SYNTHESIS OF 6-((α-thienyl)azulene FROM 2-BUTOXY-4-
(α-thienyl)-Δ³-dihydropyran

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2,5-Dibutoxy-4-(α-thienyl)-Δ³-dihydropyran was obtained by bromoalkoxylation at
the double bond and dehydrobromination of 2-butoxy-4-(α-thienyl)-Δ³-dihydropy-
ran. Acid hydrolysis of the product in the presence of N-methylaniline hydro-
chloride gave a salt of 3-(α-thienyl)glutaconic dialdehyde dianil, treatment of
which with cyclopentadienylsodium in alcohol gives the corresponding fulvene,
which is thermally cleaved to N-methylaniline and 6-(α-thienyl)azulene.

The most convenient method for the synthesis of azulene hydrocarbons is the widely-
known method of synthesis from quaternary pyridinium salts [1], but azulenes with aryl
substituents in the seven-membered ring have not been obtained by this method, apparent-
ly because of the low accessibility of the corresponding substituted pyridines. While
4-aryl- and 4-heteryl-substituted azulenes (4-phenyl, 4-α-naphthyl, and 4-α-thienyl)
are relatively accessible [2], 5-aryl-substituted azulenes are obtained in low yields
by expansion of the benzene ring of indane by arylcarbenes formed during the decomposi-
tion of aryldiazomethanes and subsequent dehydrogenation [3], and 6-arylazulenes cur-
rently remain practically inaccessible compounds. Only 6-phenylazulene, synthesized
by an extremely complex and multistep method from cyclopentane-1,2-dicarboxylic acid
[4], is known.

We propose a new method for the synthesis of 6-aryl-substituted azulenes on the
basis of dihydropyran structures with subsequent conversion of them to salts of aryl-
glutaconic dialdehyde dianils and then to fulvenes, which are thermally cyclizable to
azulenes by the Ziegler–Hafner method; this helps to avoid the dehydrogenation step,
which is basically the chief reason for the extremely low yields. Using this method,
on the basis of 2,6-dibutoxy-4-phenyl-Δ³-dihydropyran [5] we obtained 6-phenylazulene
[6], and in the present research we were able to extend this method to the total synthe-
sis of 6-(α-thienyl)azulene.

2-Butoxy-4-(α-thienyl)-Δ³-dihydropyran (I) was obtained by Diels–Alder condensa-
tion of 2-(α-thienyl)acrolein [7] with vinyl butyl ether. Treatment of I with N-bromo-
succinimide (NBS) in butyl alcohol gives 2,5-dibutoxy-3-bromo-4-(α-thienyl)tetrahydro-
pyran (II), which splits out hydrogen bromide on prolonged heating with alcoholic alkali
to give 2,6-dibutoxy-4-(α-thienyl)-Δ³-dihydropyran (III), which actually is the cyclic
acetal of 3-(α-thienyl)glutaconic dialdehyde.

Acid hydrolysis of 2,6-dibutoxy-4-(α-thienyl)-Δ³-dihydropyran (III) in the presence
of N-methylaniline hydrochloride gave the double salt of 3-(α-thienyl)glutaconic dial-
dehydrol dianil (IV), the structure of which was established on the basis of the results
of elementary analysis and the electronic and IR absorption spectra. Treatment of the
salt with excess cyclopentadienylsodium in absolute ethanol gives 6-[1-N-phenylmethyl-
amino-3-(α-thienyl)-1,3-butadien-4-yl]fulvene (V). Compound V was subjected to pyrolytic cleavage by the method proposed for unsubstituted azulene [1]. Instead of benzidine we selected triethanolamine as the solvent and carried out the pyrolysis with superheated steam at 280°C. It is possible that the relatively low yield of 6-(α-thienyl)azulene (8.5%) is due to the hydrophilic character of triethanolamine, as a consequence of which the poor solubility of fulvene V in it prevents the normal course of the intramolecular cyclization and the formation of the final product.

The structure of the 6-(α-thienyl)azulene obtained was proved by the results of elementary analysis and the electronic absorption spectrum. A mass-spectrometric determination of the molecular weight gave 210, which confirmed the composition of azulene VI.

The electronic spectrum of 6-(α-thienyl)azulene has a chief maximum at 600 nm, which corresponds to a bathochromic shift of 20 nm as compared with the absorption spectrum for unsubstituted azulene. The long-wave absorption band of α-thienylazulene VI is shifted bathochromically by 35 nm and is found at 732 nm. These shifts can be explained by the greater delocalization of the electron density of 6-(α-thienyl)azulene; this is due to the capacity for conjugation of the α-thienyl group with the seven-membered ring of the azulene system, which bears a partial positive charge. Conjugation leads to the formation of a chromophore system in which the partial positive charge is on the thiophene ring, while additional negative charge develops on the five-membered ring of azulene; this is manifested visibly also in the case of 4-(α-thienyl)azulene [2] but to a lesser degree (λmax 597 and 716 nm), inasmuch as the geometrical form of the molecule in this case causes a lower value of the electromagnetic oscillator than for the 6-substituted derivative, in which the electron-donor substituent is most remote from the acceptor — the five-membered ring.

Inasmuch as phenyl groups have a weaker electron-donor capacity, their effect on the electronic spectra of the corresponding substituted azulenes is similar to the effect of α-thienyl groups but is manifested considerably more weakly.

EXPERIMENTAL

2-Butoxy-4-(α-thienyl)-Δ3-dihydropyran (I). A 69-g (0.5 mole) sample of 2-(α-thienyl)acrolein was heated in a glass ampule with 100 g (1 mole) of vinyl butyl ether and 0.5 g of hydroquinone at 200°C for 14 h. Distillation of the reaction mixture gave 75.6 g (63.4%) of 2-butoxy-4-(α-thienyl)-Δ3-dihydropyran (I) as a pale-yellow oil with bp 154-159°C (5 mm), nD 1.5192, and d4 1.09. Found: C 65.5; H 7.4; S 13.3%; MRD 66.2. C13H16O2S. Calculated: C 65.5; H 7.6; S 13.3%; MRD 66.9.