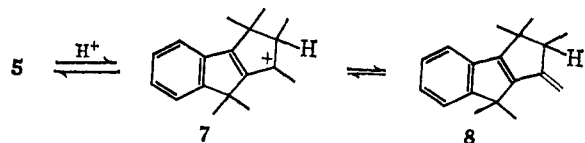
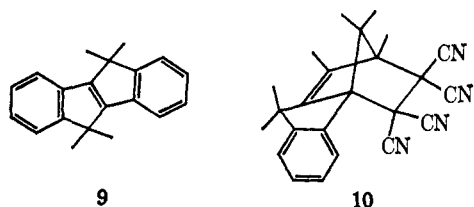


of **5** should be **7** (which can exchange *via* **8**), this experiment supports the illustrated nmr assignment for the allylic methyls in **5**.¹¹ Comparison of **5** with **9**, in

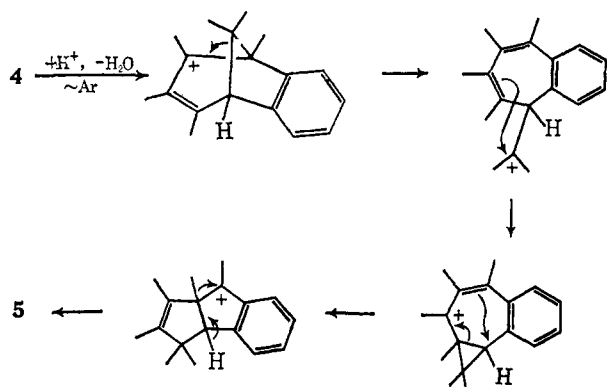


which the *gem*-dimethyls appear at τ 8.53,¹³ supports the remainder of the nmr assignment.¹¹ Finally, **5** gave a crystalline adduct with TCNE, mp 192–193°, assigned structure **10**,⁶ and similar adducts with other dienophiles.



It is believed that **5** arises from the major epimer of **4**, and a plausible (abbreviated) mechanism is shown in Scheme I. This and other possible mechanisms are

Scheme I



being tested; the scope of the rearrangement and the chemistry of the products are being investigated.¹⁴

(13) J. E. H. Hancock and D. L. Pavia, *J. Org. Chem.*, **26**, 4350 (1961).

(14) We are indebted to the National Science Foundation for financial support of this work.

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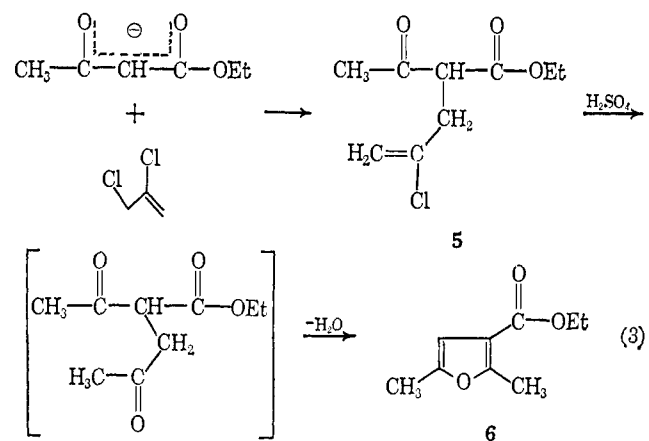
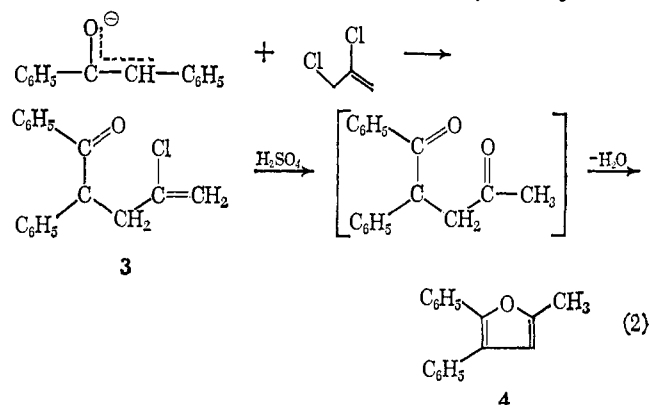
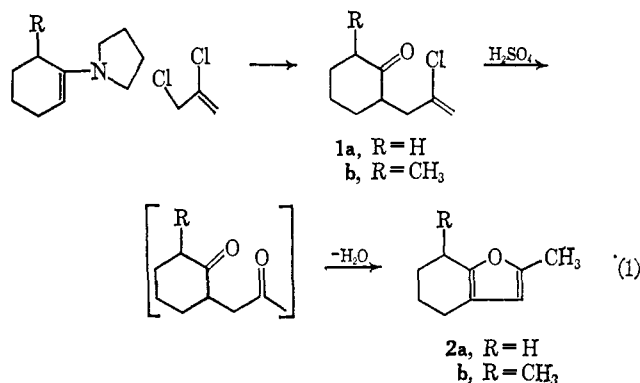
A Convenient Synthesis of Substituted Furans

Sir:

In a previous communication¹ we reported initial examples of a simple synthetic sequence leading to cyclic ketones of varying ring size. The reported synthesis utilized the β -chloroallyl group which acted both as a nucleophile and as a "masked" ketone. We have further investigated the chemistry of the β -chloroallyl group when placed in a position α to a carbonyl group and now wish to report initial examples of a con-

(1) P. T. Lansbury and E. J. Nienhouse, *J. Am. Chem. Soc.*, **88**, 4290 (1966).

venient synthesis of substituted furans. The synthesis is illustrated below in several examples² wherein enolate ions are alkylated and the resulting β -chloroallyl ketone is subjected to sulfuric acid hydrolysis. The resulting 1,4-dicarbonyl compound (not isolated) undergoes subsequent sulfuric acid dehydration analogous to the Paal-Knoor³ synthesis of oxygen, nitrogen, and sulfur heterocycles.



The "one-pot" hydrolysis-dehydration of **1a** proceeded in *ca.* 80% yield to the known⁴ 2-methyltetrahydro-4,5,6,7-benzofuran (**2a**), identified as its maleic anhydride adduct. In like manner, **1b** proceeded in excellent yield to 2,7-dimethyltetrahydro-4,5,6,7-benzofuran (**2b**). Sequence I thus suggests a potential route to elusive substituted benzofurans by aromatization of the tetrahydro-4,5,6,7-benzofuran system. In addition,

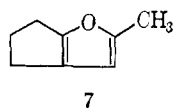
(2) All new compounds gave satisfactory elemental analysis and were further characterized by spectroscopic methods. The furans, in particular, were further characterized by their ability to form crystalline maleic anhydride adducts.

(3) (a) L. Knoor, *Ber.*, **18**, 299 (1885); (b) C. Paal, *ibid.*, **18**, 367 (1885).

(4) T. Monel and P. E. Verkade, *Rec. Trav. Chim.*, **70**, 3549 (1951).

the facile conversion of 2-methylcyclohexanone to **2b** is interesting in light of the recent observation⁵ that menthofuran, 3,6-dimethyltetrahydro-4,5,6,7-benzofuran, possesses certain physiological action on fruit flies and other insects. Hydrolysis-dehydration of α -(β -chloroallyl)deoxybenzoin¹ (**3**) in sulfuric acid gave 84% 2,3-diphenyl-5-methylfuran (**4**). The β -chloroallyl derivative of ethyl acetoacetate gave, on reaction with sulfuric acid, 2,5-dimethyl-3-carbomethoxyfuran (**6**). Sequence 3 suggests a potential route to a variety of substituted furans whose derivatives serve as excellent chemotherapeutic substances for the cure of infectious diseases in urology.⁶

2-(2-Chloroallyl)cyclopentanone, however, failed to yield the desired furan **7**. Instead, the 1,4-diketone was isolated from the reaction mixture. Presumably



furan formation is hindered by virtue of the increased angle strain which would be present in the fused five-membered ring system **7**. This observation suggests a potential route to substituted bicyclo[3.3.0]octane derivatives by a ring-forming sequence comparable to the well-known Wichterle⁷ annelation scheme.

A typical experimental procedure for the preparation of 2-methyltetrahydro-4,5,6,7-benzofuran (**2a**) is described below. A solution of 30.2 g (0.2 mole) of N-pyrrolidine-1-cyclohexene,⁸ 22.2 g (0.2 mole) of 2,3-dichloropropene, and 100 ml of dry dioxane was heated to reflux and stirred for 22 hr. Dilute hydrochloric acid (2 ml in 60 ml of water) was added and reflux was continued for 3 hr. On cooling, the contents of the flask were extracted with ether and the ether extracts were washed successively with brine, bicarbonate, and brine and dried. Distillation of the product after removal of ether afforded 16.6 g of 2-(2-chloroallyl)cyclohexanone, representing a yield of 48%; bp 86° (4.0 mm). Into a 125-ml erlenmeyer flask equipped with a magnetic stirrer was placed 30 ml of 90% v/v sulfuric acid cooled to 0°. A rapid stream of nitrogen was bubbled through the liquid while 12.0 g (0.07 mole) of 2-(2-chloroallyl)cyclohexanone was added over the period of 30 min. After stirring 1 hr at 0°, the mixture was poured into seven volumes of ice water with rapid stirring. The crude reaction product was processed by distillation *in vacuo* after extraction and drying. Distillation afforded 7.85 g (80%) of 2-methyltetrahydro-4,5,6,7-benzofuran (**2a**): $\lambda_{\text{max}}^{\text{film}}$ 3.22, 3.41, 3.50, 6.15, 6.34, 6.78, 6.92, 8.08, 8.23, 10.50, and 12.8 μ ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.62 (C=CH), 2.52 (A₂A₂', -CH₂C=C(O)CH₂-), 2.18 (C=C(O)CH₃), 1.75 (B₂B₂', -CH₂CH₂-); maleic anhydride adduct mp 78–80° (lit.⁴ mp 81–82.5°).

The above examples illustrate how the "masked" ketone of the β -chloroallyl group can be used to synthesize a variety of substituted furans. We hope that further studies, which include the aforementioned potential routes and the introduction of other hetero-

(5) (a) H. G. Daessler, *Pharmazie*, **12**, 87 (1957); (b) H. G. Daessler and G. Dube, *Anz. Schädlingskunde*, **30**, 86 (1957).

(6) M. C. Dood and W. B. Stillman, *J. Pharmacol. Exptl. Therap.*, **11**, 82 (1944).

(7) J. A. Marshall and D. J. Schaeffer, *J. Org. Chem.*, **30**, 3642 (1965), and references cited therein.

(8) J. Szmuskovicz, *Advan. Org. Chem.*, **4**, 98 (1963).

atoms, will serve to demonstrate additional versatility of this convenient synthesis.

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The Incorporation of Molecular Nitrogen into an Organic Molecule

Sir:

In the course of our studies on the preparation of benzenesulfenium ion, C₆H₅S⁺ (I), we have obtained evidence that this species reacts with molecular nitrogen under ordinary conditions. Although the ability of transition metal complexes to fix nitrogen is well documented,¹⁻⁶ I appears to be the first reported organic species to exhibit these properties.

The products of the reaction of I with molecular nitrogen exhibit little stability to conditions that might be used for purification, but several nitrogen-containing materials have been isolated in crude form. In our hands, all attempts at purification have failed. Thus, our evidence for the incorporation of nitrogen is not based on the isolation of a pure, identifiable compound. Rather, we have relied on elemental analyses, high-resolution mass spectrometry, and infrared or ultraviolet spectra to verify the presence of nitrogen. The reactions described for I are not valid for comparable reactions of alkanesulfenium salts. Furthermore, the phenomena described for I are not observed if reactions are carried out in an inert gas atmosphere.

Solutions believed to contain various sulfenium ions have been prepared by the action of sulfuric acid on 2,4-dinitrobenzenesulfonyl chloride,⁷ the reaction of silver perchlorate with the same halide,⁷ and the action of Lewis acids on sulfonyl chlorides.^{8,9} Moreover, sulfenium ions have been postulated as intermediates in disulfide interchanges which occur in biological systems and in acid solution.^{10,11} In our studies, solutions of what is believed to be I were prepared by the reaction of silver 2,4,6-trinitrobenzenesulfonate or perchlorate with benzenesulfonyl bromide.^{12,13}

Benzenesulfonyl bromide (prepared *in situ* from bromine and diphenyl disulfide) in methylene chloride was mixed at room temperature with an equivalent amount of silver 2,4,6-trinitrobenzenesulfonate in nitromethane through which a continuous stream of dry nitrogen was bubbling. Silver bromide and a transient blue color were observed immediately. The silver bromide was

(1) M. E. Vol'Pin and V. B. Shur, *Nature*, **A209**, 1236 (1966).

(2) H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305 (1966).

(3) H. Brintzinger, *ibid.*, **88**, 4307 (1966).

(4) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, **79** (1967).

(5) A. Sacco and M. Rossi, *ibid.*, **316** (1967).

(6) A. Misono, Y. Uchida, T. Saito, and K. M. Song, *ibid.*, **419** (1967).

(7) N. Kharasch, C. M. Buess, and W. King, *J. Am. Chem. Soc.*, **75**, 6035 (1953).

(8) C. M. Buess and N. Kharasch, *ibid.*, **72**, 3529 (1950).

(9) S. N. Nabi and M. A. Khaleque, *J. Chem. Soc.*, 3626 (1965).

(10) R. E. Benesch and R. Benesch, *J. Am. Chem. Soc.*, **80**, 1666 (1958).

(11) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

(12) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).

(13) D. J. Pettitt, Ph.D. Thesis, University of California, Riverside, Calif., 1964.