alkyl chlorides. Their data on $C_4H_{10}O$ alcohols are shown in Table II.[15] For the borneols, the peak for loss of OH is about $^1/_{20}$th as intense as the M − HOH peak.

Table II. A Comparison of the Loss of HOH *vs.* OH for Isomeric Butyl Alcohols[a]

Compound	M − HOH intensity	M − OH rel intensity
n-Butyl alcohol	1	0.074
Isobutyl alcohol	1	1.3
sec-Butyl alcohol	1	2.8
tert-Butyl alcohol	1	6.3

[a] Taken from the data of ref 13.

From the data of Table II, it seems reasonable to conclude that, when a stable carbonium ion results, loss of hydroxy radical can occur. We would expect that ion **10** would fall in the class of a fairly stable carbonium ion and could conceivably be formed in the manner shown. If our conclusions are correct, it leaves open the question as to how many other electron impact dehydrations are also two-step eliminations of water. This hypothesis may also explain why so many bicyclic alcohols which are endo and exo isomers show nearly identical mass spectra.[16] Work is continuing in this area to attempt to verify these ideas.

Acknowledgments. We are grateful to the Research Corporation for their support of this work and Dr. T. C. Ehlert for his assistance.

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(15) Comparing two mass spectral peaks for relative abundance may or may not be valid depending on whether these ions are further reacting to approximately the same extent.

(16) D. R. Dimmel and J. Wolinsky, *J. Org. Chem.*, 32, 2735 (1967).

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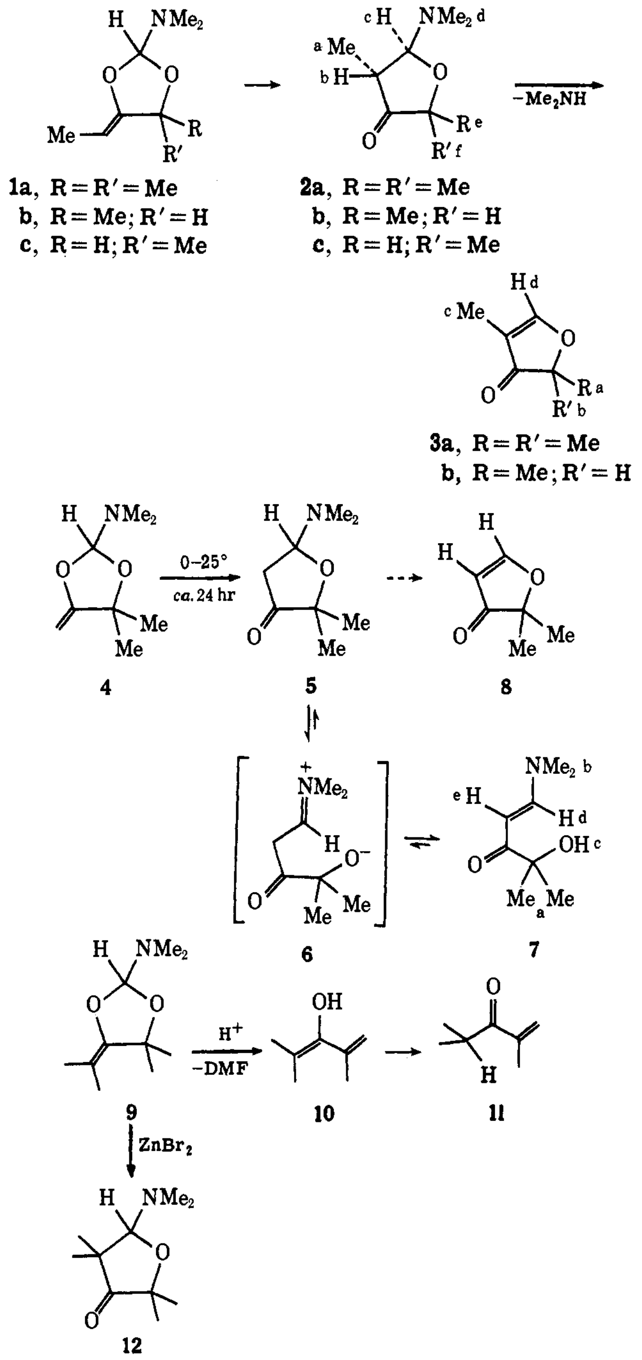
Synthesis of 3(2*H*)-Furanones

Sir:

3(2*H*)-Furanones have been used as building blocks for the synthesis of muscarins[1] and are valued by perfumers owing to their pleasant and varied odors.[2] We here describe a new and efficient route to these heterocycles,[3] which uses 2-dimethylamino-4-methylene-1,3-dioxolanes[4] as the key intermediates.

Experimentally, the reactions are simple and can be monitored conveniently by nmr. For instance, on being heated in a 1 *M* dimethylformamide solution to 60°, **1a** disappears with a half-life of less than 1 hr to form the α-amino ether **2a** (Scheme I) (nmr δ (TMS) a 1.00 (3 H, d, $J = 7$ Hz), b 2.5 (complex, largely obscured by other signals), c 4.42 (1 H, d, $J = 9$ Hz), d 2.39 (s, 6 H), e, f 1.11 (s, 3 H), 1.20 ppm (s, 3 H)). As a β-ketoamine which is rendered even more labile by an α-ether grouping, **2a** would be expected to be very reactive and indeed was found to suffer loss of dimethylamine almost before its formation from **1a** was complete, yielding 2,2,4-trimethyl-3(2*H*)-furanone (**3a**): nmr δ (TMS, DMF) a, b 1.28 (s, 6 H), c 1.64 (3 H, d, $J \sim 1$ Hz), d 8.2 (br, 1 H); ir 1710, 1760 cm^{-1}; mass spectrum 126, 71, 69, 58, 57, 55. Alternatively, the transformation of **1a** into **3a** can be brought about simply by leaving a solution of **1a** in CCl_4 for 1 week at room temperature.

Scheme I



Analogously, the epimeric mixture of aminoacetals **1b** + **1c** was heated to 60° and found to rearrange into **2b** (or **2c**) [nmr a 0.99 (3 H, d, $J = 7$ Hz), b 2.3 (com-

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(1) Reviews: S. Wilkinson, *Quart. Rev., Chem. Soc.*, 15, 153 (1961); C. H. Eugster, *Advan. Org. Chem.*, 2, 427 (1960).

(2) R. Teranishi in "Gustation and Olfaction," G. Ohloff and A. F. Thomas, Ed., Academic Press, New York, N. Y., 1971, p 165; see also R. E. Rosenkranz, K. Allner, R. Good, W. v. Philipsborn, and C. H. Eugster, *Helv. Chim. Acta*, 46, 1259 (1963); A. Hofmann, W. v. Philipsborn, and C. H. Eugster, *ibid.*, 48, 1322 (1965); L. Re and G. Ohloff, U. S. Patent 3,576,014 (1971).

(3) Work described in part at the SCB Symposium in Louvain, Belgium, Sept 1971; see also H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 11, 324 (1972).

(4) H. M. R. Hoffmann, K. E. Clemens, E. A. Schmidt, and R. H. Smithers, *J. Amer. Chem. Soc.*, 94, 3201 (1972).

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 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$_2$O or MeOD the peak at 4.4–4.5 ppm disappeared from the nmr and an O–D peak appeared at 2510 cm^{-1} in the ir; mass spectrum *m/e* 157, 142 (M − Me), 139 (M − H$_2$O), 112 (M − HNMe$_2$), 98 (Me$_2$NCH=CHCO), 59 (Me$_2$COH), 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 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$_3$CO$_2$D 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 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 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]

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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.