A New Synthesis of Thiophenes

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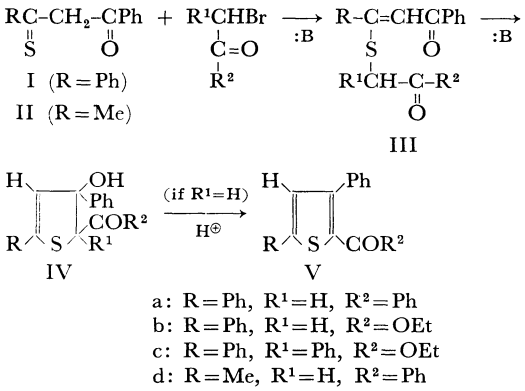
A new route to thiophenes from 2-thiocarbonylenamines and α-bromocarbonyl compounds was reported recently.[1] In an exploration of the reactions of readily available monothio-β-diketones,[2] we eventually found an analogous way to thiophenes as outlined below. This seems to be easier and more versatile than the published methods. Physical data of products obtained (III—V) are listed in Table 1.



a: R=Ph, R^1=H, R^2=Ph
b: R=Ph, R^1=H, R^2=OEt
c: R=Ph, R^1=Ph, R^2=OEt
d: R=Me, R^1=H, R^2=Ph

A mixture of α-(thiobenzoyl)acetophenone (I, 5.0 mmol) and phenacyl bromide (5.0 mmol) dissolved in benzene (30 m*l*) was treated with triethylamine (15.0 mmol) at room temperature for 1 hr. Addition of water followed by extraction with benzene gave IVa in a quantitative yield. A solution of IVa (1.40 mmol) and concentrated hydrochloric acid (0.5 m*l*) in methanol (50 m*l*) was heated to reflux for 30 min and extracted with benzene to afford Va quantitatively. An S-alkylated compound IIIb (70%) was isolated in the reaction of I with ethyl bromoacetate under the same condition. In contrast, however, the use of sodium hydride (10.0 mmol) suspended in benzene (50 m*l*) in place of triethylamine yielded a cyclization product IVb (50%), whose treatment with hydrochloric acid gave Vb quantitatively.

S-alkylated products IIIc and IIId were isolated also in triethylamine-treatment of a mixture of I and ethyl α-bromophenylacetate and that of α-(thioacetyl)acetophenone (II) and phenacyl bromide in 55% and 54% yield, respectively. These are easily cyclized by more basic reagents. Treatment of IIIc (1.25 mmol) with sodium ethoxide (4.4 mmol) in ethanol (50 m*l*) at room temperature for 3 hr gave a dihydrothiophene IVc (42%), whereas that of IIId (5.0 mmol) with sodium hydroxide (10.0 mmol) in water (2.0 m*l*) and ethanol (50 m*l*) mixture yielded a thiophene Vd (60%).

The IR spectra of IIIb, IIIc and IIId showed characteristic two bands at *ca.* 1640 and 1530 cm^{-1}, which would reasonably be ascribed to the mesomeric group $-S-\dot{C}=CH-\dot{C}=O \longleftrightarrow -\overset{\oplus}{S}=\dot{C}-CH=\dot{C}-\overset{\ominus}{O}$. The $R^1-\dot{C}H-CO-R^2$ group exhibited normal absorption.

TABLE 1. MPS AND SPECTRAL PROPERTIES OF NEW COMPOUNDS[a]

Compd	Mp °C	IR[b] cm^{-1}	NMR δ ppm from TMS in $CDCl_3$
IVa	148—150	3450, 1688	5.08[c] (s, 1H), 5.40 (s, 1H), 6.15 (s, 1H), 7.2—7.8 (m, 15H)
Va	96.5—98	1634	7.1—7.8 (m)
IIIb	96—98	1738, 1635, 1532	1.17 (t, 3H), 3.26 (s, 2H), 4.02 (q, 2H), 7.11 (s, 1H), 7.3—7.6 (m, 8H), 7.9—8.2 (m, 2H)
IVb	130—132	3445, 1726	1.25 (t, 3H), 3.95[c] (s, 1H), 4.21 (q, 2H), 4.75 (s, 1H), 6.01 (s, 1H), 7.2—7.7 (m, 10H)
Vb	71—73	1708	1.26 (t, 3H), 4.25 (q, 2H), 7.2—7.8 (m, 11H)
IIIc	73—76	1733, 1634, 1530	1.09 (t, 3H), 3.95 (q, 2H), 4.65 (s, 1H), 7.03 (s, 1H), 7.2—8.1 (m, 15H)
IVc	116—118	3445, 1706	1.33 (t, 3H), 4.36[c] (broad s, 1H), 4.41 (q, 2H), 6.53 (s, 1H), 7.2—7.8 (m, 15H)
IIId	139—141	1690, 1622, 1524	2.42 (d,[d] 3H), 4.27 (s, 2H), 6.99 (q,[d] 1H), 7.3—8.1 (m, 10H)
Vd	68.5—69	1623	2.56 (d,[d] 3H), 6.92 (q,[d] 1H), 7.0—7.7 (m, 10H)

a) All gave correct analytical data. b) Taken in KBr tablets.
c) Signal disappears on treatment with D_2O. d) J=1.0 Hz.

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2) a) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965); b) E. Uhlemann and Ph. Thomas, *J. Prakt. Chem.*, **34**, 180 (1966).