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A New Type of Clathrate Host: Tris-(5-acetyl-3-thienyl)methane

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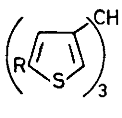
Summary The title compound is shown to give 2:1 clathrates with a wide variety of organic compounds.

GOLD'FARB and his co-workers[1] have noted that chloroform reacts with 2-acetylthiophen in the presence of an excess of aluminium chloride to give solely tris-(5-acetyl-3-thienyl)-methane (**1**). They reported that the sublimed material was an amorphous solid with an indistinct m.p. of 50—58 °C but which recrystallised well from benzene, ethanol, or pyridine incorporating 0·5 mol of the solvent.

We concur with this proposed structure from n.m.r. data which prove the 2,4-substitution [δ 2·49 (d) and 2·77 (br) (thiophen H; $J_{2,4}$ 1·3 Hz), 4·41 (s, CH), and 7·49 (s, Me)] and find that the compound is readily prepared in 50—100 g amounts by minor modifications to the reported procedure. Furthermore, a systematic study has so far not revealed a solvent which is not incorporated. The following results were obtained (2:1 ratio solute: solvent unless noted): C_6H_6 m.p. 106—110 °C; toluene 109—110; *o*-xylene 120—121; *m*-xylene 97—98; *p*-xylene 112—113; mesitylene 77—78; PhEt 106—110; cumene 85—89; PhBu^t (3:1 solute: solvent) 136—139; PhF 106—110; PhCl 116—119; PhBr 128—130; PhI 131—132; naphthalene 140—142; cyclohexane 98—100; decalin 74—75; cyclooctene 98—99; MeOH 108—114; EtOH 108—114; Pr^{i}OH 106—111; Bu^{s}OH 97—110; Bu^{t}OH 103—107; n-decanol 121—123; PhOMe 102—106; Me_2CO 111—113; MeCOEt 111—114; MeCOPh 101—104; EtOAc 100—101; MeCN 108—111; AcOH 102—104; pyridine 104—107; piperidine 102—105; Et_3N 114—115; $MeNO_2$ 109—112; Me_2SO 113—116; CH_2Cl_2 109—115; $CHCl_3$ 100—107; CCl_4 (6:1 solute: solvent) 98—99; $HCONMe_2$ 110—113. In only two cases of bulky solvents (t-butylbenzene and carbon tetrachloride) was the stoicheiometry other than 2:1

Solids can also be incorporated from solutions in appropriate solvents (*e.g.* naphthalene is incorporated from mesitylene solution) while solvents which readily dissolve the host molecule yield the requisite clathrate by addition of light petroleum (*e.g.* chloroform) or water (*e.g.* dimethyl sulphoxide). No evidence of host–guest interaction in solution in various solvents was seen, since n.m.r. spectra showed normal absorptions. The m.p.s of the clathrates (often considerably higher than the b.p.s of the guest molecule) suggest that 'three-legged' solvents are less favourable (*e.g.* compare mesitylene and isopropylbenzene with their homologues), and the higher melting *ortho*-isomer is preferentially, but not exclusively (*ca.* 5:1), incorporated from a 50:50 mixture of *o*- and *m*-xylene.



	R	% Yield	Mp (b.p.)/°C
(1)	Ac	60-65	See text
(2)	EtCO	86	147-150
(3)	Pr^{n}CO	53	76
(4)	Pr^{i}CO	11	153-155
(5)	MeO_2C	52	See text
(6)	EtO_2C	20-25	(264 at 0·7 mmHg)
(7)	HON=C(Me)		232-234
(8)	Et	95	(135-140 at 0·3 mmHg)

A variety of analogues [(**2**)—(**6**)] of the parent system have been made by Gold'farb's method as well as the oxime (**7**) and the ethyl derivative (**8**) [by Huang-Minlon reduction of (**1**)]. Surprisingly, only the methyl ester (**5**) showed any sign of clathration properties; it was obtained as a viscous oil by chromatography but it crystallised slowly from ethanol, cyclohexane, or carbon tetrachloride (m.p.s 74—77, 83—86, and 84—86 °C, respectively) incorporating the solvent in each case in a 2:1 ratio.

Finally, attempts, with racemic s-butyl alcohol, to utilise the potentially chiral crystalline clathrates of (**1**) were ineffective for resolution.

This system therefore appears to be another member of that diverse group of compounds which show the unique property of clathration.[2]

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[1] A. P. Yakubov, Yu. K. Sudarushkin, L. I. Belenkii, and Ya. L. Gold'farb, *J. Org. Chem.* (*U.S.S.R.*), 1973, **9**, 1549.

[2] S. G. Frank, *J. Pharm. Sci.*, 1975, **64**, 1585.