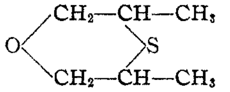
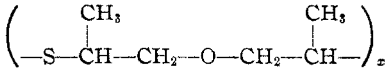
sulfide to react with olefins in the presence of amines,[3] under which conditions an ionic "normal" addition occurs. In studies of the base-catalyzed reaction of hydrogen sulfide with diolefinic substances, we have observed the formation not only of oily, apparently essentially linear, adducts, but also of cyclic molecules. The yields are comparatively high and undoubtedly could be improved. Thus, from diallyl ether and hydrogen sulfide in the presence of di-*n*-butylamine, was obtained a 43% yield of 2,6-dimethyl-1,4-thioxane



as well as a linear polymer of the structure



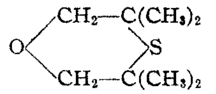
$$\left(-S-\overset{CH_3}{\overset{|}{CH}}-CH_2-O-CH_2-\overset{CH_3}{\overset{|}{CH}}-\right)_x$$

which is terminated either with allyl or mercapto groups or both. The relative amounts of the two products, as well as the magnitude of x in the second formula, can be varied by the operating conditions. Three illustrative examples are given in the following paragraphs.

2,6-Dimethyl-1,4-thioxane.—Diallyl ether (73.6 g., 0.75 mole), hydrogen sulfide (30 g., 0.88 mole) and di-*n*-butylamine (10 g., 0.078 mole) were heated together at 100° for eighty-nine hours in a 200-cc. 18-8 stainless steel bomb. By distillation the product was shown to contain 43% by weight of a water-white liquid boiling at 113–114° at 160 mm. pressure; $n^{20}D$ 1.4850. Analyses indicate that this liquid is 2,6-dimethyl-1,4-thioxane

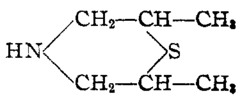
	Found	Calculated
S, %w	23.5, 23.6	23.3
SH, as S, %w	<0.01	0
Mol. wt. (cryo-benzene)	147	132
Mol. wt. (cryo-dioxane)	120	

2,2,6,6-Tetramethyl-1,4-thioxane.–Dimethallyl ether (94 g., 0.75 mole), hydrogen sulfide (30 g., 0.88 mole) and *n*-butylamine (3.6 g., 0.05 mole) were heated together in a stainless steel bomb for twenty-three hours at 110°. The product upon distillation yielded 22% of a colorless liquid: b. p. 130–132° at 190 mm., $n^{20}D$ 1.4748. This liquid appears to be 2,2,6,6-tetramethyl-1,4-thioxane



	Found	Calculated
S, %w	19.7	20.2
SH, as S, %w	0.29	0
Mol. wt., (cryo-benzene)	150	158

2,6-Dimethyl-1,4-thiazane.—Diallylamine (14.6 g., 0.15 mole) and hydrogen sulfide (5.1 g., 0.15 mole) were heated in a Pyrex bomb tube for thirty hours at 100°. Upon distillation 49% of the product boiled between 44 and 62°, mainly at 60°, at 0.2–0.5 mm.; $n^{20}D$ 1.5882. Analyses of this fraction indicate that it is 2,6-dimethyl-1,4-thiazane



	Found	Calculated
S, %w	24.5	24.4
SH, as S, %w	0.14	0
Mol. wt. (cryo-benzene)	129	131
N, %w (Dumas)	10.4	10.7

This synthesis is undoubtedly applicable to the formation of other heterocyclic rings such as 2,4-dimethyl-1,3-oxathiolane from allyl vinyl ether and 2,6-dimethyl-1,4-dithiane from diallyl sulfide. Davis and Fettes[4] have recently reported the production of related heterocyclics by treating dichloro compounds with sodium disulfide.

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(3) German Patent 669,961, to I. G. Farben.; also Keyssner, U. S. Patent 2,163,176 (June 20, 1939).

(4) Davis and Fettes, THIS JOURNAL, **70**, 2611 (1948).

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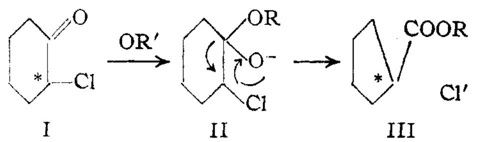
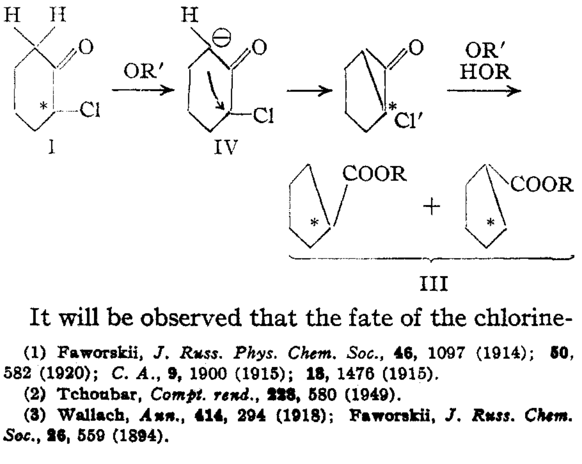
ON THE MECHANISM OF THE FAWORSKII[1] REARRANGEMENT OF α-HALO KETONES

Sir:

There has been considerable effort to establish the mechanism of the base-catalyzed rearrangement of α-halo ketones. The mechanism which has received most support is one closely related to that of the benzilic acid rearrangement[2]



An alternative involves a cyclopropanone intermediate[3]



It will be observed that the fate of the chlorine-

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(1) Faworskii, *J. Russ. Phys. Chem. Soc.*, **46**, 1097 (1914); **50**, 582 (1920); *C. A.*, **9**, 1900 (1915); **18**, 1476 (1915).

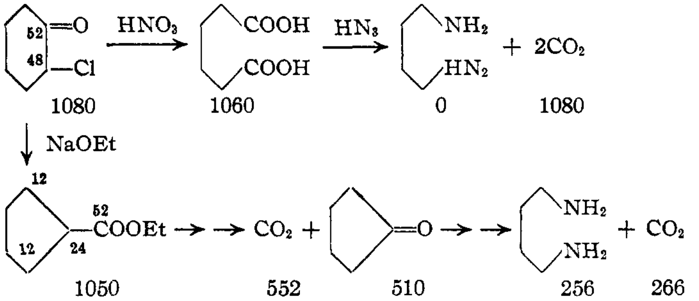
(2) Tchoubar, *Compt. rend.*, **228**, 580 (1949).

(3) Wallach, *Ann.*, **414**, 294 (1918); Faworskii, *J. Russ. Chem. Soc.*, **26**, 559 (1894).

bearing carbon atom of the 2-chloro-1-cyclohexanone I is different depending on the path followed. In the first case it becomes exclusively the α-carbon atom of the cyclopentanecarboxylic acid III; in the second case it appears in both the α- and β-positions of III. Hence it should be possible to select between the two mechanisms using chlorocyclohexanone appropriately tagged with C-14.

Chlorocyclohexanone labeled as shown below was prepared by an unambiguous synthesis. To establish that no chlorine had migrated from the tagged to the untagged α-carbon atom during synthesis, the tagged chlorocyclohexanone was oxidized with nitric acid to adipic acid. The adipic acid was degraded to putrescin and carbon dioxide by the Schmidt reaction. The absence of radioactivity in the putrescin proved that only carbon atoms 1 and 2 of the chlorocyclohexanone were labeled.

The tagged chloroketone reacted with sodium ethoxide in ethanol to yield the ester which was hydrolyzed to cyclopentanecarboxylic acid. The acid was brominated, then hydrolyzed to the corresponding α-hydroxy acid which was oxidized smoothly with potassium permanganate to cyclopentanone and carbon dioxide. The cyclopentanone on successive Schmidt reactions yielded putrescin and carbon dioxide. The figures on the carbon atoms indicate percentages of total radioactivity which are consistent with the radioactivities observed in the degradation products (figures below the formulas are observed counts per minute per one-tenth millimole as barium carbonate).



It is apparent that the present results support strongly the cyclopropanone mechanism or some other mechanism in which carbon atoms 2 and 6 are at some time equivalent. It must be admitted that there is a possibility of the chlorine migrating from the labeled to the unlabeled α-carbon atom of I, perhaps by nucleophilic displacement on chlorine by the carbanion IV. Such migration, proceeding very rapidly compared to the Faworskii rearrangement, would account for our results. Experiments are in progress to check this point.

It is also apparent that the cyclopropanone mechanism cannot be applied to the rearrangement of all α-halo ketones. Thus although 1-benzoyl-1-chlorocyclohexane can give no anion corresponding to IV, it does rearrange slowly to 1-phenylcyclohexane-1-carboxylic acid.[4] However, it seems possible that the rearrangement of α-halo ketones proceeds through the cyclopropanone intermediate whenever possible.

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[4] Tchoubar, *Compt. rend.*, **208**, 1020 (1939).

* Harvard University Ph.D. 1946; Research Fellow 1948–.

REARRANGEMENTS AND REVISIONS IN THE TETRAHYDROCARBAZOLE SERIES

Sir:

Recent mention in the literature[1,2] of 11-hydroxytetrahydrocarbazolenine[3] prompts us to report some results in this field.

It was shown previously[4] that the action of alkali on 9-acetyl-10,11-dihydroxyhexahydrocarbazole (I) does not yield 11-hydroxytetrahydrocarbazolenine (II), but spiro-[cyclopentane-1,2′-pseudoindoxyl] (III). By catalytic oxidation of tetrahydrocarbazole in ethyl acetate over platinum and subsequent gentle hydrogenation[5] we have now prepared authentic II in 75% yield (big, colorless prisms, m. p. 159°. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 77.0; H, 6.95; N, 7.42. Found: C, 77.21; H, 7.08; N, 7.48. Absorption spectra: ultraviolet, $\lambda_{max.}$ (log ϵ): 260 (3.42); $\lambda_{min.}$ (log ϵ): 235 (3.20); infrared, 3.02 μ (OH), 6.25 μ (Ph—N=C<)). II, treated with alkali, undergoes a benzilic acid type of rearrangement to III, and is the intermediate in the conversion of I to III. Either acid, heat or acetic anhydride likewise caused rearrangement to III (yield 85%) evidently by a different route, but in addition two more products were isolated of which one formed colorless plates (m. p. 255° and, after resolidification, 313°. *Anal.* Calcd. for $C_{24}H_{18}N_2$: C, 85.25; H, 6.51; N, 8.3; mol. wt., 338. Found: C, 85.15; H, 6.89; N, 8.40; mol. wt. (Rast), 325). We have found II and the colorless high melting product to be identical, respectively, with the "10-hydroxy-1,2,3,10-tetrahydrocarbazole" and the "2,3-dihydrocarbazole" previously reported.[6]

I, because of the N-acetyl group, with acetic anhydride shows a Wagner–Meerwein shift to give V (formerly thought to be IV[3]) which, after deacetylation and nitration, can be methylated to yield VII.[3] We have synthesized VI by condensing N-methyloxindole with tetramethylene bromide (colorless hexagons, m. p. 63°. *Anal.* Calcd. for $C_{13}H_{15}ON$: C, 77.61; H, 7.96. Found:

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[1] Beer, McGrath, Robertson and Woodier, *Nature*, **164**, 362 (1949).

[2] Barnes, Pausacker and Schubert, *J. Chem. Soc.*, 1381 (1949).

[3] Perkin and Plant, *ibid.*, **123**, 688 (1923).

[4] Witkop, THIS JOURNAL, **71**, 614 (1950).

[5] The method has been previously employed with natural products containing the indole system (Witkop, to be published).

[6] Plant and Tomlinson, *J. Chem. Soc.*, 298 (1933).