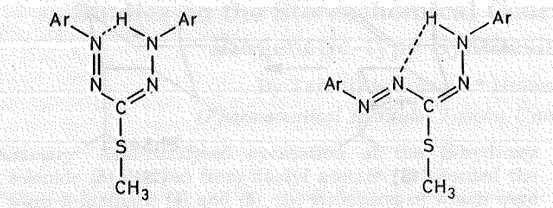



(**1**) Ar = Ph
(**2**) Ar = *p*-tolyl
(**3**) Ar = *o*-tolyl

The di-(*p*-tolyl) (**2**) and di-(*o*-tolyl) (**3**) homologues of (**1**) and the corresponding $-SCD_3$ analogues have been prepared.[6] Red needles of (**2**) dissolve in chloroform to give a pink solution ($\lambda_{max}$ 550 nm, $\epsilon$ 1406 $m^2$ $mol^{-1}$) which slowly turns brownish to give a new band at 425 nm with a concomitant decrease in the absorbance at longer wavelength, in exact analogy with the behaviour of (**1**). Presumably (**2**) has the same solid state configuration (d.r.s.: $\lambda_{max}$ 550 nm) as (**1**), *viz.* *syn*,s-*trans* (**2b**). The compound (**3**), however, crystallizes as yellow plates (d.r.s.: $\lambda_{max}$ 423 nm) and the *X*-ray structural analysis‡ establishes an *anti*,*s-trans* configuration [as (**3c**)]. During several days in the dark the initially yellow solution of (**3c**) in chloroform ($\lambda_{max}$ 420 nm, $\epsilon$ 2936 $m^2$ $mol^{-1}$) slowly formed a brown equilibrium mixture (isosbestic point 485 nm) with a pink isomer (**3b**) having a peak at 560 nm. Under the same conditions the initially pink (**2b**) reaches equilibrium with the yellow isomer (**2c**).

The $^1H$ n.m.r. spectrum of a freshly prepared (pink) solution of (**2**) in $CDCl_3$ shows a single resonance (6H) for the two equivalent *p*-tolyl Me groups. Although this would be consistent with structure (**2a**), formazans known to have this structure in the solid state[7] show an imino proton at $\delta$ ($CDCl_3$, $Me_4Si$) 14—16 and $\nu$ (N–H) *ca.* 3030 $cm^{-1}$ in fresh solutions. Spectroscopic data for (**1**), (**2**), and (**3**) do not provide evidence for such strong hydrogen bonding (Table) and configuration (**2b**) [already shown to exist in crystals of (**1**)][5] should be considered, the equivalence of the two Me groups being achieved by interconversion, fast on the n.m.r. time scale, between two equivalent forms of (**2b**) by rotation about the C–N single bond (*trans* → *cis*) to give the quasi-aromatic *syn*,s-*cis* structure (**2a**) as an intermediate.§ During the slow isomerization of pink (**2a**) to yellow (**2c**) two new *p*-tolyl Me resonances develop until after 3 days in the dark three lines are found, still integrating *in toto* for 6H. The new resonances are attributed to the magnetically non-equivalent *p*-tolyl Me groups of isomer (**2c**) produced by a *syn* → *anti* isomerization: structure (**2d**) is less favoured owing to repulsion of the lone pairs on nitrogens 1 and 4. The magnetically non-equivalent *o*-tolyl Me groups in a fresh (yellow) solution of (**3**) show two resonances of equal intensity derived from form (**3c**), as expected from the *X*-ray analysis of the yellow crystals of (**3**). On standing in the dark isomerization about the C=N bond occurs yielding the pink *syn*,s-*cis* (**3a**) tautomeric pair which gives rise to an additional *o*-tolyl Me resonance in the spectrum of the equilibrium mixture. During the isomerization (**2a**) → (**2c**) a new *S*-Me resonance appears at virtually the same chemical shift value as that given by a fresh solution of (**3c**); (**3c**) → (**3a**) gives a new *S*-Me line corresponding to a fresh solution of (**2a**) (Table). The equilibrium mixture in either case contains roughly equal proportions of the two isomers to give very similar $^1H$ n.m.r. spectra, contrasting mainly in the difference in chemical shifts of the two *o*-tolyl Me resonances (**3c**; *e.g.*,

TABLE. $^1H$ Chemical shift values (p.p.m.) of imino and methyl resonances at ambient temperature [$\delta(CDCl_3)$ and, in parentheses, $\delta(C_6D_6)$; $Me_4Si$, 100 MHz]. $\nu$(N–H)/$cm^{-1}$ for KBr pressed disks and $CCl_4$ solutions.

| | | Solid | Fresh solution | | Equilibrium mixture after 70 h | |
|---|---|---|---|---|---|---|
| (**1**) | –N*H* | | 10·26 | (10·02) | 10·26 | (10·02) |
| | | | | | 9·46 | (9·24) |
| | –SC*H*$_3$ | | 2·54[a] | (2·29)[a] | 2·54[a] | (2·29)[a] |
| | | | | | 2·40[a] | (1·92)[a] |
| | $\nu$(N–H) | 3338 | 3342 | | 3342, 3253 | |
| (**2**) | –N*H* | | 10·22 | (10·06) | 10·19 | (10·06) |
| | | | | | 9·43 | (9·26) |
| | –SC*H*$_3$ | | 2·52[a] | (2·32)[a] | 2·52[a] | (2·32)[a] |
| | | | | | 2·39[a,b] | (1·95)[a] |
| | ArC*H*$_3$ | | 2·39 | (2·09) | 2·39 | (2·09) |
| | | | | | 2·42 | (2·09)[b] |
| | | | | | 2·34 | (2·03) |
| | $\nu$(N–H) | 3341 | 3344 | | 3344, 3254 | |
| (**3**) | –N*H* | | 9·53 | (9·41) | 9·52 | (9·41) |
| | | | | | 10·28 | (10·21) |
| | –SC*H*$_3$ | | 2·43[a] | (1·95)[a] | 2·43[a] | (1·95)[a] |
| | | | | | 2·51[a] | (2·35)[a] |
| | ArC*H*$_3$ | | 2·40 | (1·98) | 2·40 | (1·98) |
| | | | 2·72 | (2·69) | 2·72 | (2·69) |
| | | | | | 2·53 | (2·29) |
| | $\nu$(N–H) | 3270 | 3269 | | 3269, 3361 | |

[a] Resonance disappears in spectrum of $-SCD_3$ analogue. [b] Apparent from peak integration.

‡ *Crystal data:* (**3**), $C_{16}H_{16}N_4S$, $M_r$ = 298·40, monoclinic, space group $P2_1/n$, $a$ = 7·993(4), $b$ = 20·910(9), $c$ = 10·154(5) Å, $\beta$ = 110·43(5)°, $U$ = 1590(1) Å$^3$, $D_m$ = 1·29 (by flotation), $D_c$ = 1·25 g $cm^{-3}$, $Z$ = 4, $F(000)$ = 632. The structure was solved by direct methods using the SHELX-76 program system (G. M. Sheldrick, Cambridge) from data collected by the $\omega$—2$\theta$ scan technique in the range 3 ⩽ $\theta$ ⩽ 20° on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation [$\lambda$ = 0·7107 Å, $\mu$(Mo-$K_\alpha$) = 1·63 $cm^{-1}$]. Refinement by full-matrix least-squares gave $R$ = 0·064 for 1319 observed reflections with $I_{rel} > 2\sigma I_{rel}$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ *Added in proof:* However, the $^{13}C$ n.m.r. spectrum of (**2**) and the n.m.r. spectrum of the compound labelled at N-1 and N-5 with $^{15}N$ provide unambiguous support for structure (**2a**). Details will be reported in the full paper.



$C_6D_6$ 0·71 p.p.m.) compared with those of *p*-tolyl in the same configuration (**2c**; 0·06 p.p.m.), presumably owing to the magnetic anisotropy effect of the azo-group on one of the *o*-tolyl Me groups. The approach to an equilibrium mixture starting from either the *syn*,s-*cis* (**2a**) or the *anti*,s-*trans* (**3c**) isomer can be followed by observing the change in $\nu$ (N–H) since the intramolecular N–H · · · N and N–H · · · S hydrogen bonds differ significantly in strength with $\Delta\nu$ (N–H) *ca.* 90 $cm^{-1}$ (Table). Changes in the imino proton resonance (Table) also reflect this difference in internal hydrogen bonding.

Several authors have speculated on the nature of the pink and yellow isomers of (**1**)[4,6,8,9] and, indeed, of formazans in general.[2,3,10] Our results explain the isomerism occurring in (**1**) and may be applied to that found in many other formazans. They lead us to reject the assignments proposed by Burns and Duncan[9] but they support the speculative configurations proposed by Kuhn and Weitz.[3]

We thank Dr. K. R. Koch for helpful discussions, the C.S.I.R. (Pretoria) and the University of Cape Town for research grants, and the C.S.I.R. for the collection of diffractometer data.

(*Received*, 28*th April* 1980; *Com.* 439.)

[1] H. M. N. H. Irving, 'Dithizone,' Analytical Sciences Monographs No. 5, The Chemical Society, London, 1977, p. 84.
[2] I. Hausser, D. Jerchel, and R. Kuhn, *Chem. Ber.*, 1949, **82**, 515; W. Otting and F. A. Neugebauer, *Z. Naturforsch., Teil B*, 1968, **23**, 1064; *Chem. Ber.*, 1969, **102**, 2520.
[3] R. Kuhn and H. M. Weitz, *Chem. Ber.*, 1953, **86**, 1199.
[4] P. S. Pel'kis and R. G. Dubenko, *Dokl. Akad. Nauk SSSR*, 1956, **110**, 798; *Ukr. Khim. Zh.* (*Russ. Ed.*), 1957, **23**, 64, 69.
[5] J. Preuss and A. Gieren, *Acta Crystallogr., Sect. B*, 1975, **31**, 1276.
[6] H. Irving and C. F. Bell, *J. Chem. Soc.*, 1954, 4253; A. H. Nabilsi, Ph.D. Thesis, University of Leeds, 1972.
[7] E. Dijkstra, A. T. Hutton, and L. R. Nassimbeni, submitted for publication in *Acta Crystallogr.* It is shown that 3-nitro-1,5-di(2,6-dimethylphenyl)formazan adopts this quasi-aromatic structure in the solid state.
[8] W. Ferguson, B.Sc. Thesis, University of Oxford, 1957; C. H. Carlin, Ph.D. Thesis, The Johns Hopkins University, Baltimore, 1966.
[9] G. R. Burns and J. F. Duncan, *Chem. Commun.*, 1966, 116.
[10] A. W. Nineham, *Chem. Rev.*, 1955, **55**, 355; G. V. D. Tiers, S. Plovan, and S. Searles, Jr., *J. Org. Chem.*, 1960, **25**, 285; C. Schiele, K. Halfar, and G. Arnold, *Tetrahedron*, 1967, **23**, 2693; P. B. Fischer, B. L. Kaul, and H. Zollinger, *Helv. Chim. Acta*, 1968, **51**, 1449; L. Mester, A. Stephen, and J. Parello, *Tetrahedron Lett.*, 1968, 4119; G. Arnold and C. Schiele, *Spectrochim. Acta, Part A*, 1969, **25**, 685.

# Catalytic Control of Reactions of Dipoles and Carbenes;[1] an Easy and Efficient Synthesis of Cycloheptatrienes from Aromatic Compounds by an Extension of Buchner's Reaction

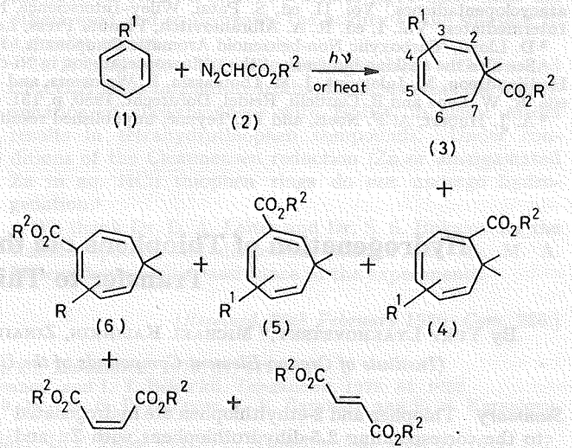
By ANDRÉ J. ANCIAUX, ALBERT DEMONCEAU, ANDRÉ J. HUBERT,* ALFRED F. NOELS,* NICOLE PETINIOT, and PHILIPPE TEYSSIÉ

(*Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman*, 4000 *Liège, Belgium*)

*Summary* Rhodium salts from strong carboxylic acids [particularly rhodium(II) trifluoroacetate] are novel and highly efficient catalysts for the preparation of substituted cycloheptatriene carboxylates from aromatic hydrocarbons and diazo-esters, and in contrast with the classical Buchner procedures these rhodium catalysts lead specifically to the 1-isomer (**3**), avoiding its subsequent prototropic conversion into conjugated isomers.

SINCE Buchner's classical work, the formation of cycloheptatrienes by cycloaddition of carbenes to aromatic substrates has been thoroughly investigated owing to its great mechanistic[2] and also preparative interest (particularly in the field of natural products).[3] Hitherto, however, finding selective, efficient processes for the direct preparation of substituted cycloheptatrienes from carbenes (*i.e.* generated by decomposition of diazo-compounds) has been a problem, the reaction yielding in all cases complex mixtures of products which are very difficult to separate (see the Scheme).

We now report that rhodium(II) carboxylates of strong organic acids are highly efficient in promoting the addition




SCHEME

of carbenes to aromatic substrates, permitting ready and sometimes regioselective access to substituted cycloheptatrienes. For example, tetrakis(trifluoroacetato)-dirhodium(II) (rhodium trifluoroacetate) catalyses the formation of the non-conjugated cycloheptatriene (**3**) from the diazo-esters (**2**) with an unexpectedly high selectivity. The yield, generally good, is practically quantitative in the case of benzene and toluene (Table). Moreover, with substituted benzenes, (**1**; R ≠ H) the distribution of isomers reveals that the attack, in several cases, is remarkably regioselective (Table).

In a typical preparation of cycloheptatriene-1-carboxylates, the diazo-ester (5 mmol) was continuously added, within 2 h, with a motor-driven syringe (Sage, model 352), to the solution containing the catalyst ($2—4 \times 10^{-2}$ mmol) in the aromatic substrate (0·1 mol), at room temperature with magnetic stirring. The product was analysed by g.l.c. using an internal standard. In preparative experiments, the product was distilled *in vacuo* after evaporation of the solvent. The cycloheptatriene fractions were identified by comparison with reported data where possible and by the usual spectroscopic methods (i.r., mass, n.m.r.), all compounds yielding satisfactory elemental analysis.

It should be emphasized that it is the kinetic isomer that is selectively produced (arising from sigmatropic hydrogen-shifts) and not the thermodynamic one. Thus, naphthalene yields the corresponding norcaradiene-intermediate addition product (instead of the final cycloheptatriene) in good yield: up to 85% with rhodium(II) methoxyacetate as catalyst and butyl diazoacetate. It is also noteworthy that the efficiency of the catalysts is strongly dependent on the electron-withdrawing ability of the carboxylate ligand, *e.g.*, for benzene:acid, $pK_a$ (% yield): $CF_3CO_2H$, 0·23 (100%); $C_6F_5CO_2H$, 1·48 (89%); $MeOCH_2CO_2H$, 3·57 (30%); $MeCO_2H$, 4·76 (7%); $Bu^tCO_2H$, 5·03 (5%). This is another example of the important role played by these halogenocarboxylate ligands in co-ordination chemistry.[4]

TABLE. Formation of the methyl cyclohepta-2,4,6-triene-carboxylates (**3**) from (**1**) (100 mmol), methyl diazoacetate (5 mmol), and rhodium(II) trifluoroacetate (0·02 mmol) at 22 °C.

| Substrate (**1**) | Yield | Distribution of isomers of (**3**)[a] | | | | | |
|---|---|---|---|---|---|---|---|
| Benzene | 100 | | (100) | | | | |
| Toluene | 95 | 4 | (56) | 3 | (23) | 2 | (17) |
| *o*-Xylene | 80 | 2, 3 | (43) | 3, 4 | (39) | 4, 5 | (18) |
| *m*-Xylene | 90 | 2, 4 | (12) | 2, 6 | (43) | 3, 5 | (43) |
| *p*-Xylene | 90 | 2, 5 | (85) | 3, 6 | (10) | | |
| Anisole | 73 | 3 | (8) | 4 | (56) | | |
| Chlorobenzene | 72 | 4 | (80) | 3 | (15) | 2 | (5) |
| Fluorobenzene | 46 | 4 | (80) | 3 | (12) | 2 | (8) |
| Pyridine | 0 | Strongly inhibiting ligand | | | | | |

[a] The first number refers to the position of the substituents relative to the carboxylate group; numbers in parentheses are the proportions (mole %) of the corresponding isomer present in the mixture of the carboxylates (**3**) mixture. The balance to 100% is made up of unidentified isomers.

In contrast with the observation that for olefin cyclopropanation with rhodium(II) carboxylates, lipophilic non-bonded interactions determined the reactivity,[1] the present results clearly indicate that for carbene addition to aromatic molecules it is electronic factors which control the reactivity of the rhodium carbenoid.

In conclusion, these systems, besides their interest in offering a new approach to a better mechanistic understanding of the behaviour of carbenoids, are of great preparative value and are quite versatile in their applications; *e.g.*, polystyrene is easily carboxylated in solution.[5]

We thank the 'Services de la Programmation de la Politique Scientifique' for support, FNRS (Belgium) and IRSIA for fellowships (N.P. and A.D.), and Dr. R. Weber and Mrs. M. Degueldre (Laboratory of Prof. M. Renson, University of Liège) for mass spectrometry measurements.

(*Received*, 7*th May* 1980; *Com.* 485.)

[1] For Part 1 and references to related publications see A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot, and Ph. Teyssié, *J. Org. Chem.*, 1980, **45**, 695; N. Petiniot, A. J. Anciaux, A. F. Noels, A. J. Hubert, and Ph. Teyssié, *Tetrahedron Lett.*, 1978, 1239.
[2] For general references on Büchner synthesis and diazo-ester reactions, see V. Dave and E. W. Warnhoff, *Org. React.*, 1970, **18**, 217; D. S. Wulfman, G. Linstrumelle, and C. F. Cooper, 'Synthetic Application of Diazoalkanes, Diazocyclopentadienes and Diazoazacyclopentadienes,' Vol. II, ed. S. Patai, Wiley–Interscience, New York, 1978, ch. 18; D. S. Wulfman and B. Poling, 'Reactive Intermediates,' Vol. 1, ed. R. A. Albramovitch, Plenum Press, London - New York, 1980, ch. 5.
[3] D. Lloyd, 'Carboxylic Non-benzenoid Aromatic Compounds,' Elsevier, Amsterdam, 1966, pp. 122 and 125.
[4] See also the striking influence of the trifluoroacetate ion in Ni-catalysed polymerisation of butadiene: Ph. Teyssié, A. Devaux, P. Hadijandreou, M. Julemont, J. M. Thomassin, E. Walckiers, and R. Warin, 'Preparation and Properties of Stereoregular Polymers,' eds. R. W. Lenz and F. Ciardelli, Reidel, Dordrecht, 1980, p. 131.
[5] A. J. Hubert, A. F. Noels, and Ph. Teyssié, unpublished results.

# Hydrogenation of Thiophens *via* the Consecutive Electron and Proton Transfer to Thiophenium Ions

By YURY LYAKHOVETSKY,* MICHAEL KALINKIN, ZINAIDA PARNES, FLURA LATYPOVA, and DMYTRY KURSANOV

(*Institute of Organo-Element Compounds of the U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.*)

*Summary* Thiophen and 2-ethylthiophen are hydrogenated to the corresponding 2,5-dihydrothiophens with Zn and $CF_3CO_2H$ *via* a mechanism involving the protonation of the thiophen ring to the respective thiophenium ion, followed by the transfer of two electrons from Zn and the second proton from the acid.



THIOPHENS were shown to undergo hydrogenation with $HSiEt_3$ and $CF_3CO_2H$.[1] A mechanism was proposed involving protonation of the substrate to form the thiophenium ion, the latter abstracting a hydride ion from $HSiEt_3$ to yield the hydrogenated product.[1,2] Though the detailed mechanism of the second step of the reaction has not yet been ascertained, it is formally possible to consider the hydride transfer as a transfer of two electrons and a proton and, thus, $HSiEt_3$ as performing two donating functions, one of them being electron donating and the other proton donating. Thus, it seemed reasonable to try to develop a process in which these two donating functions would be divided between two separate donors, the first being the donor of electrons and the second supplying protons, especially as a proton donor is required for the first step of the reaction. We report here that the reaction using the pair Zn + $CF_3CO_2H$ is suitable. 2-Ethylthiophen (**1**) in $CF_3CO_2H$ solution reacts with Zn to give a mixture of 2-ethyl-2,5-dihydrothiophen (**2**) and 2-ethyltetrahydrothiophen (**3**), (**2**) being in considerable excess. Solvents such as benzene, toluene, hexane, or dichloromethane increase the yield of (**2**), while the yield of (**3**) remains unchanged or even slightly decreases (Table).

TABLE. Hydrogenation of (**1**) by Zn and $CF_3CO_2H$ at room temperature.[a]

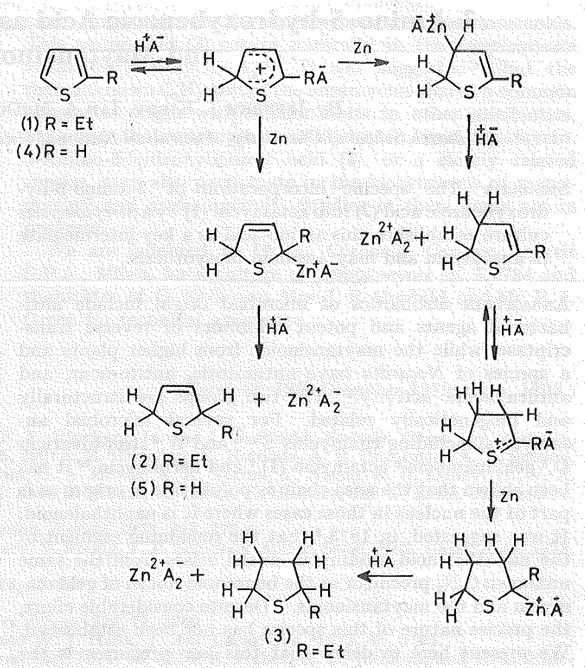
| Molar ratio (**1**):Zn:$CF_3CO_2H$ | Reaction time/h | Solvent | Yield/% (**2**) | Yield/% (**3**) |
|---|---|---|---|---|
| 1:50:100 | 3 | — | 41 | 11 |
| 1:92:50 | 2·5 | Benzene | 58 | 8 |
| " | 3 | Toluene | 61 | 8 |
| " | 3 | Hexane | 55 | 10 |
| " | 3 | Dichloromethane | 70 | 6 |
| " | 5 | Ether | 0 | 0 |

[a] High dilution and large amounts of Zn were used in order to decrease the extent of bimolecular side reactions.

Hydrogenation of unsubstituted thiophen (**4**) results in 2,5-dihydrothiophen (**5**), but the rate of the reaction is noticeably less. When the reaction of (**4**) was carried out in benzene under the conditions analogous to those used for the hydrogenation of (**1**), 10 h of vigorous agitation resulted in a 7% yield of (**5**) and a considerable amount of (**4**) remained unchanged. Under the more drastic conditions, boiling $CF_3CO_2H$ without solvent and in the presence of $LiClO_4$, the yield of (**5**) was 42% after 4 h.

The products were identified by g.l.c.–m.s. [$M^+$: (**2**) 114 and (**3**) 116] and, after isolation by preparative g.l.c., by mass [$M^+$: (**5**) 86] and Raman spectroscopy [C=C stretching: ν (**2**) 1638 $cm^{-1}$ and (**5**) 1637 $cm^{-1}$].[3] Since the Raman spectrum did not absolutely specify the double bond position in (**2**) a chemical method was employed for additional support: (**2**) did not react with $HSiEt_3$ in $CF_3CO_2H$ solution which is characteristic of an isolated double bond.[1] The quantitative measurements were performed by g.l.c.

A plausible mechanism for the reaction is illustrated in the Scheme. The following experimental findings support the possibility that the process begins with protonation of the substrate. (i) The reaction does not occur when $CF_3CO_2H$ is replaced by $MeCO_2H$ or a mixture of conc. HCl and benzene. The concentration of thiophenium ions is very small in these media as shown by the lack of reaction with $HSiEt_3$. (ii) The rate of hydrogenation of (**1**) is considerably higher than that of (**4**). The introduction of the donating ethyl-radical into the thiophen ring increases the basicity of the molecule and, thus, the concentration of the thiophenium ion. (iii) No reaction was observed in ether, a solvent which is more basic than the others used and so decreases the acidity of the solution to a greater extent.




SCHEME. A = $CF_3COO$.

It is interesting that the hydrogenation with Zn and $CF_3CO_2H$ leads to 2,5-dihydrothiophens, whereas the hydrogenation of alkylthiophens with $HSiEt_3$ in acidic media results in tetrahydrothiophen compounds. Under conditions of the Clemmensen reduction (Zn or amalgamated Zn in aq. HCl) thiophen rings do not undergo hydrogenation.[4]

We thank Dr. L. A. Leites and Dr. S. S. Bukalov for the Raman spectra and discussions thereof and Ms. M. A. Moscovskaya for her assistance in the experiments.

(*Received*, 26*th February* 1980; *Com.* 220.)

[1] D. N. Kursanov, Z. N. Parnes, G. I. Bolestova, and L. I. Belen'kii, *Tetrahedron*, 1975, **31**, 311.
[2] Z. N. Parnes, Yu. I. Lyakhovetsky, M. I. Kalinkin, D. N. Kursanov, and L. I. Belen'kii, *Tetrahedron*, 1978, **34**, 1703.
[3] W. H. Green and A. B. Harvey, *Spectrochim. Acta, Part A*, 1969, **25**, 723; G. D. Gal'pern, L. R. Barykina, and E. N. Karaulova, *Izv. Acad. Nauk SSSR, Ser. Khim.*, 1967, 2123.
[4] M. A. Youtz and P. P. Perkins, *J. Am. Chem. Soc.*, 1929, **51**, 3511; L. F. Fieser and R. G. Kennelly, *ibid.*, 1935, **57**, 1611; S. Z. Taits and Ya. L. Gol'dfarb, *Izv. Acad. Nauk SSSR, Otd. Khim. Nauk*, 1960, 1698; Ya. L. Gol'dfarb, S. Z. Taits, and V. N. Bulgakova, *ibid*, 1963, 1299.