Tetrahedron. Vol. 30, pp. 4113 to 4115. Pergamon Press 1974. Printed in Great Britain

THIO-ACIDS—V[1]

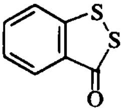
SOME REACTIONS OF 3-OXO-1,2-DITHIOLES

M. A.-F. ELKASCHEF,*† F. M. E. ABDEL-MEGEID and A. A. ELBARBARY
National Research Centre, Dokki, Cairo, Egypt

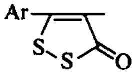
(*Received in the UK* 26 *June* 1974; *Accepted for publication* 4 *July* 1974)

Abstract—Diphenyldiazomethane with compound (**1**) gave dibenzoyl, while **2** and **3** gave the corresponding 3-oxo(2H)thiophenes **5**. With copper-bronze **1** gave 2,2′-di-(thiobenzoate) (**4**), while **2** gave 2,7-diphenylthiepin (**6a**) and 2,5-diphenylthiophene (**7a**), but **3** gave only 2,5-di-(p-methoxyphenyl)thiophene (**7b**). With Grignard reagents **1** gave the corresponding methanol derivative **14**, while **2** gave the thiobenzoylethylenes **13a** and **b**, but **3** gave 2,7-di-(*p*-methoxyphenyl)-4,4,5,5-tetraphenyl(4H)thiepin (**15**). The reaction mechanisms are discussed.

The reactions of 3-oxo-1,2-dithioles with several reagents have been investigated,[2-8] but their reactions with diazoalkanes and copper-bronze have not been studied, while the reactions with Grignard reagents[8] have received little attention.

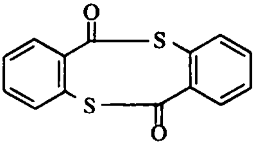


1



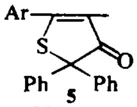
2: Ar = Ph
3: Ar = $C_6H_4OCH_3(p)$

We found that 4,5-benzo-3-oxo-1,2-dithiole (**1**) reacted with diphenyldiazomethane to give dibenzoyl and with copper-bronze to give 2,2′-di-(thiobenzoate) (**4**), which on hydrochloric acid hydrolysis afforded thiosalicyclic acid.



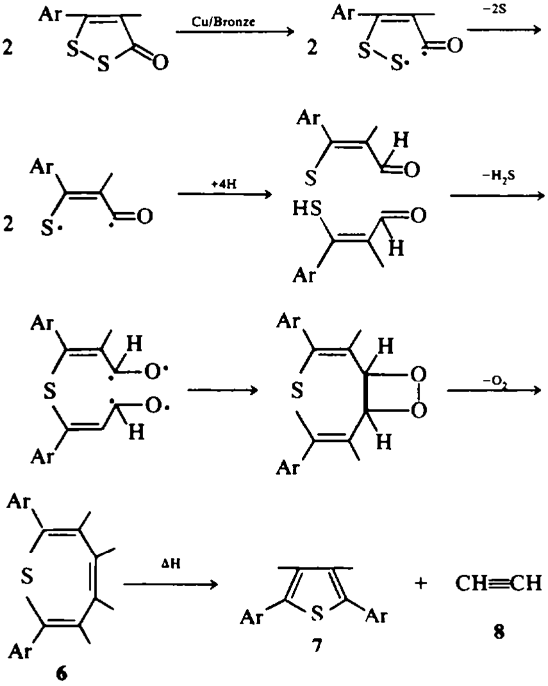
4

5-phenyl- and 5-*p*-methoxyphenyl-3-oxo-1,2-dithiole (**2** and **3**, respectively) with diphenyldiazomethane afforded 2,2,5-triphenyl- and 5-*p*-methoxyphenyl-2,2-diphenyl-3-oxo(2H)-thiophene (**5a** and **b**, respectively).



5
a: Ar = Ph
b: Ar = $C_6H_4OCH_3(p-)$

With copper-bronze, compound **2** afforded 2,7-diphenylthiepin (**6a**) together with 2,5-diphenylthiophene (**7a**), while compound **3** afforded, on similar treatment, only 2,5-di-(*p*-methoxyphenyl)thiophene (**7b**), which probably has arisen from the more thermally unstable 2,7-di-(*p*-methoxyphenyl)thiepin (**6b**) according to the following reaction sequence:



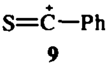
a: Ar = Ph; **b**: Ar = $C_6H_4OCH_3(p-)$

The NMR spectrum of compound **6a** gave a signal at δ 7·5 corresponding to 10 aromatic protons and a signal at δ 7·2 corresponding to the 4 heptagonal ring protons. Its mass spectrum gave a peak for the parent ion (**6a**$^+$) at *m/e* 262, a strong peak at 236

---

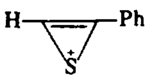
†Present address: Département de Chimie, Faculté des Sciences, Université d'Alger, Alger, Algerie.

(**6a** − CH≡CH; M − 26) corresponding to **7a**$^+$ (proving the splitting of **6** into **7** and **8**). Two other peaks appeared at *m/e* 134 and 121 corresponding to the fragments **9** and **10**, respectively.



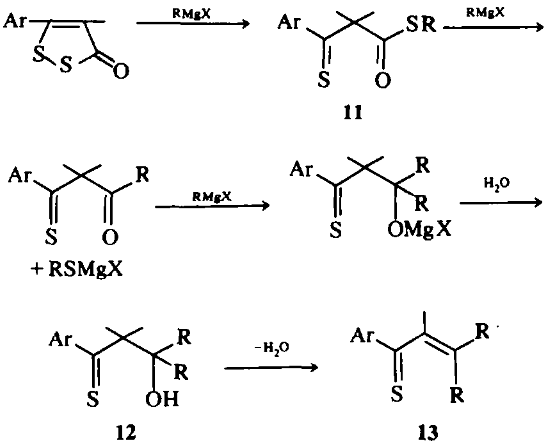
$S{=}\overset{+}{C}{-}Ph$

9



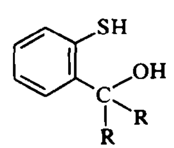
10

Boberg and Schardt[8] found that dithiolones with Grignard reagents in the proportion 1:1 afforded the respective thiol esters **11**. We found, however, that using excess of the Grignard reagents gave the following reaction sequence:



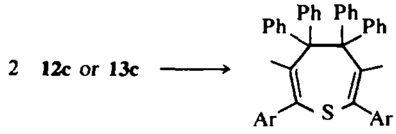
a: Ar = Ph, R = Ph
b: Ar = Ph, R = $C_{10}H_7(\alpha\text{-})$
c: Ar = $C_6H_4OCH_3(p\text{-})$, R = Ph

Compound **2** gave α-phenylchalcone (**13a**, O instead of S) and diphenyl disulphide when reacted with phenylmagnesium bromide. With α-naphthylmagnesium bromide compound **2** reacted also in a similar way to give 1,1 - di - (α - naphthyl) - 2-thiobenzoylethylene (**13b**). Formation of intermediate **12** is confirmed by the product 2 - (1 - phenylthiol)-α,α-dinaphthylmethanol (**14**) obtained from the reaction of compound **1** with excess of α-naphthylmagnesium bromide.



14

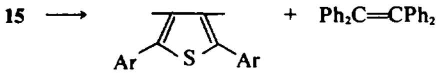
Compound **3**, with excess of phenylmagnesium bromide afforded 2,7 - di - (*p* - methoxyphenyl) - 4,4,5,5 - tetraphenyl(4H) - thiepin (**15**) as a result of cyclisation of **12c** or **13c**.



15

Ar = $C_6H_4OCH_3(p\text{-})$

Compound **15** when brominated afforded its tetrabromide (**16**). Compound **15**, being similar to compound **6**, is expected to undergo thermal cleavage and in fact when it was boiled in nitrobenzene it gave tetraphenylethylene and 2,5 - di - (*p* - methoxyphenyl)thiophene (**7b**)



7b

EXPERIMENTAL

M.ps are uncorrected and measured on a kofler apparatus. Microanalyses: by Microanalytical Lab., N.R.C., Cairo, and Michel Beller Lab., West Germany. Molecular weights: by electrothermal method (New-Mayer) at Microanalytical Unit, Faculty of Science, Cairo University. NMR: by Varian A-100 spectrophotometer.

Action of diazomethane on **1**. A mixture of **1** (1 g; 0·006 mole) in dry benzene (50 ml) and diphenyldiazomethane (3 g; 0·015 mole) was refluxed for 5 hr. The mixture was concentrated and left to cool. The solid product (0·4 g; 40%) that was separated by filtration was proved to be unreacted **1**. M.p. and mixed m.p. with an authentic sample of **1** 76°. The filtrate was evaporated to dryness. The residual solid (0·3 g; 50%) was recrystallized from EtOH, m.p. and mixed m.p. with an authentic sample of dibenzoyl[9] 95°.

Action of diazomethane on **2**. Compound **2** (2 g; 0·0103 mole) in dry benzene (50 ml) reacted with diphenyldiazomethane (4 g; 0·206 mole). The solid **5a** obtained (1·8 g; 53%) had m.p. 162° from EtOH. (Found: C, 81·5; H, 5·2; S, 9·2. $C_{22}H_{16}OS$ (328) requires: C, 80·5; H, 4·9; S, 9·7%. M. wt. Found: 338).

Action of diazomethane on **3**. A mixture of **3** (2 g; 0·0096 mole) in dry benzene (80 ml) was refluxed for 10 hr. The solid **5b** obtained (1·7 g; 50%) had m.p. 171–172° from EtOH. (Found: C, 77·0; H, 5·5; S, 9·0. $C_{23}H_{18}O_2S$ requires: C, 77·1; H, 5·0; S, 8·9%).

Action of copper-bronze on **1**. A mixture of **1** (3 g; 0·0168 mole) in dry xylene (150 ml) and copper-bronze (4 g) was refluxed for 10 hr. The mixture was filtered while hot and the solvent was evaporated till dryness. The residual solid **4** (1·7 g; 74%) had m.p. 183°[10,11] from EtOH. (Found: C, 61·4; H, 2·9; S, 23·3%. Calcd. for $C_{14}H_8S_2O_2$: C, 61·8; H, 2·9; S, 23·5%).

Action of hydrochloric acid on **4**. A mixture of **4** (2 g; 0·0073 mole) and 20% HCl (20 ml) was refluxed for 8 hr. The mixture was filtered after cooling and the solid obtained (2·1 g; 95%) recrystallized from light petroleum (b.p. 80–110°), m.p. and mixed m.p. with an authentic sample of thiosalicylic acid 164°.

Action of copper-bronze on **2**. A mixture of **2** (3 g; 0·015 mole) in dry xylene (100 ml) and copper-bronze (3 g) was refluxed for 10 hr, then filtered while hot and the filtrate was distilled under reduced pressure. The residual oil was chromatographed on alumina column. Elution with cyclohexane gave the first fraction, a white solid **7a** (0·9 g; 50%), m.p. (from EtOH) and mixed m.p. with an authentic sample of 2,5-diphenylthiophene[12] 151°.

Elution with cyclohexane-benzene (50:50) gave the second fraction, a pale brown solid **6a** (0·8 g; 40%), m.p. 130–131° from n-hexane. (Found: S, 12·2. $C_{18}H_{14}S$ (262) requires S, 12·2%. M.wt. Found: 267).

Treatment of **6a** *with bromine.* Compound **6a** (0·1 g; 0·0004 mole) was isolated unchanged after refluxing for 3 hr with a soln of Br_2 (6 ml; 0·12 mole) in glacial AcOH (50 ml).

Action of copper-bronze on **3**. A mixture of **3** (2 g; 0·0096 mole) in dry xylene (100 ml) and copper-bronze (3 g) was refluxed for 8 hr and filtered while hot. The solvent was distilled off under reduced pressure. The residual oil gave only one fraction when chromatographed on alumina column. Elution with cyclohexane gave **7b** (0·5 g; 26%), recrystallized from n-hexane, m.p. and mixed m.p. with an authentic sample of 2,5 - di - (*p* - methoxyphenyl)thiophene[13] 215°.

Action of phenylmagnesium bromide on **2**. A soln of PhMgBr (0·046 mole) in dry ether (40 ml) was added dropwise to a soln of **2** (2·91 g; 0·015 mole) in dry benzene (50 ml). The mixture was left overnight, then refluxed for 4 hr, cooled and poured onto ice-HCl mixture. The organic layer was separated, dried (Na_2SO_4), and the solvents were removed under reduced pressure. The residual oil was chromatographed on alumina column. Elution with n-hexane gave the first fraction, diphenyl disulphide (1·7 g; 53%), recrystallized from MeOH, m.p. and mixed m.p. with an authentic sample of diphenyl disulphide[14] 61°.

Elution with n-hexane–benzene (50:50) gave the second fraction **13a** (O instead of S) (0·7 g; 16%), recrystallized from n-hexane, m.p. 92°.[15] (Found: C, 88·7; H, 5·5%. Calcd. for $C_{21}H_{16}O$: C, 88·7; H, 5·6%).

Action of α-naphthylmagnesium bromide on **2**. Compound **2** (1·94 g; 0·01 mole) in dry benzene (50 ml) was treated with a soln of oc-naphthylmagnesium bromide (0·04 mole) in dry ether (40 ml). The organic layer was collected and the solvents were distilled under reduced pressure. The residual oil solidified to give **13b** (1·2 g; 30%), m.p. 199–200° from EtOH-benzene. (Found: C, 87·1; H, 5·1; S, 8·4. $C_{29}H_{20}S$ (400) requires: C, 87·0; H, 5·0; S, 8·0%. M.wt. Found: 397).

Action of α-naphthylmagnesium bromide on **1**. Compound **1** (3 g; 0·018 mole) in dry benzene (50 ml) was treated as before with a soln of oc-naphthylmagnesium bromide (0·1 mole) in dry ether (50 ml) to yield **14** (1·5 g; 22%), m.p. 201° from MeOH-benzene. (Found: S, 8·2. $C_{27}H_{20}OS$ requires: S, 8·2%).

Action of phenylmagnesium bromide on **3**. Compound **3** (2·25 g; 0·0108 mole) in dry benzene (100 ml) was treated as before with a soln of PhMgBr (0·045 mole) in dry ether. The residual oil was chromatographed on alumina column. Elution with n-hexane gave **15** (0·9 g; 26%), m.p. 173–175° from EtOH. (Found: C, 84·05; H, 6·6; S, 5·5. $C_{44}H_{36}O_2S$ requires: C, 84·1; H, 5·7; S, 5·1%).

Action of bromine on **15**. A soln of Br_2 (6 ml; 0·12 mole) in glacial AcOH (20 ml) was added dropwise to a hot soln of **15** (0·3 g; 0·0005 mole) in glacial AcOH (50 ml). The mixture was distilled off under reduced pressure. The residual oil solidified using EtOH to yield **16** (0·2 g; 44%), m.p. 156° from EtOH. (Found: Br, 34·3. $C_{44}H_{36}O_2SBr_4$ requires: Br, 33·75%).

Thermal decomposition of **15**. A mixture of **15** (0·5 g; 0·0008 mole) and nitrobenzene (100 ml) was refluxed for 10 hr. The solvent was distilled off under reduced pressure and the residual oil was chromatographed on alumina column. The first product was eluted with n-hexane to yield tetraphenylethylene (0·06 g; 23%) m.p. (from EtOH) and mixed m.p. with an authentic sample of tetraphenylethylene[16] 224°.

Elution with n-hexane–benzene (7:3) gave the second product **7b** (0·04 g; 17%), m.p. and mixed m.p. with an authentic sample of **7b**[13] showed no depression.

REFERENCES

[1] Part IV. M. A.-F. Elkaschef, M. H. Nosseir and A. I. Atwa, *J. Chem. U.A.R.* **9**, 175 (1966)

[2] S. Smiles and E. W. McClelland, *J. Chem. Soc.* **121**, 86 (1922)

[3] E. W. McClelland and J. Longwell, *Ibid.* **123**, 3310 (1923)

[4] F. Boberg, *Liebigs Ann.* **678**, 67 (1964)

[5] E. Klingsberg, *J. Am. Chem. Soc.* **85**, 3244 (1963)

[6] B. Böttcher and F. Bauer, *Liebigs Ann* **568**, 227 (1950)

[7] E. Baumann and E. Fromm, *Ber. Dtsch. Chem. Ges* **30**, 110 (1897)

[8] F. Boberg and R. Schardt, *Liebigs Ann.* **728**, 44 (1969).

[9] H. T. Clarke and E. E. Dreger, *Organic Syntheses Coll.* Vol. **1**, 87

[10] R. Anschütz and E. Rhodius, *Ber Dtsch. Chem. Ges* **47**, 2733 (1914)

[11] W. Baker, A. S. El-Nawawy and W. D. Ollis, *J. Chem. Soc.* 3163 (1952)

[12] E. Fromm, P. Fantle and E. Leibsohn, *Liebigs Ann.* **457**, 271 (1927).

[13] E. Campaigne and W. O. Foye, *J. Org. Chem.* **17**, 1405 (1952)

[14] F. Krafft and W. Vorster, *Ber. Dtsch. Chem. Ges* **26**, 2815 (1893)

[15] I. Smedley, *J. Chem. Soc.* **97**, 1494 (1910)

[16] R. E. Buckles and M. Matlack, *Organic Syntheses* **31**, 104 (1951)