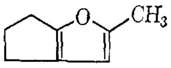
the facile conversion of 2-methylcyclohexanone to **2b** is interesting in light of the recent observation[5] that menthofuran, 3,6-dimethyltetrahydro-4,5,6,7-benzofuran, possesses certain physiological action on fruit flies and other insects. Hydrolysis–dehydration of α-(β-chloroallyl)deoxybenzoin[1] (**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-carbethoxyfuran (**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 Wichterle[7] annelation scheme.



7

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**): $\lambda_{\max}^{\text{film}}$ 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 (A_2A_2', $-CH_2C{=}C(O)CH_2-$), 2.18 ($C{=}C(O)CH_3$), 1.75 (B_2B_2', $-CH_2CH_2-$); 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 heteroatoms, will serve to demonstrate additional versatility of this convenient synthesis.

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Received June 23, 1967

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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, $C_6H_5S^+$ (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-dinitrobenzenesulfenyl chloride,[7] the reaction of silver perchlorate with the same halide,[7] and the action of Lewis acids on sulfenyl 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 benzenesulfenyl bromide.[12,13]

Benzenesulfenyl 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

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removed by filtration under nitrogen, leaving a brown solution, Ia. Selected examples of proof of nitrogen incorporation follow.

Addition of Ia to dry ether yielded a cream solid that could not be redissolved without decomposition. An infrared spectrum of this material in a Nujol mull showed a weak band at 2260 cm^{-1}. When a solution comparable to Ia was prepared under helium, precipitation of the product with ether yielded only a sticky green tar which showed no discernible infrared bands in the 2700–2000-cm^{-1} region, where diazonium groups absorb.

Solution Ia reacted with compounds typically used in diazonium coupling reactions. Resorcinol dimethyl ether yielded a deep red oil with infrared and nmr spectra which were nearly superimposable on those of a red oil prepared from a diazonium salt of *o*-aminobenzenethiol and resorcinol dimethyl ether. The visible spectra differed, however, for the oil from Ia exhibited a maximum at 5400 A, while that from the authentic diazonium salt was at 5100 A.

Solution Ia reacted with azulene to give a black solid that decomposed upon all attempts at purification by crystallization or chromatography. Furthermore, this solid decomposed when heated above 120° with the evolution of quantities of gaseous material. The mass spectrum of the trapped gases consisted of six peaks at m/e 27, 28, 30, 44, 48, and 64, with m/e 28 being the largest. Under high resolution, appreciable quantities of molecular nitrogen were observed at m/e 28.

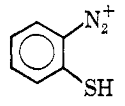
A solution analogous to Ia was prepared at $-78°$ using silver perchlorate in the absence of nitromethane. The deep red methylene chloride solution was allowed to warm slowly in the presence of nitrogen to $-10°$, whereupon the color changed to deep blue. At this point, 1 equiv of resorcinol dimethyl ether was added, and the color of the solution changed to a light purple. After silver bromide was separated, the solution was concentrated *in vacuo*, leaving an oily, purple, ether-soluble residue. The visible spectrum of this oil exhibited a maximum at 5600 A. Elemental analysis was performed after extraction with pentane. *Anal.* Found: C, 56.2; H, 6.2; N, 2.5.

Since the only nitrogen in the system was in the molecular form, we have excluded the possibility that solvents or reactants were sources of incorporated nitrogen.

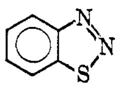
When the same process was carried out in an argon atmosphere the cold reaction mixture was also a deep red, but the "coupling" product was salmon pink. This residue was added to pentane, yielding a white emulsion. On standing overnight, exposed to air, a small amount of purple solid precipitated. The pentane solution yielded a heavy yellow syrup that would not crystallize. *Anal.* Found (for the solid): C, 34.0; H, 3.5; N, 0.6. Found (for the oil): C, 58.2; H, 5.5; N, 0.6. The nitrogen content was not significantly higher than that found in starting materials.

These results indicate that nitrogen is involved in the reaction during the preparation of solutions of I. It appears that the red color, similar to that observed by Kharasch, *et al.*,[7] may be ascribed to the benzenesulfenium ion, while the blue color formed at higher temperatures may represent the first nitrogen-containing intermediate.

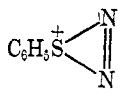
If nitrogen were incorporated into the aromatic ring, a conventional diazonium salt such as II would have formed. However, the visible spectrum of a known diazonium coupling product casts doubt on this possibility. Also, it has been shown[14] that II may easily be converted to a stable thiadiazole, III, but, under conditions in which it should form, it has been undetected in our system.



II



III



IV

$C_6H_5SN_2^+$

V

$(C_6H_5SN{=}NAr)H^+$

VI

The alternative to ring incorporation of nitrogen is bonding directly to sulfur. The most likely alternatives are then the cyclic and linear structures IV and V. The coupling products may then be represented as salts of the type VI.

Further studies are required in order to ascertain the nature of the coupling products and to investigate general applicability of the benzenesulfenium ion in the fixation of nitrogen.

Acknowledgment. This research was supported by Grant GP 5737 from the National Science Foundation.

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A Structurally Selective Method for the Preparation of Certain Diels–Alder Adducts

Sir:

The Diels–Alder reaction[1] is probably the most general method for the synthesis of substituted cyclohexenes. Although characterized by high stereospecificity,[2] its structural selectivity is less pronounced. The combination of unsymmetrically substituted components usually leads to mixtures of structural isomers,[3] a situation causing chagrin in synthetic work, particularly when the minor isomer is the desired product.

We have developed a method which allows the preparation of certain Diels–Alder adducts in a structurally specific manner. Addition of α,β-unsaturated carbonyl compounds to dienes results in γ,δ-unsaturated products (*e.g.*, **3**) which in principle should be available by Claisen rearrangement of allyl vinyl ethers (*e.g.*, **1**). Support for the feasibility of a transition state with the geometry of **2** comes from the observation that the two aldehydes **4** and **5** are in thermal equilibrium.[4] Acrolein dimer[5] was transformed to the olefin **1**[6] by Wittig condensation

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