actually, the latter substance was obtained, and hence the classical scheme applies to this process.

Since the reaction between cinnamyl bromide and potassium thiocyanate might have been accompanied by structural change, we proved that the constitution of our starting material was really (III) by hydrogenating it; the same *compound* (VI) was obtained as by condensation of γ -phenylpropyl bromide and potassium thiocyanate. Further, the structure (III) is supported by the fact that it gives benzoic acid on oxidation.



When (III) is warmed it is converted into the *isothiocyante*, the structure of which was established by the fact that with aniline it gives a disubstituted thiourea (VIII) identical with that formed from cinnamylamine (VII) and phenyl *isothiocyante*. Further, in order to ensure that the "cinnamylamine" did not have the isomeric structure (IX), which might have arisen in its preparation from cinnamyl chloride and potassium phthal-

imide, followed by hydrolysis, since the first stage of the reaction involves directly one carbon atom of the allylic system (in the second stage, no allylic rearrangement can take place, for the hydrolysis does not involve the allylic system), we hydrogenated the "cinnamylphthalimide," obtaining *phthalo- γ -phenylpropylimide* (X), identical with that prepared from potassium phthalimide and γ -phenylpropyl bromide. The structure (XI) is thereby confirmed for the phthalimide.

EXPERIMENTAL.

Cinnamyl Thiocyanate (III).—Potassium thiocyanate (12 g.), dissolved in 75% alcohol (40 c.c.), was mixed with cinnamyl bromide (Rupe and Buerger, *Ber.*, 1910, **43**, 173) (20 g.) in alcohol (40 c.c.) at a low temperature. The whole mass solidified to a thick crystalline cake, which was triturated with alcohol (20 c.c.), and then, after $\frac{1}{2}$ hr., with water (200 c.c.). The white needles obtained were recrystallised from light petroleum; m. p. 68°; yield, 15 g. (Found: N, 8.2. $C_{10}H_9NS$ requires N, 8.0%). Cinnamyl chloride may be used instead of the bromide. Oxidation of the *thiocyanate* (0.123 g.) in acetic acid (10 c.c.) by chromic acid (1 g. in 40 c.c. of acetic acid) gave benzoic acid (20 mg.).

γ -Phenylpropyl Thiocyanate (VI).—(a) Solutions of ammonium thiocyanate (9.5 g.) in 75% methyl alcohol (40 c.c.) and of γ -phenylpropyl bromide (20 g.) (Rupe and Buerger, *loc. cit.*; b. p. 128°/28 mm.) in methyl alcohol (100 c.c.) were mixed, kept during 3 days at room temperature, then boiled for 1 hr., poured into water, and extracted with ether; the residue was distilled in a vacuum; yield, quantitative; b. p. 180°/30 mm. (Found: N, 7.6. $C_{10}H_{11}NS$ requires N, 7.9%). The *thiocyanate* has an intensely vesicant effect.

(b) Cinnamyl thiocyanate (III) (3 g.) in boiling propyl alcohol (35 c.c.) was treated with hydrogen for 2 hrs. in presence of palladised barium sulphate. The filtered solution, which had become extremely irritating, was evaporated. The oily residue was triturated with ice-cold methyl alcohol, leaving undissolved initial material; from the filtrate, nearly 2 g. of γ -phenylpropyl thiocyanate were obtained, b. p. 180°/30 mm.

Cinnamyl isoThiocyanate (V).—The thiocyanate (4.5 g.) was heated under reflux in a vacuum for 1 hr., and the product distilled, affording 2.5 g. of a yellow oil, b. p. 162°/12 mm. (Found: C, 68.0; H, 5.1; N, 7.6. $C_{10}H_9NS$ requires C, 68.6; H, 5.1; N, 8.0%).

s-Phenylcinnamylthiourea (VIII).—Aniline (1 g.) and cinnamyl *isothiocyanate* (1 g.) were mixed in ethereal solution. On addition of alcohol, crystallisation set in; recrystallisation from ethyl acetate–ligroin afforded 0.7 g. of the thiourea, m. p. 119°, identical with that prepared from phenyl *isothiocyanate* and cinnamylamine (Posner, *Ber.*, 1893, **26**, 1860).

Phthalo- γ -phenylpropylimide (X).—(a) Potassium phthalimide (18.5 g.) and γ -phenylpropyl bromide (20 g.) were heated at 150° for 6 hrs. The mass, which smelled strongly of β -phenylpropaldehyde, was triturated with dilute potash solution, sucked dry, and treated with water and ether. The residue crystallised immediately and was recrystallised from methyl alcohol containing a little acetone; prismatic crystals, m. p. 61°; yield, 12 g. (Found: N, 5.6, 5.5. $C_{17}H_{15}O_2N$ requires N, 5.6%).

(b) Phthalocinnamylimide (XI) (3 g.) was hydrogenated as above, and the filtered solution evaporated; the remaining oil crystallised after 2 days, and on recrystallisation from methyl alcohol afforded prisms (2.5 g.), m. p. and mixed m. p. with product from (a) 61°. The substance (XI) was prepared (Posner, *loc. cit.*) by heating potassium phthalimide (18.5 g.) and cinnamyl chloride (15.2 g.) at 160° for 4 hours; recrystallised from propyl alcohol, it formed needles (6 g.), m. p. 156°.

Some of the above work was carried out in the laboratory of the Friedrich Wilhelm University, Berlin, in collaboration with H. Corte.