Tetrahedron Letters No.5, pp. 297-300, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THIOPHENE DERIVATIVES FROM CENTAUREA AND RUDBECKIA SPP.

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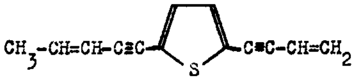
(Received 10 December 1964)

We wish to report the isolation of the thiophene derivative (I) from various Centaurea spp., the derivative (VIII) from Rudbeckia spp. and the confirmation of these structures by simple syntheses.

Extraction of the roots of Centaurea jacea L. with pentane-ether followed by chromatography over silica gave a yellow oil (b.p. 93°/0.05 mm.) which was pure by thin-layer chromatography in two systems.[1] Analytical results were difficult to obtain but indicated $C_{13}H_{12-16}S$.

The infra-red spectrum of the oil showed a -C≡C- group(s) (2201 cm.$^{-1}$), a -CH=CH- system (trans, 1610, 950 cm.$^{-1}$), a $-CH=CH_2$ group (990, 905 cm.$^{-1}$) and a 2,5-disubstituted thiophene residue (800 cm.$^{-1}$). The ultraviolet absorption spectrum 334, 354 (sh.) mμ, (log ε, 4.51, 4.31) indicated a thiophene ring with at least four unsaturated centres in conjugation. The n.m.r. spectrum showed resonances at τ 3.0 (2 protons; 3,4-positions of the thiophene ring), τ 3.6 - 4.8 (5 protons, complex series, -CH=CH-; $-CH=CH_2$) and τ 8.1 (3 protons, doublet, $\underline{CH_3}$-CH=).

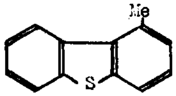
Since we were able to isolate the dien-tetrayne (II)[2] from the same extraction, structures based on this skeleton seemed likely. There were three possible thiophene structures of this type which were consistent with the spectroscopic evidence above but these could not be correlated with such analytical evidence as we had been able to obtain.



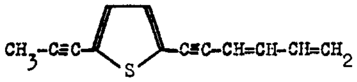
(I)

$CH_3-CH=CH-(C\equiv C)_4-CH=CH_2$

(II)



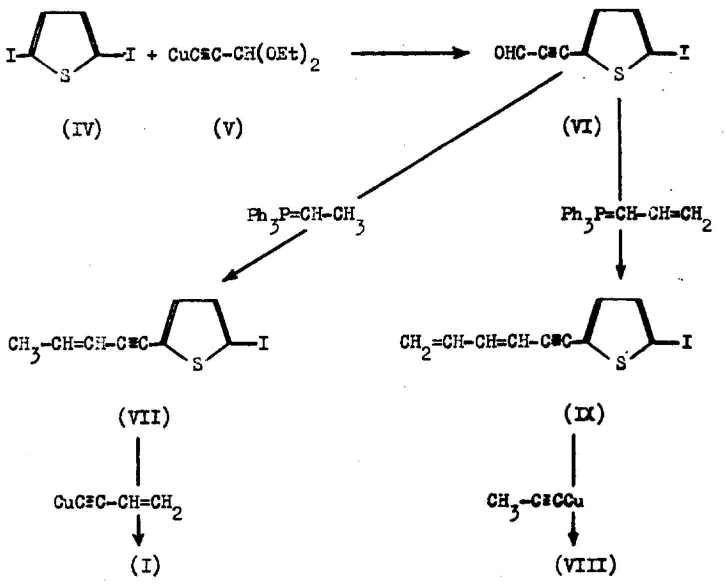
(III)



(VIII)

Structure (I) was supported by the mass spectrum. This showed a parent molecular ion of 198 ($C_{13}H_{10}S$) which was correct for a molecular formula such as (I) but the splitting pattern was identical with that of 1-methyldibenzothiophene (III). This must have arisen by rearrangement during the mass determination since the other spectral evidence was clearly inconsistent with (III).

The synthesis of (I) (and VIII, below) are good examples of the utility of the heterocyclic acetylene synthesis which we have recently described.[3] 2,5-Diiodothiophene[4] (IV) was treated with one equivalent of the cuprous salt of propargylaldehyde diethyl acetal (V) under nitrogen in pyridine under reflux to give, after acid hydrolysis during the work-up, 2-iodo-5(prop-2-yn-1-al)thiophene (VI), (52%), m.p. 82-83°, u.v. max. 264, 324, 331 mμ (log ε 3.88, 4.31, 4.32). Treatment of (VI) with a Wittig reagent from ethyl bromide gave compound (VII) (trans isomer, 28%) which was reacted with the cuprous salt of vinyl acetylene in the same manner to give (I), identical in all respects with the natural material.



The thiophene derivative (VIII) which we have isolated[5] from the roots of <u>Rudbeckia nitida</u> Nutt. and <u>Rudbeckia laciniata</u> L. by similar techniques was also synthesised from the intermediate (VI). Treatment with a Wittig reagent from allyl bromide gave the yne-diene (IX) which was reacted with the cuprous salt of methyl acetylene to give (VIII), (22%; b.p. 110°/0.06 mm., u.v. max. 334, 357 mμ, log ε 4.42, 4.47) identical with the natural material. The detailed spectroscopic arguments which led to structure (VIII) will be presented in a full communication.

We have isolated (I) and (II) from other sources, e.g. <u>Centaurea nigra</u> L., <u>Centaurea cineraria</u> L. and <u>Centaurea pulcherrima</u> Wright. Very recently, Bohlmann and co-workers[6] have reported the isolation of a compound from <u>Serratula radiata</u> M. Bieb and five other species which has been assigned structure (I) on evidence from hydrogenation experiments and spectral measurements and a compound described as (VIII) on the same basis from <u>Rudbeckia amplexicaulis</u> Vahl. No synthetic studies were reported.

Satisfactory analyses were obtained for all compounds except (VII) and (IX) which could not be distilled.

We are grateful to Dr. J. H. Beynon and Mr. A. E. Williams of Imperial Chemical Industries Ltd., (Dyestuffs Division) for mass spectra, and financial support from British Petroleum Ltd. (R.E.A.).

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