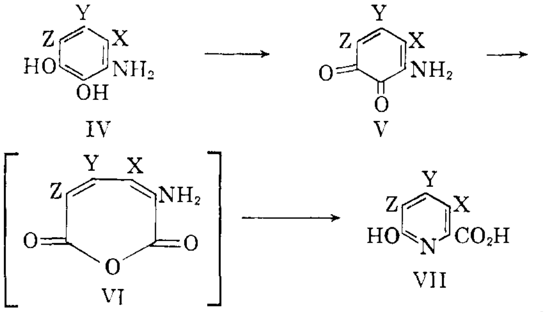
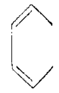
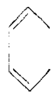
strong ultraviolet light hydrolysis of each anhydride (VI) brings about isomerization to a hydroxypicolinic or an isocarbostyrilcarboxylic acid (VII). Percentage yields for the transformations of IV to VII are: a, 16; b, 11; c, 16; d, 65; e, 31.



a, $X = Y = Z = H$ d, $X = H$, XZ = 

b, $X = CO_2H$, $Y = Z = H$

c, $X = NH_2$, $Y = CH_3$, $Z = H$

e, $X = C_6H_5NH$, YZ = 

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[12] This investigation was carried out during the tenure of a Predoctoral Fellowship from the National Heart Institute, United States Public Health Service, 1959–1960.

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CHEMISTRY OF THE METAL CARBONYLS. V. THE DESULFURIZATION OF THIOPHENE[1]

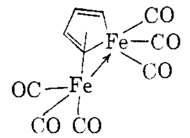
Sir:

At elevated temperatures, thiophene and iron carbonyls undergo a novel reaction resulting in removal of the sulfur atom from the thiophene ring and its substitution by the iron atom of an iron tricarbonyl group.

A 250-ml. flask was fitted with a Soxhlet extractor and a reflux condenser to the top of which was attached a tube for the introduction of prepurified nitrogen. After the apparatus had been flushed with nitrogen, a 150 ml. (1.9 moles) sample of thiophene, in which no impurities could be detected by vapor phase chromatography, was placed in the flask and a 10 g. (20 mmoles) sample of triiron dodecacarbonyl was placed in the thimble of the Soxhlet. The flask and its contents were heated for 15 hr., during which time the iron carbonyl was extracted continuously. Black solid formed in the flask and the green color due to triiron dodecacarbonyl eventually disappeared. After the flask and its contents cooled to room temperature, filtration afforded a pale red or orange filtrate, from which excess of thiophene was removed (25°, 15 mm.) leaving an orange solid and a red oil. The residue was dissolved in 10 ml. of pentane and chromatographed on a 2 × 50 cm. column of Merck alumina, thereby giving a yellow band preceded by a small red band. Elution with pentane and removal of solvent afforded a trace of a red oil from the first eluate and an orange solid from the later eluate. The orange solid (450 mg., 5% yield) obtained (m.p. 52–54°), as well as that formed in a repeat experiment, was found to have the composition $C_{10}H_4O_6Fe_2$.

Anal. Calcd. for $C_{10}H_4O_6Fe_2$: C, 36.1; H, 1.2; Fe, 33.7; S, 0.00; mol. wt., 332. Found: C, 36.2, 35.6; H, 1.3, 1.4; Fe, 32.9, 33.1; S, 0.00, 0.00; mol. wt., 348 (determined from vapor pressure of a dichloromethane solution).

The orange solid, pale red when impure, shows carbonyl bands in its infrared spectrum (tetrachloroethylene solution, Perkin Elmer Model 21 spectrophotometer fitted with CaF_2 prism) at 2079 (s), 2042 (vs), 2006 (vs.), 1998 (vs) and 1962 (vw) cm^{-1}. Since it has been reported[2] that under certain conditions acetylene and iron carbonyls react to give an orange solid (m.p. 54–55°,[2a] 53°[2b]) of composition $C_{10}H_4O_6Fe_2$, it seemed possible that this compound, which has been assigned[2a,b] structure (I), was identical with the compound formed from thiophene and iron carbonyls. Accordingly, the preparation of I from acetylene



I

was repeated by the method described elsewhere.[2a] The orange solid thus obtained had an infrared spectrum (3500–800 cm.$^{-1}$) exactly coincident with that of the orange solid obtained from thiophene and iron carbonyls; the identity of the two solids also was shown by the identity of their individual and mixed melting points.

In our hands the reaction between thiophene and iron pentacarbonyl or triiron dodecacarbonyl carried out in a flask without use of a Soxhlet gave products similar to those described above, but in poorer yield. Solid black residues from the reactions afforded hydrogen sulfide on treatment with dilute hydrochloric acid. The red oil mentioned above and formed in very small amounts appears to be a mixture worthy of further investigation. One component, sulfur and iron containing, shows in its infrared spectrum (tetrachloroethylene solution, CaF_2 prism) carbonyl bands at 2072 (s), 2035 (vs), 2000 (vs), 1989 (vs) and 1956 (vw) cm.$^{-1}$. This infrared band pattern in the carbonyl region also is shown by products obtained from reactions, at present under study, between a number of organosulfur compounds and iron carbonyls.

Formation of I from an iron carbonyl and thiophene may not be unrelated to the mechanism of certain metal-desulfurization processes in organic chemistry. Moreover, the reaction described here suggests that derivatives of thiophene might function as intermediates for the synthesis of new heterocyclic iron compounds having covalent iron-iron bonds. It is of further interest to note that

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[1] Previous article in this series, R. B. King and F. G. A. Stone, THIS JOURNAL, **82**, 4557 (1960).

[2] (a) W. Hübel and E. Weiss, *Chemistry and Industry*, 703 (1959); (b) W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); (c) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 989 (1960).

previous workers[3] have claimed that thiophene and iron pentacarbonyl afford the π-complex thiophene-iron dicarbonyl, described as a pale red solid with a melting point of 51° and characterized by carbon, hydrogen and oxygen analysis. However, although the literature describes numerous well authenticated π-complexes involving iron tricarbonyl groups, similar complexes of iron dicarbonyl groups are rare.

(3) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chemistry and Industry*, 1592 (1958).

(4) Department of Chemistry, University of California, Los Angeles.

(5) National Science Foundation predoctoral fellow, 1958–61.

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EVIDENCE FOR CYCLOPENTYNE AS A REACTION INTERMEDIATE IN THE COUPLING OF PHENYLLITHIUM WITH 1-CHLOROCYCLOPENTENE[1]

Sir:

Evidence has been presented previously for the intervention of benzyne[2,3] and cyclohexyne[4] as intermediates in nucleophilic substitution reactions of phenyl and cyclohexenyl halides, respectively. In studies designed to determine the minimum ring size for operation of the elimination–addition mechanism, we have now found that an entity with the symmetry properties of *cyclopentyne* must be involved in the formation of 1-phenylcyclopentene from 1-chlorocyclopentene-1-^{14}C and phenyllithium. The occurrence of cyclopentyne as a reaction intermediate was suggested some time ago. Favorskii proposed that tris-trimethylenebenzene, formed by the action of sodium in ether on 1,2-dibromocyclopentane, arose from the trimerization of cyclopentyne.[5] Very recently Wittig[6] appears to have trapped cyclopentyne as a Diels–Alder adduct in a similar reaction.

The general plan of attack was similar to that employed previously[4] with 1-chlorocyclohexene-2-^{14}C, except that the degradation scheme and controls were more nearly complete.

Our starting material was adipic-16-$^{14}C_2$ acid.[7] The preparation of 1-phenylcyclopentene-*x*-^{14}C from this material as well as the degradative schemes and ^{14}C analyses for 1-phenylcyclopentene-*x*-^{14}C and 1-chlorocyclopentene-1-^{14}C are summarized in Fig. 1. Clearly, the reaction of phenyllithium with 1-chlorocyclopentene-1-^{14}C proceeds with rearrangement, and the extent of formation of 1-phenylcyclopentene-1-^{14}C is almost exactly that which would be expected for cyclopentyne (I) as an intermediate. The 14.9% of 1-phenylcyclopentene-5-^{14}C formed in the reaction most probably arises from a phenyllithium-induced allylic rearrangement of the double bond of the first-formed 1-phenylcyclopentene-2-^{14}C (III). The starting chloride, 1-chlorocyclopentene-1-^{14}C, had 97.3% of the ^{14}C in the 1-position.

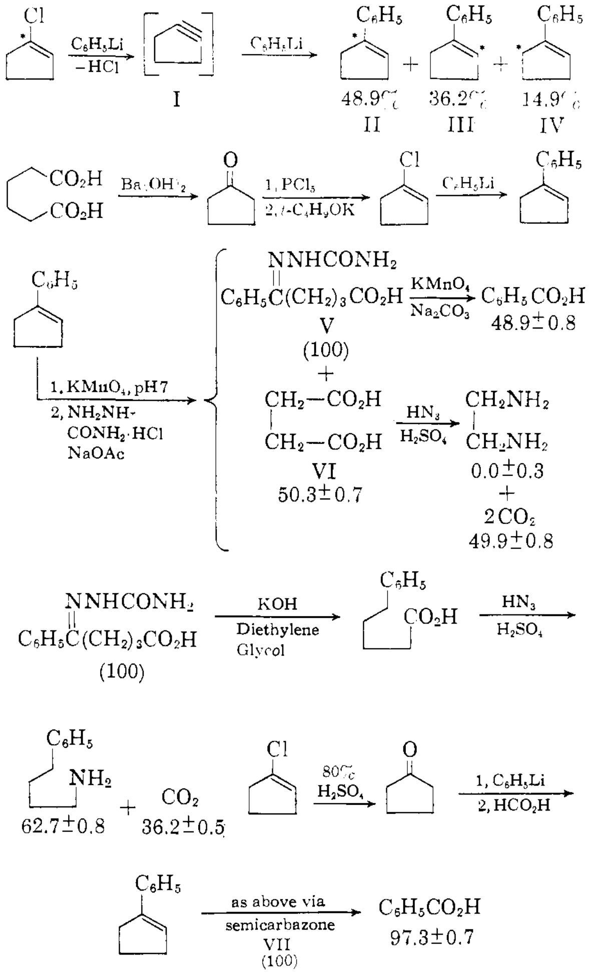

Fig. 1.—Degradative schemes for 1-phenylcyclopentene-*x*-^{14}C and 1-chlorocyclopentene-1-^{14}C. Specific activities for key compounds: 5-phenyl-5-oxopentanoic-*x*-^{14}C acid semicarbazone (V), 2.331 ± 0.002 μc./mmole; succinic-*x*-^{14}C acid, diluted (VI), 0.470 ± 0.002 μc./mmole; 5-phenyl-5-oxopentanoic-5-^{14}C acid semicarbazone, diluted (VII), 1.150 ± 0.004 μc./mmole. The figures under the formulas represent the found percentages of ^{14}C content relative to the corresponding key compounds from which they were derived.

Our attempts to extend this type of study to halides with still smaller rings so far have been unsuccessful. 1-Bromocyclobutene does indeed react with phenyllithium, but the only reaction products that have been isolated are phenylacetylene and cyclobutene. The mechanism of the unusual fragmentation reaction that affords phenylacetylene is not yet known. Efforts to induce substitution by way of the elimination-addition

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(1) Supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the Donors of this Fund.

(2) (a) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, THIS JOURNAL, **75**, 3290 (1953); (b) J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenow, *ibid.*, **78**, 601 (1956); (c) E. F. Jenny and J. D. Roberts, *Helv. chim. acta*, **38**, 1248 (1955).

(3) *Cf.* the recent review of R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(4) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **1**, 343 (1957).

(5) A. E. Favorskii, *J. Gen. Chem.* (*U. S. S. R.*), **6**, 720 (1936).

(6) G. Wittig, A. Krebs and R. Pohlke, *Angew. Chem.*, **72**, 324 (1960).

(7) Supplied by Merck and Company, Limited.