is well documented. A previous report of the synthesis of 5,7-dimethoxyindole[2] *via* decarboxylation of the corresponding 2-carboxylic acid of mp 178°, reported the indole as having mp 159–160°. In our hands, 5,7-dimethoxyindole was prepared in an unequivocal manner and the literature melting point and report of its preparation are apparently in error.

Experimental Section[3]

3,5-Dimethoxy-2β-dinitrostyrene.—To a solution of 3,5-dimethoxy-β-nitrostyrene[4] (5.1 g, 0.024 mole) in Ac_2O (90 ml) was added, with stirring, powdered $Cu(NO_3)_2$ (7.2 g) portionwise over 70 min. Red fumes were evolved and the temperature rose to 70°. Stirring was continued for 1 hr, the reaction mixture was poured over ice, and the resultant product collected by filtration. Recrystallization from EtOH yielded 4.32 g (75%) of pale yellow needles, mp 179–181°. *Anal.* ($C_{10}H_{10}N_2$) C, H, N.

5,7-Dimethoxyindole.—Fe powder (30 g) was added to 3,5-dimethoxy-2β-dinitrostyrene (8.6 g, 0.033 mole) in AcOH (150 ml, 80%). An exothermic reaction occurred on slightly warming the mixture. The mixture was allowed to stand 1 hr, diluted with H_2O, and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried ($MgSO_4$), filtered, and evaporated to dryness to yield an oil 4.3 g. Chromatography on silica gel yielded 3.3 g (57%) of product, mp 81–83°. Recrystallization for Et_2O–pet ether gave a sample, mp 83–84°; nmr (60 Mcps, $CDCl_3$), 6.45 multiplet, 2 H, 6.76 doublet, 1 H, and 7.1 triplet 1 H (aromatic protons) and 8.4 ppm broad band 1 H, (amine proton). *Anal.* ($C_{10}H_{11}NO_2$) C, H, N.

(2) V. Oskar Sus, M. Glos, K. Moller, and H. D. Eberhardt, *Justus Liebigs Ann. Chem.*, **583**, 150 (1953).

(3) Melting points were taken in capillaries and are uncorrected.

(4) H. Lloyd, E. A. Kielar, R. Hight, S. Uyeo, H. Falles, and W. Wildman, *J. Org. Chem.*, **27**, 373 (1960).

Dithienylpiperidylthenilates

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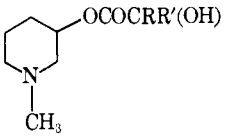
Compounds of type 1 have been shown to be potent anticholenergics and psychotomimetics.[1] Increases in pharmacologic response when R = phenyl is changed to thienyl have been noted.[2] We wish to show that compounds of type **1** can be synthesized despite the



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marked instability of the thenilic acids.[3a,b]

Experimental Section[4]

Methyl Thenilates (Table I).—A suspension of 0.01 mole of the thenil[5] in 20 ml of H_2O and 0.05 mole of KOH was stirred and refluxed under N for 30 min longer than required to effect soln. The cooled soln was acidified with concd HCl to congo red and immediately extracted with Et_2O. The dried (Na_2SO_4) extracts were treated with excess CH_2N_2 and stirred for 30 min, and solvents were removed at reduced pressure. The residue was recrystallized from pet ether (bp 60–90°).

Table I

Methyl Esters of Thenilic Acids

No.	R,R'	Mp °C	Yield, %	Formula[b]
2	2-Thienyl	92–94	69	$C_{11}H_{10}O_3S_2$
3	3-Thienyl	80–81	70	$C_{11}H_{10}O_3S_2$
4	5-Chloro-2-thienyl	*a*	92	$C_{11}H_8Cl_2O_3S_2$
5	2-Thianapthyl	103–104	62	$C_{19}H_{14}O_3S_2$

[a] Liquid, molecular distilled at 130° (0.01 torr). [b] All compounds analyzed correctly for C,H,S.

Table II

N-Methyl-3-piperidyl Esters of Thenilic Acids

No.	R,R'	Mp °C	Yield, %	Formula[a]
6	2-Thienyl	201–204	24	$C_{16}H_{20}ClNO_3S_2$
7	3-Thienyl	228–231	48	$C_{16}H_{20}ClNO_3S_2$
8	5-Chloro-2-thienyl	203–205	37	$C_{16}H_{18}Cl_3NO_3S_2$
9	2-Thianapthyl	233–234	42	$C_{24}H_{24}ClNO_3S_2$

[a] All compounds analyzed correctly for C,H,N,S.

***N*-Methyl-3-piperidyl Esters (Table II).**—A mixture of 0.01 mole of methyl thenilate, 0.01 mole of *N*-methyl-3-piperidinol, and 0.01 g of NaOMe in 40 ml of dry heptane was refluxed 6 hr under N_2. The cooled soln was washed with H_2O, dried (Na_2SO_4), and taken to dryness by rotary evaporator. The residue was dissolved in 20 ml of *i*-PrOH, and 20 ml of Et_2O saturated with dry HCl was added. The amino ester hydrochloride was recrystallized from 90% EtOH–H_2O.

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(1) J. H. Biel, L. G. Abood, W. K. Hoya, H. A. Leiser, P. A. Nuhfer, and E. F. Kluchesky, *J. Org. Chem.*, **26**, 4096 (1961).

(2) J. H. Biel, E. P. Sprengeler, H. A. Leiser, J. Horner, A. Drukker, and H. L. Friedman, *J. Amer. Chem. Soc.*, **77**, 2250 (1955).

(3) (a) S. Z. Cardon and H. P. Lankelma, *ibid.*, **70**, 4248 (1948); (b) E. Campaigne and R. C. Bourgeois, *ibid.*, **75**, 2702 (1953).

(4) Analysis indicated only by the symbols of the elements were within 0.4% of the theoretical values.

(5) 2,2,-Thenil and 3,3,-thenil are known. Bis(5-chloro)-2,2′-thenil and 2,2′-thianapthil were prepared analogously.

Acetylenics. 1. Aromatic Amines Containing the Acetylenic Triple Bond

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Some recent work in our laboratories on oxybutynin-like compounds which were shown by Thibodeau[1] to exhibit unusually long duration of action against Tremorine-produced tremors, prompted us to undertake a systematic study of the acetylenic bond in centrally and perepherally active drugs. As part of this study, some aromatic amines (Table I), similar to known phenethylamines derivatives, but containing the acetylenic bond were synthesized.

Experimental Section

Method A.—1-phenyl-3-bromo-1-propyne (I) (52 g, 0.25 mole) was added to 2.5 mole of liquid NH_3 or the appropriate amine in a pressure reactor. The whole was heated at 35° for 30 min and the unreacted amine allowed to excape. Et_2O (150 ml) was added to the residue and the whole was filtered, dried, and evapd. The residue was again taken up in Et_2O and a solution of HCl gas in Et_2O was added until pptn was complete. The solid was recrystd from Me_2CO or EtOAc.

Method B.—Phenylacetylene (0.3 mole), paraformaldehyde (0.31 mole), Me_2NH(II) (0.6 mole), and $Cu(OAc)_2$ (0.2 g) in 150 ml of dioxane were refluxed with stirring under a Dry Ice conden-

(1) G. Thibodeau, University of Montreal, personal communication.