95% ethyl alcohol, and 5 ml of water was refluxed for 0.5 hr. The solution was cooled, diluted with water, and acidified with dilute hydrochloric acid. The resulting yellow precipitate, upon recrystallization from petroleum ether (bp 66–75°), yielded 0.4 g of 2-pyrrolethiocarbanilide (**3**), mp 94.5–95.5°, identified by its infrared spectrum and by mixture melting point with an authentic sample of **3**.

Oxidation of 2-phenylpyrrolo[1,2-*c*]-1-thiohydantoin (4) to 2-phenylpyrrolo[1,2-*c*]hydantoin (5).—To 1 g of **4** and 1 g of sodium acetate trihydrate in 10 ml of acetic acid,[11] 2 ml of hydrogen peroxide (30%) was added, and the mixture was stirred for 24 hr. After addition of another 2 ml of hydrogen peroxide (30%), stirring was continued for a further 42 hr. The mixture was then diluted with 100 ml of water and filtered. The precipitate, washed with water and dried (0.7 g), had an infrared spectrum identical with that of **5** and, after recrystallization from 95% ethyl alcohol, melted at 225–226°. The melting point was not depressed by mixing with an authentic sample of **5**.

2-Phenylpyrrolo[1,2-*c*]-3-thiohydantoin (6).—To a solution of 6.1 g (0.03 mole) of 1-pyrrolethiocarbanilide (**1**) in 20 ml of tetrahydrofuran 2.5 g of a 56% sodium hydride dispersion in mineral oil (0.06 mole NaH) was added, and the mixture was stirred until evolution of hydrogen had stopped. After dilution with 150 ml of cyclohexane, a solution of 4 g of phosgene in 50 ml of cyclohexane was added dropwise, and the resulting mixture was stirred at room temperature for 21 hr, and at reflux for a further 2 hr. Filtration of the product yielded a yellow solution to which were added ether washings of the precipitate. When this solution was cooled and filtered, 2 g of **6**, yellow crystals, mp 144–144.5°, was obtained. Evaporation of the filtrate to dryness under reduced pressure and recrystallization of the residue from 95% ethyl alcohol gave a further 2.4 g of **6**, mp 143–144° (total yield 65%). An analytical sample melted at 144–144.5°.

Anal. Calcd for $C_{12}H_8N_2OS$: C, 63.16; H, 3.53; N, 12.28; S, 14.02. Found: C, 62.99; H, 3.57; N, 12.37; S, 13.90.

Oxidation of 2-Phenylpyrrolo[1,2-*c*]-3-thiohydantoin (6) to 2-Phenylpyrrolo[1,2-*c*]hydantoin (5).—The reaction was carried out exactly as previously described for the conversion of **4** to **5**. The product was 0.8 g of crude **5**, identified by its infrared spectrum. After recrystallization from 95% ethyl alcohol the melting point was 225–227°, undepressed on admixture with authentic **5**.

2-Phenylpyrrolo[1,2-*c*]dithiohydantoin (7).—A mixture of 4.0 g (0.02 mole) of **1**, 1.7 g of a 56% sodium hydride dispersion in mineral oil (0.04 mole NaH), and 20 ml of tetrahydrofuran was stirred until evolution of hydrogen had stopped. After addition of 130 ml of cyclohexane, followed by dropwise introduction of a solution of 2.3 g (0.02 mole) of thiophosgene in 50 ml of cyclohexane, the reaction mixture was stirred at room temperature for 3 hr, and at reflux for a further 3 hr. It was then cooled and filtered, and the residue was washed with ethyl ether. Removal of the solvents under reduced pressure from the combined filtrate and ether washings and crystallization of the residue from petroleum ether (bp 66–75°) produced 2.0 g of dark purple crystals, mp 127–131°. Recrystallization from methyl alcohol raised the melting point to 133.5–134.5° (1.2 g, 24%). An analytical sample melted at 134–134.5°.

Anal. Calcd for $C_{12}H_8N_2S_2$: C, 59.02; H, 3.30; N, 11.47; S, 26.21. Found: C, 58.73; H, 3.42; N, 11.81; S, 26.10.

Compound **7** was also obtained as follows.

A. **From 2-Phenylpyrrolo[1,2-*c*]hydantoin (5).**—A mixture of 1 g of **5**, 4 g of phosphorus pentasulfide, and 30 ml of xylene[16] was refluxed for 36 hr. Filtration and evaporation of the filtrate to dryness under reduced pressure produced a residue which was refluxed with 100 ml of petroleum ether (bp 66–75°) for 10 min. A new filtration, followed by cooling of the solution, yielded 0.5 g of dark purple crystals, mp 132.5–133.5°, the infrared spectrum of which was identical with that of the product of the immediately preceding reaction. After recrystallization from methanol, the melting point was 133.5–134.5°, undepressed on admixture with **7** prepared by the previous reaction.

B. **From 2-Phenylpyrrolo[1,2-*c*]-1-thiohydantoin (4).**—The reaction was run as described immediately before, except that 2 g of phosphorus pentasulfide, and a 22-hr refluxing period were used. The product was 0.4 g of **7**, mp 133–134°.

C. **From 2-Phenylpyrrolo[1,2-*c*]-3-thiohydantoin (6).**—A mixture of 1 g of **6**, 1 g of phosphorus pentasulfide, and 30 ml of dioxane[15] was refluxed for 5 hr. The same treatment as before led to 0.6 g of **7**, mp 133–134°.

Oxidation of 2-Phenylpyrrolo[1,2-*c*]dithiohydantoin (7) to 2-Phenylpyrrolo[1,2-*c*]hydantoin (5).—The reaction was run exactly as described for the conversion of **4** to **5**. The product was 0.5 g of crude **5** identified by its infrared spectrum. Upon recrystallization from 95% ethyl alcohol, the melting point became 225–227°, and was not depressed on admixture with authentic **5**.

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On the Mechanism of the Synthesis of Phenylcyclopropanes from Allylic Chlorides and Phenyllithium

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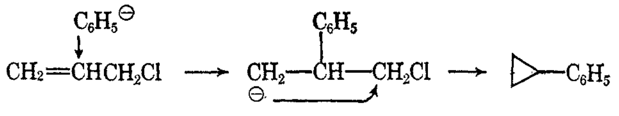
Wawzonek, Studnicka, Bluhm, and Kallio[1] have recently reported that allyl chloride reacts with phenyllithium in ether to give some phenylcyclopropane, and that some γ-substituted allyl chlorides give substituted phenylcyclopropanes. They suggested a mechanism involving β attack by a phenyl anion as shown below.



While the mechanism provides an economical interpretation of the available facts, it is sufficiently novel that critical tests of it seem in order.

A mechanism with a cyclopropene intermediate is suggested by the known formation of cyclopropenes from allylic chlorides and strong bases.[2] In this mechanism, addition of phenyllithium would have to compete with the known proton abstraction reaction of cyclopropenes,[2a] but the particularly large strain of a cyclopropene with no substituents on the double bond[3] might provide sufficient driving force to enable the addition to compete.

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[1] S. Wawzonek, B. Studnicka, H. J. Bluhm, and R. E. Kallio, *J. Am. Chem. Soc.*, **87**, 2069 (1965).

[2] (a) G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963); (b) F. Fisher and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965); (c) G. L. Closs and K. D. Krantz, *ibid.*, **31**, 638 (1966).

[3] (a) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962); (b) R. Turner, Abstracts of Papers, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p 41-O.

The two mechanism shown above have been distinguished by use of deuterium oxide to quench the reaction mixture. The ratio of phenylcyclopropane to other products (measured by glpc) was 9:91, regardless of whether the deuterium oxide was added immediately after mixing the reactants or after the reaction mixture had been held for 2 hr under reflux. The phenylcyclopropane contained no detectable deuterium, in spite of the known stabilities of cyclopropyllithiums in ether.[4] The cyclopropene mechanism is thus virtually ruled out, and the Wawzonek mechanism or some variant of it remains the simplest interpretation of the facts. One modification of this mechanism which might improve it would be to eliminate the intermediate carbanion (*i.e.*, to make the reaction one concerted process). It is not obvious that there should be simple addition to the double bond in the sense observed, since phenyllithium does not add to simple olfins.[5] The higher yields of cyclopropanes when γ-alkyl substituents are present[1] are also in the wrong direction with respect to the expected relative stabilities[6] of the intermediate carbanions proposed by Wawzonek.

Another mechanism which cannot be ruled out is heterolytic dissociation of the allylic chloride followed by reaction of the allylic cation at the 2 position with phenyllithium. The reaction path lacks good precedent, but could be regarded as the mechanistic reverse of the formation of allylic cations from cyclopropyl halides.

Experimental Section[7]

Reaction of Allyl Chloride with Phenyllithium.—To a stirred solution of 100 ml of 1.2 *M* (0.12 mole) phenyllithium in 70:30 benzene–ether was added dropwise, over a 10-min period, 7.65 g (0.10 mole) of allyl chloride. The reaction temperature was maintained at 20–25° by use of an ice bath. Immediately after the addition, 10 ml of deuterium oxide (99.5%) was added cautiously. The mixture was poured into water, and then extracted with ether. The organic phase was dried over sodium sulfate, filtered, and concentrated. Phenylcyclopropane was collected by preparative glpc on a 10-ft column of 20% Apiezon L on Anakrom ABS at 155°, flow rate 100 ml/min. Analytical glpc on a 10-ft 10% Apiezon L column at 150° and 80 ml/min showed major peaks at 2.7, 4.15, and 7.8 min, the last being phenylcyclopropane. The relative peak areas were 1.84:8.54:1.00, respectively. In a similar run, the reaction mixture was heated under reflux for 2 hr before addition of deuterium oxide, and in this case, the peak areas observed were 1.83:8.49:1.00. The phenylcyclopropane peak was established by the identity of the infrared spectrum with that of an authentic sample[8] and by the identity of the nmr (carbon tetrachloride) spectrum with the published spectrum.[9] There was no absorption in the infrared from 1950 to 2800 cm^{-1} to show any deuterium incorporation, and a falling-drop deuterium analysis also showed no deuterium in the sample from immediate deuterium oxide work-up.

Acknowledgment.—The authors are indebted to the National Science Foundation for support of this work, and to Professor Wawzonek for details of his experimental procedure.

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The Acylation of Cycloheptene[1]

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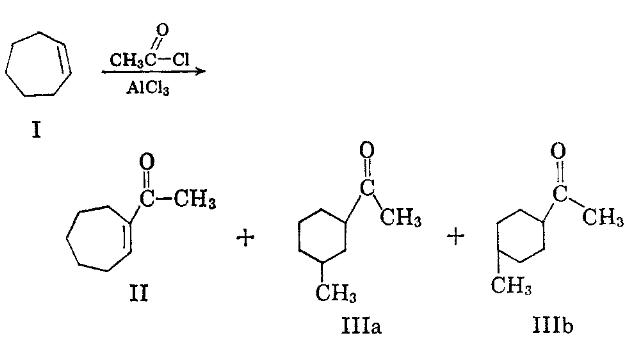
The aluminum chloride catalyzed acylation of cycloheptene (I) has been shown[2-6] to produce a variety of products depending upon the reaction conditions. At 10°, acetylation with acetyl chloride in methylene chloride gave[4] 1-acetylcycloheptene (II), while at reflux temperatures in cyclohexane or isopentane, Friess and Pinson[5] and Nenitzescu and his co-workers[6] obtained 3- and 4-methylacetylcyclohexane (IIIa,b). It was suggested[6] that the saturation of the rearranged products was the consequence of an intermolecular hydrogen transfer from the solvent.



In the course of attempting to synthesize II using polyphosphoric acid (PPA),[7] it was surprising to find, instead, the products shown in Table I. Although the ketones, 2-methyl-1-acetylcyclohexene (IV) and 2-methyl-3-acetylcyclohexene (V) represent rearrangement of the cycloheptyl ring skeleton, they do not correspond to the rearranged products obtained by the aluminum chloride catalyzed reaction. The ester VI and hydrocarbon VII were produced without a skeletal rearrangement.

The formation of these products can be visualized as arising from several carbonium ion processes. Electrophilic attack on the olefin by the acylium ion, from the reaction of acetic acid with PPA, would give rise to the intermediate ion, IIa. Rearrangement to the tertiary ion involving a 1,2-hydride ion shift[8] and elimination of proton H_a or H_b would yield the ketonic products IV and V.

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[1] (a) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. (b) Taken in part from a dissertation submitted by R. J. Dolinski to the University of Detroit Graduate School in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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