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THIENOAZATROPONE: SYNTHESIS OF 7-CHLORO-8H-THIENO[3,2-c]AZEPIN-8-ONE

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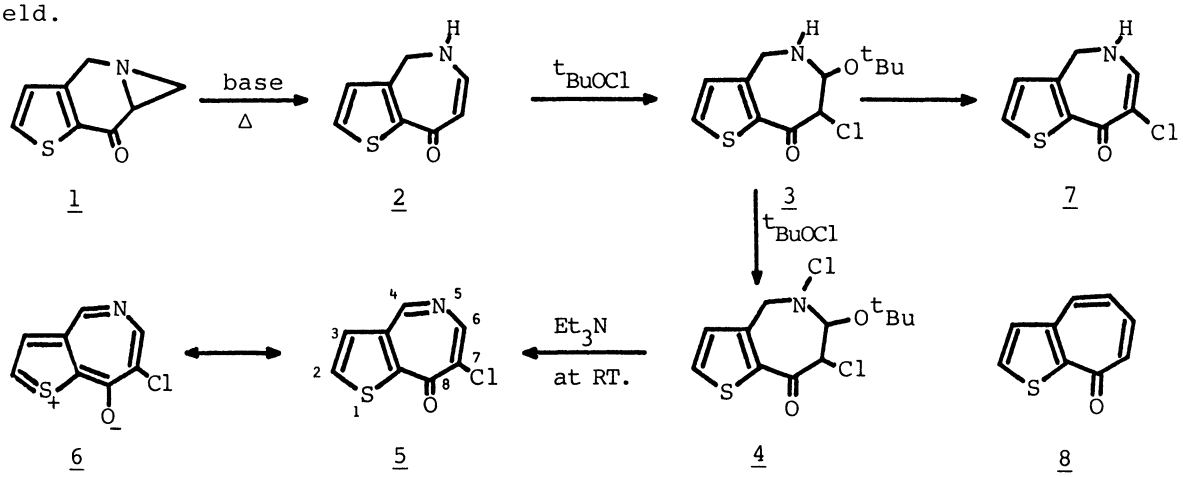
A thienoazatropone, 7-chloro-8H-thieno[3,2-c]azepin-8-one(5) is synthesized from 4,5-dihydro-8H-thieno[3,2-c]azepin-8-one(2) using t-butyl hypochlorite. In addition, some physical properties of 5 are disscussed.

In a series of our synthetic investigations of the nitrogen-containing seven-membered ring compounds, we are interested in the fused π-conjugated system of thiophene which is classified as π-excess heteroaromatic ring and cationic 4-aza-tropone which is, at least to our knowledge, yet unknown.

Previously, we reported that the synthesis of 6,7-dihydroazirino[1,2-a]thieno-[2,3-d]pyrid-8-one(1) and base-catalyzed ring-opening reactions of the aziridine ring of 1 gave 4,5-dihydro-8H-thieno[3,2-c]azepin-8-one(2).[1] Now we wish to report the synthesis of novel heterocyclic system, 7-chloro-8H-thieno[3,2-c]azepin-8-one(5), which has a thiophene-fused 4-azatropone structure, from 2. Thienoazatropone 5 is considered as 5-aza-analogue of 8H-cyclohepta[b]thiophen-8-one(8), which is also yet unknown heterocyclic conjugated system.

Two molar equivalents of t-butyl hypochlorite is added to a dichlolomethane solution of 2 at -10°C. After 2 hr, the treatment of this resulting solution with excess triethylamine at room temperature for 1 hr gives a crude product of 5, which is purified by means of a column chromatography on silica gel to give pale yellow crystals[2] (mp.175-177°C; Mass m/e 197(M^+,100%); IR 1599,1590,1560,1527cm^{-1}) in 80% yield.



On the other hand, 7-chloro-4,5-dihydro-8H-thieno[3,2-c]azepin-8-one(7)[2] (mp. 133.5-134°C;IR 1592cm^{-1};NMR($CDCl_3$+DMSO-d_6) δ4.33(d,$J_{4,5}$=6.5Hz,2H,H_4),6.90(d,$J_{2,3}$=5.0 Hz,1H,H_3),7.47(d,$J_{5,6}$=7.4Hz,1H,H_6),7.53(d,$J_{2,3}$=5.0Hz,1H,H_2),8.42(br,1H,H_5)) is ob-

tained in quantitative yield when one molar equivalent of t-butyl hypochlorite is used in this reaction sequence in under similar conditions.

The formation of 5 from 2 would be explained by possible intervention of the two intermediates(3 and 4). In the first step, addition reaction of t-butyl hypochlorite to the C_6-C_7 double bond of 2 would give intermediate 3. The formation of 7 elucidates the intermediate 3 and the regioselectivity of the addition which may be controlled by the nucleophilic property of 2 as an enamine. Subsequently, the well-known N-chlorination[3] occurs to give intermediate 4.

The structure of 5 is confirmed on the basis of its spectral data. The NMR spectrum of 5 exhibits two singlets of seven-membered ring protons at δ8.71 and 9.02, and an AB quartet(J=5.0Hz) of thiophene ring protons at δ7.61 and 7.90. These four protons are assigned by the use of shift-reagent, $Eu(fod)_3$. This is shown in Figure 1.

Comparison of electronic spectrum of 5 in ethyl alcohol with that in dichloromethane reveals that the lowest energy absorption is assigned as an intramolecular charge-transfer band(Fig. 2).[4]

From these results, e.g., remarkably low chemical shift of four ring protons, especially, chemical shifts of H_4 and H_6 which are much lower than α-protons of pyridine, and the intramolecular charge-transfer band in its electronic spectra, thienoazatropone system 5 is considered as a partly polarized species as shown by the resonance structure 6, which is quite analogous to the conjugation in azulene.

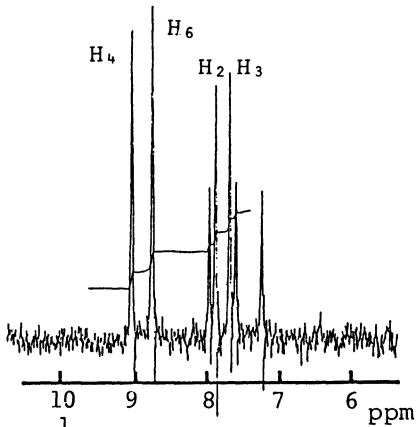


Fig 1. ^{1}H-NMR(60MHz) spectrum of 5 in $CDCl_3$.

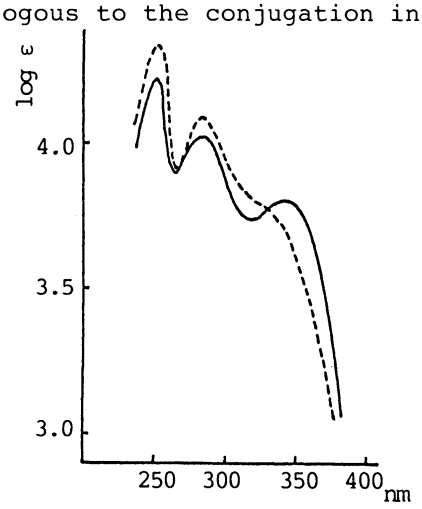


Fig 2. Electronic spectra of 5 in ethyl alcohol(———) and in dichloromethane(- - - - -).

Further investigation on the chemical reactivities of 5 is now in progress.

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References

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