plex) c 4.40 (1 H, d, J = 9 Hz), d 2.42 (s, 6 H), e 1.21 (3 H, d, J = 6.8 Hz), f 3.80 (1 H, q, J = 6.8 Hz)][5] and thence into 2,4-dimethyl-3(2*H*)-furanone (**3b**): nmr a 1.3 (3 H, d, J = 7 Hz), b 4.41 (1 H, q, J = 7 Hz), c 1.61 (3 H, d, $J \sim$ 1 Hz), d 8.14 (1 H, m); m/e 112; ir 1700, 1760 $\mathrm{cm^{-1}}$.

In striking contrast to **1a–c** the highly reactive 4,4-dimethyl-2-dimethylamino-5-methylene-1,3-dioxolane (**4**) showed no trace of **8** when being warmed to room temperature. Instead, a more deep-seated rearrangement took place and after removal of the solvent 1-dimethylamino-4-hydroxy-4-methyl-1-penten-3-one (**7**) was isolated as a clear viscous liquid in quantitative (100%) yield: nmr δ (TMS, CCl_4, 25°) a 1.23 (s, 6 H), b 3.0 (br s, 6 H), c 4.5–4.6 (br s, 1 H), d 7.59 (1 H, d, J = 12 Hz), e 5.06 (1 H, d, J = 12 Hz). Above 35° (solvents $CFCl_3$, CCl_4) **7** showed a sharp dimethylamino resonance at δ 2.96 which broadened on cooling to room temperature and split into two singlets below 15°. Based on the coalescence temperature 15.5 ± 1° and $\Delta\nu$ = 31 Hz at −20° the barrier to rotation in **7** is $\Delta G^{\ddagger}$ = 13.7 kcal/mol, in excellent agreement with the rotation barriers reported for structurally related enamines.[6] On addition of D_2O or MeOD the peak at 4.4–4.5 ppm disappeared from the nmr and an O–D peak appeared at 2510 $\mathrm{cm^{-1}}$ in the ir; mass spectrum m/e 157, 142 (M − Me), 139 (M − H_2O), 112 (M − $HNMe_2$), 98 ($Me_2NCH{=}CHCO$), 59 (Me_2COH), and further peaks at 158, 97, 96, 82, 74, 72, 71, 70, 56, and 55.

Interestingly, the postulated intermediate **5** could not be detected in the nmr spectrum which throughout the rearrangement showed the signals of **4** and **7** only, even if the reaction was allowed to take place under the mildest possible conditions, *i.e.*, between 0 and 10°. However, the ir spectrum of **7** contained a weak shoulder at 1730 $\mathrm{cm^{-1}}$, not inconsistent with a small amount of **5** (carbonyl stretching of a cyclopentanone) at equilibrium.[7] In any event, under acidic conditions (catalytic amounts of CF_3CO_2D at 25° or on heating in methanol and even on addition of methyl iodide) the enamino ketone **7** was cleanly converted into 2,2-dimethyl-3(2*H*)-furanone (**8**),[8] which after extraction with ether was isolated as a sweet smelling oil: nmr 1.36 (s, 6 H), 5.49 (1 H, d, J = 2.5 Hz), 8.09 (1 H, d, J = 2.5 Hz); ir 1700, 1760 $\mathrm{cm^{-1}}$; mass spectrum 112, 97, 71, 69, 58, 54, 43, and 41.

In analogy to the transformations described above the fully methylated heterocycle **9** might have been expected to yield the cyclic α-amino ether **12** on heating. However, as we have shown previously, loss of dimethylformamide from **9** occurs readily and affords the simple aliphatic enol **10** in high concentrations, before the thermodynamically stable ketone **11** is formed finally.[9]

Interestingly, the E1 type formation of **10** can be suppressed in the presence of $ZnBr_2$ which is introduced most conveniently *via* the preparation of **9** itself, without isolation of any intermediates. Thus, 2,4-dibromo-2,4-dimethyl-3-pentanone (5 g, 0.02 mol) and zinc–copper couple (3.7 g, 0.06 mol) in dimethylformamide (25 ml) were allowed to react at −15° in the reactor–extractor[4] and then isopentane (25 ml) was introduced as a seal against deleterious traces of oxygen and moisture. The reaction mixture was protected from light and gently stirred for 1 week at room temperature. Continuous extraction of the products from the mother liquor with isopentane at −40° gave an extract containing dimethylformamide (40%), **11** (5%), unchanged **9** (5%), and 2,2,4,4-tetramethyl-5-dimethylaminotetrahydrofuran-3-one (**12**), which was freed from **11** and most of the solvent dimethylformamide by slow vacuum distillation at room temperature into a Dry Ice trap: yield of **12**, 2.05 g (60%); nmr δ (TMS, CCl_4) 1.02 (s, 3 H), 1.08 (s, 3 H), 1.15 (s, 3 H), 1.23 (s, 3 H), 2.31 (s, 6 H), 4.05 (s, 1 H); ir ν_{CO} 1745 $\mathrm{cm^{-1}}$ (vs); mass spectrum m/e 185.1390; calcd for $C_{10}H_{19}NO_2$, 185.1416.

To conclude, 2-dimethylamino-4-methylene-1,3-dioxolanes seem ideally disposed toward formation of 3-(2*H*)-furanones, since they contain a preformed ammonium enolate zwitterion which can readily undergo C-alkylation and suffer loss of dimethylamine with equal ease, given the possibility of elimination.[10]

Acknowledgments. We are grateful to the Petroleum Research Fund, administered by the American Chemical Society, the Science Research Council, London, and the Dr. Carl Duisberg-Stiftung and Schering AG Berlin for support of our work.

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(5) Note that $J_{b,c}$ = 9 Hz for **2a** as well as **2b** (**2c**). Steric considerations suggest that H_b and H_c are trans in both compounds.

(6) A. Mannschreck and U. Koelle, *Tetrahedron Lett.*, 863 (1967); M. L. Blanchard, A. Chevalier, and G. J. Martin, *ibid.*, 5057 (1967).

(7) In the corresponding enamino ketones from **2a–c** a methyl or a bulky acyl grouping would have to be cis to the dimethylamino grouping; this situation seems sterically unfavorable [*cf.* G. Stork, A. Brizzolara, H. Landesman, J. Smuszkowicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963); W. D. Gurowitz and M. A. Joseph, *Tetrahedron Lett.*, 4433 (1965)].

(8) For additions of carbon nucleophiles to the β-aminoacryl moiety in alkaloid synthesis see E. Wenkert, *Accounts Chem. Res.*, **1**, 78 (1968).

(9) H. M. R. Hoffmann and E. A. Schmidt, *J. Amer. Chem. Soc.*, **94**, 1373 (1972); E. A. Schmidt and H. M. R. Hoffmann, *ibid.*, in press.

(10) The recently described synthesis of isobullatenone and a demethylated analog appears to proceed by a similar sequence of reactions; see M.-A. Barrow, A. C. Richards, R. H. Smithers, and H. M. R. Hoffmann, *Tetrahedron Lett.*, 3101 (1972).

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The Thieno[3,4-*c*]furan and Thieno[3,4-*c*]pyrrole Systems. Unusual Nonclassical Heterocycles

Sir:

We have previously reported the synthesis of tetraphenylthieno[3,4-*c*]thiophene (**1**), a stable derivative of a 10π-electron heterocycle for which the only uncharged resonance contributors are structures containing tetracovalent sulfur.[1] We now report the generation of novel analogs (**2** and **3**) of **1** in which one of the two sulfur atoms is replaced by an oxygen or a nitrogen, respectively.

Treatment of tetrabenzoylethane[2] with hydrogen chloride in acetic acid afforded, in 90% yield, 2,5-diphenyl-3,4-dibenzoylfuran (**4**), mp 128–129°. Borohydride reduction of **4** gave an epimeric mixture of the corresponding diols (**5**). Reaction of **5** with phos-

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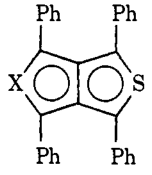
(1) M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969), and other references cited therein.

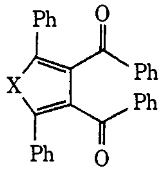
(2) A. Andres, Dissertation, Strassburg, 1911.

phorus pentasulfide in carbon disulfide[3] gave, after alumina chromatography, the cis sulfide **6**, mp 246–248°, in 19% yield.[4] Periodate oxidation[5] of **6** gave (92%) the corresponding sulfoxide **7**, mp 241–243° dec.

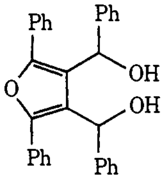
When **7** was refluxed in acetic anhydride under nitrogen, a pale violet color appeared; attempted work-up (tlc) indicated the formation of a complex mixture which has not yet been resolved. However, when the same dehydration of **7** was carried out in the presence of dimethyl acetylenedicarboxylate, adduct **8**, mp 228–230°, was readily isolated in 70% yield, indicating the intermediary formation of the thienofuran **2**. The assigned structure **8** was supported by the presence of a strong (33%) M − 16 peak in its mass spectrum, and was confirmed by the deoxygenation of **8** by hot triethyl phosphite to give the isothianaphthene diester **9**.[6]



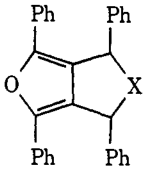
1, X = S
2, X = O
3, X = NCH$_3$



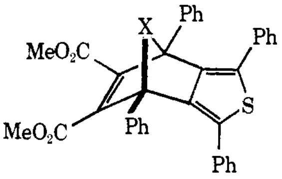
4, X = O
10, X = NCH$_3$



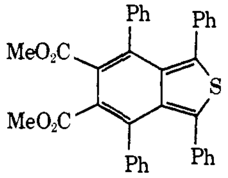
5



6, X = S
7, X = SO



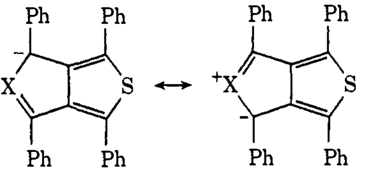
8, X = O
11, X = NCH$_3$



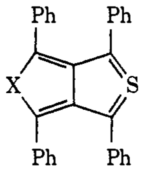
9

The reaction of tetrabenzoylethane with methylamine in acetic acid afforded (90%) 1-methyl-2,5-diphenyl-3,4-dibenzoylpyrrole (**10**), mp 198–200°. Treatment of diketone **10** with phosphorus pentasulfide in refluxing toluene (1.5 hr), followed by evaporation of the solvent, gave an amorphous brown solid. Digestion of this solid with hot 10% aqueous sodium hydroxide afforded a bright red powder, which is stable to air for weeks in the dry state. This material, which shows a strong peak at *m/e* 441 and a strong absorption maximum in benzene at 526 nm, consists primarily of thienopyrrole **3**, as shown by its rapid reaction with dimethyl acetylenedicarboxylate in chloroform to give (>85%) adduct **11**, mp 247–248°. The structure of adduct **11** was supported by the shielded value (δ 1.72) of its *N*-methyl group, and confirmed by its conversion (98% yield) to isothianaphthene **9** by oxidation with *m*-chloroperbenzoic acid.[7]

Heterocycles **2** and **3** may be viewed electronically as hybrids of 1,3-dipolar (**2a** and **3a**) and tetravalent thiophene contributors (**2b** and **3b**). The greater stability of **3** relative to **2** is not unexpected in view of the greater electronegativity of oxygen as compared to nitrogen. Although we cannot rule out the possibility of a triplet ground state for the transient thienofuran **2**, we have observed that benzene solutions of the more stable thienopyrrole **3** give no esr signal, thereby indicating a singlet ground state. In this regard, it may be noted that recent SCF-MO calculations, assuming no sulfur d orbital participation, have predicted a triplet ground state for thieno[3,4-*c*]pyrrole.[8]



a



b

2, X = S
3, X = NCH$_3$

Acknowledgment. We thank the National Institutes of Health (for a Predoctoral Fellowship to M. A. Sprecker) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(3) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).

(4) Satisfactory analyses were obtained for all new compounds reported with melting points. Nmr and mass spectra were found to be consistent with assigned structures.

(5) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(6) We thank Dr. M. Behforouz for an authentic sample of **9** prepared from the reaction of **1** with dimethyl acetylenedicarboxylate (unpublished results).

(7) This reaction undoubtedly proceeds by formation of the *N*-oxide of **11** followed by a facile elimination of nitrosomethane. For a closely related decomposition of an aziridine *N*-oxide to an olefin, see J. E. Baldwin, A. K. Bhatnager, Se Chun Choi, and T. J. Shortridge, *J. Amer. Chem. Soc.*, **93**, 4082 (1971).

(8) L. Klasinc and N. Trinajstic, *Tetrahedron*, **27**, 4045 (1971).

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The Synthesis of Stable "Tetravalent Sulfur" Heterocycles

Sir:

Syntheses of several stable, nonclassical 10π-electron heterocycles have been reported[1] recently in the literature, these compounds being of particular interest because of the tetravalent environment of the sulfur. We now wish to describe a simple synthetic route to the thieno[3,4-*c*]pyrazole system (**3**). Yields of the order of 85% in each of two steps makes this unusual aromatic system available in sufficient quantity for detailed chemical studies.

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(1) (a) M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969); (b) J. M. Hoffman and R. H. Schlessinger, *ibid.*, **91**, 3953 (1969); J. D. Bower and R. H. Schlessinger, *ibid.*, **91**, 6891 (1969); (c) F. H. M. Deckers, W. N. Speckamp, and H. O. Huisman, *Chem. Commun.*, 1521 (1970); (d) D. W. H. MacDowell, A. T. Jeffries, and M. B. Meyers, *J. Org. Chem.*, **36**, 1416 (1971).