Debromination of α,α'-Dibromo Ketones with a Zinc–Copper Couple in Dimethylformamide and Dimethylacetamide. A New Reaction Yielding 2-Dimethylamino-4-methylene-1,3-dioxolanes

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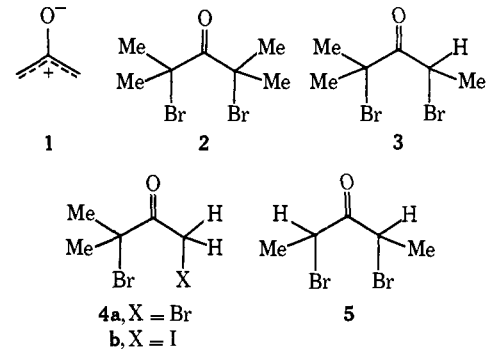
Abstract: The synthesis of 2-dimethylamino-4-methylene-1,3-dioxolanes, *i.e.*, **6**, **7**, **8**, **9a**, **9b**, **10**, and **11**, has been accomplished by debromination of α,α'-dibromo ketones with a zinc–copper couple in dimethylformamide and dimethylacetamide. An apparatus has been devised which allows the preparation and isolation of these highly sensitive heterocyclics at low temperature. The formation of the cycloadducts is (i) stereospecific with respect to the methyl group attached to the exocyclic olefinic carbon in **7**, **9a**, and **9b**, which is cis to the vicinal oxygen, and (ii) orientationally uniform in that the oxygen of the erstwhile dimethylformamide and dimethylacetamide is attached exclusively to the more highly alkylated oxyallyl terminus.

In exploring various routes to stabilized allylic cations[2] we have discovered a surprisingly simple and general reaction which in starting from a ketone affords 2-dimethylamino-4-methylene-1,3-dioxolanes in two stages. Formally, these heterocyclics can be regarded as 1,3-dipolar adducts of dimethylacetamide and oxyallyl **1**, a species which has been of increasing synthetic[3a–c] and theoretical[3d,e] interest although its existence as a planar and free entity seems still hypothetical. Since our adducts are *inter alia* 1-aminoacetals[4] and since dimethylformamide and dimethylacetamide must rank among the weakest dipolarophiles on record,[5] it comes as no surprise that the new compounds show outstanding reactivity which necessitates special care in their preparation and isolation.

Synthesis and Spectral Identification. The α,α'-dibromo ketones 2,4-dibromo-2,4-dimethyl-3-pentanone (**2**), 2,4-dibromo-2-methyl-3-pentanone (**3**), 1,3-dibromo-3-methyl-2-butanone (**4a**), and 2,4-dibromo-3-pentanone (**5**) were readily obtained by treating the corresponding ketones which are commercially available with bromine. The mixed bromoiodo ketone **4b**, 3-bromo-1-iodo-3-methyl-2-butanone, was prepared from **4a** *via* displacement with iodide ion.



On slow addition of the dihalo ketones to a stirred suspension of a highly active zinc–copper couple[6] in dimethylformamide at −30 to −40°, dehalogenation ensued with formation of zinc dihalide and the desired products. Considerable experimental difficulties were encountered in isolating and purifying the sensitive adducts. Clearly, not only is $ZnBr_2$ an aggressive Lewis acid, which tends to attack the cycloadducts even when they are kept at −78° overnight in dimethylformamide solution, but the propensity of the products to form azeotropes with dimethylformamide, noted previously by various workers when dealing with simple 1-aminoacetals,[4b,c] or even to decompose on distillation under high vacuum[4a] had to be overcome as well. In order to reduce the undesirable effect of $ZnBr_2$, we initially converted it into $Zn(NO_3)_2$ with $AgNO_3$ or precipitated it as $Zn(C_9H_9N)Br_2$ complex with quinoline and distilled the products together with solvent at 0° or below. However, attempts to concentrate the distillate by further fractionation were not successful and all solutions obtained contained at least 90% dimethylformamide, which partly obscured the nmr and ir spectra of the products and complicated their identification. It proved to be a key observation that the cycloadducts could be extracted continuously from the

(1) (a) Graduate fellow, 1968–1971; (b) graduate fellow, 1970–present; (c) graduate fellow, 1967–1970.

(2) H. M. R. Hoffmann, G. F. P. Kernaghan, and G. Greenwood, *J. Chem. Soc. B*, 2257 (1971), and references cited therein; see also G. Greenwood and H. M. R. Hoffmann, *J. Org. Chem.*, 37, 611 (1972).

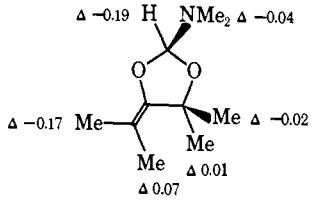
(3) (a) N. J. Turro, *Accounts Chem. Res.*, 2, 25 (1969); (b) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Amer. Chem. Soc.*, 91, 2283 (1969); (c) R. G. Doerr and P. S. Skell, *ibid.*, 89, 4684 (1967); (d) R. Hoffmann, *ibid.*, 90, 1475 (1968); see, however, (e) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, 92, 3854 (1970).

(4) For selected references, see (a) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Justus Liebigs Ann. Chem.*, 641, 1 (1961); (b) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Chem. Ber.*, 96, 2671 (1963); (c) H. Bredereck, G. Simchen, S. Rebsdat, W. Kantlehner, P. Horn, R. Wahl, H. Hoffmann, and P. Grieshaber, *ibid.*, 101, 41 (1968); G. Simchen, H. Hoffmann, and H. Bredereck, *ibid.*, 101, 51 (1968); (d) H. Brechbühler, H. Büchi, E. Hatz, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 48, 1746 (1965); (e) W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinauer, R. Nehring, W. Thier, and H. Hellmann, *Angew. Chem., Int. Ed. Engl.*, 5, 875 (1966); (f) *cf.* also H. H. Bosshard, E. Jenny, and H. Zollinger, *Helv. Chim. Acta*, 44, 1203 (1961); H. Vorbrüggen, *Angew. Chem., Int. Ed. Engl.*, 2, 211 (1963); Z. Arnold and M. Kornilov, *Collect. Czech. Chem. Commun.*, 29, 645 (1964); (g) reviews: R. H. DeWolfe, "Carboxylic Ortho Acid Derivatives," Academic Press, New York, N. Y., 1970, Chapter 7; J. Gloede, L. Haase, and H. Gross, *Z. Chem.*, 9, 201 (1969); R. Feinauer, *Synthesis*, 16 (1971).

(5) R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, 2, 565 (1963); *Helv. Chim. Acta*, 50, 2421 (1967).

(6) E. LeGoff, *J. Org. Chem.*, 29, 2048 (1964).

Table I. Nmr Spectra and Aromatic Solvent Induced Shifts, $\Delta = \tau_{C_6H_6} - \tau_{CCl_4}$ (ASIS),[7] of 2-Dimethylamino-4-methylene-1,3-dioxolanes[a]



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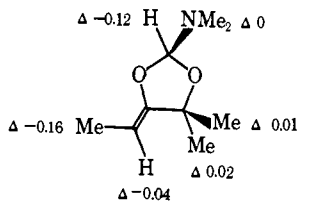

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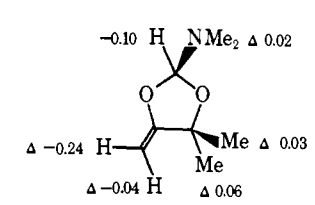

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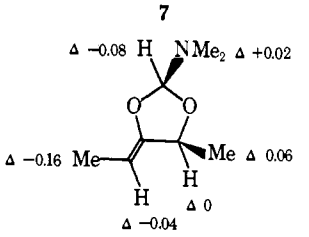
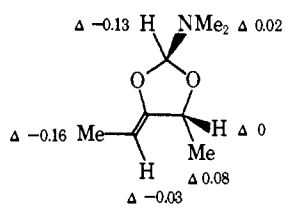


9a



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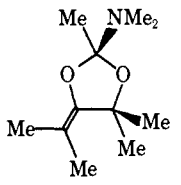

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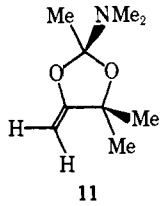

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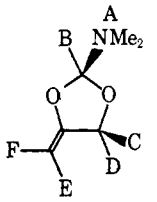


Adduct	A (s, 6 H)	B	C[b]	D[b]	E	F
6	7.74	4.57 s (1 H)	8.53 s (3 H)	8.65 s (3 H)	8.44 s (3 H)	8.40 s (3 H)
7	7.74	4.43 s (1 H)	8.66 s (3 H)	8.75 s (3 H)	6.04 q (1 H)	8.48 d (3 H), J = 7 Hz
8	7.71	4.37 s (1 H)	8.59 s (3 H)	8.68 s (3 H)	6.33 d (1 H), J = 2 Hz	6.02 d (1 H)
9a	7.77	4.54 s (1 H)	8.78 d (3 H), J = 7 Hz	5.65 q (1 H)	6.08 q (1 H)	8.51 d (3 H), J = 7 Hz
9b	7.81	4.52 s (1 H)	5.63 q (1 H), J = 7 Hz	8.85 d (3 H)	6.07 q (1 H)	8.50 d (3 H), J = 7 Hz
10	7.77	8.61 s (3 H)[c]	8.52 s (3 H)[c]	8.65 s (3 H)[c]	8.43 s (3 H)[c]	8.40 s (3 H)[c]
11	7.73	8.62 s (3 H)	8.56 s (3 H)	8.65 s (3 H)	6.27 d (1 H), J = 2 Hz	5.95 d (1 H)

[a] Recorded at 100 MHz on the τ scale using 10% solutions in CCl_4; the spectra of **6**, **7**, **8**, **9a**, and **9b** were also recorded in benzene in order to determine $\Delta = \tau_{C_6H_6} - \tau_{CCl_4}$. [b] Tentative assignments based on the spectrum of **9a** and **9b**; *cf.* text. [c] Tentative assignments.

dimethylformamide mother liquor with a solvent such as pentane or 2-methylbutane at low temperature. The hydrocarbon solvent was then removed readily at reduced pressure leaving the 2-dimethylamino-4-methylene-1,3-dioxolanes together with only about 25% of dimethylformamide. Both preparations and continuous extraction can be combined conveniently in an apparatus which we have devised for this purpose (Figure 2).

The adducts so obtained were thermally too unstable for elemental analysis and also extremely sensitive to air and even light. However, high resolution nmr demonstrated that the dimethylformamide adducts **6**, **7**, **8**, and **9a,b** were remarkably pure, *i.e.*, at least 95% aside from the remaining dimethylformamide (*ca.* 25%), as illustrated in Figure 1 for heterocycle **7**.

While the chemical shifts and coupling constants (*cf.* Table I) speak for themselves, our stereochemical assignments require detailed comment. *A priori*, the methyl group at the olefinic terminus in **7** and **9a,b** could be cis and/or trans to the enolic ether grouping, and it is rather interesting that in all cases *only one stereoisomer was formed.*

Of course, one must question whether any firm stereochemical assignment is possible when only one of two possible isomers is available. In the present instance a clear-cut assignment could be reached on the following basis.

(i) In adduct **6** the singlets at τ 8.40 and 8.44 can be assigned to the methyl protons at the olefinic terminus. The ASIS (aromatic solvent induced shift;[7] *cf.* Table I) of these two singlets is markedly different, $\Delta^{CCl_4}_{C_6H_6}$ being −0.17 and +0.07, respectively. Since an olefinic proton cis to a neighboring enol ether oxygen is deshielded relative to the trans proton,[8] the signal at τ 8.40 can be assigned to the cis methyl group and the ASIS $\Delta^{CCl_4}_{C_6H_6}$ −0.17 is diagnostic of a cis methyl group in our adducts (*cf.* Table I).

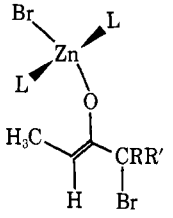
(ii) The olefinic protons of adduct **8** show an aromatic solvent induced shift of Δ −0.24 and −0.04. Since the signal associated with Δ −0.04 represents the upfield part of the olefinic quartet and can be assigned to the proton trans to the neighboring oxygen,[8] the ASIS of Δ −0.04 reveals a trans proton in adducts **7**, **9a**, and **9b**.

(iii) In heterocycle **8** the olefinic protons resonate at τ 6.02 and 6.33, the downfield signal being due to the proton cis to the vicinal oxygen.[8] Since the additive shielding increment of a geminal methyl group in an olefin is −0.45 ppm[8] (Z_{gem} = 0.45 using the δ scale), a methyl group trans to the vicinal oxygen is predicted to shift the olefinic proton resonance downfield to τ = 6.02 − 0.45 = 5.57, while a cis methyl should shift the trans proton to τ 6.33 − 0.45 = 5.88. The observed chemical shifts in **7**, **9a**, and **9b** are τ 6.04, 6.08, and 6.07, respectively, and are in better agreement with the given assignment.

(7) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967); *cf.* also D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).
(8) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *ibid.*, **25**, 691, 2023 (1969); also see S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).

Adducts **9a** and **9b** were formed on debromination of 2,4-dibromo-3-pentanone (**5**) in dimethylformamide and are isomeric with respect to the ring methyl group which can be either cis to the dimethylamino grouping as in **9a** or trans as in **9b**. For simple 2,4-dialkyl-1,3-dioxolanes which lack the exocyclic methylene group, it has been shown recently that the cis isomer can be assigned on the basis that (i) it is kinetically and thermodynamically preferred by a slight margin, (ii) its C-2 proton resonance appears upfield *vis-à-vis* the trans form, and (iii) the chemical shift of its 2-alkyl substituent (Me, *i*-Pr, and *tert*-Bu) is downfield from the corresponding signal in the trans isomer.[9] In our case the major isomer was found to (i) predominate by a factor of 5:3, (ii) exhibit its C-2 proton resonance upfield, and (iii) exhibit its dimethylamino proton resonance downfield from the minor isomer (*cf.* Table I). Hence, there is little doubt that our major isomer is the *cis*-2,4-disubstituted-1,3-dioxolane as in **9a**, and it seems likely that the methyl protons in position C, *i.e.*, cis to the dimethylamino grouping, generally appear at lower field than in position D in all other compounds (*cf.* Table I, footnote *b*).

Mechanism of Formation of the Cycloadducts. Two structural features of our cycloadducts deserve special comment. (i) The methyl group attached to the exocyclic carbon–carbon double bond in **7**, **9a**, and **9b** is cis to the vicinal oxygen, no trans isomer being formed. (ii) The oxygen originating from dimethylformamide is attached exclusively to the oxyallyl carbon terminus which can sustain the greater fraction of positive charge. A probable intermediate in the debromination is the zinc enolate **12**, in which the olefinic methyl group is



12, R = H, CH_3; R′ = CH_3; L = DMF, DMAc

stereospecifically cis to the OZnBr.[10] SNi departure of the allylic bromine from **12** or a related 2-oxyallylic bromide formed subsequently is likely to generate a relatively long-lived and therefore selective allyl cation, which we have trapped with conjugated dienes in other solvents[11] and in the case at hand combines with the nucleophilic oxygen of the solvent at the terminus of greater positive charge and then closes to the observed cycloadducts.

It is worthy of note that the cycloaddition outlined has considerable synthetic potential since, of all the acyclic α,α'-dihalo ketones which we have studied so far, only the two most simple derivatives, namely those of acetone and ethyl methyl ketone, have failed to react in the fashion described. The new adducts provide a bevy of reactive synthetic intermediates, and we shall show that they can serve as precursors of model allyl cations as well as enolate ions.

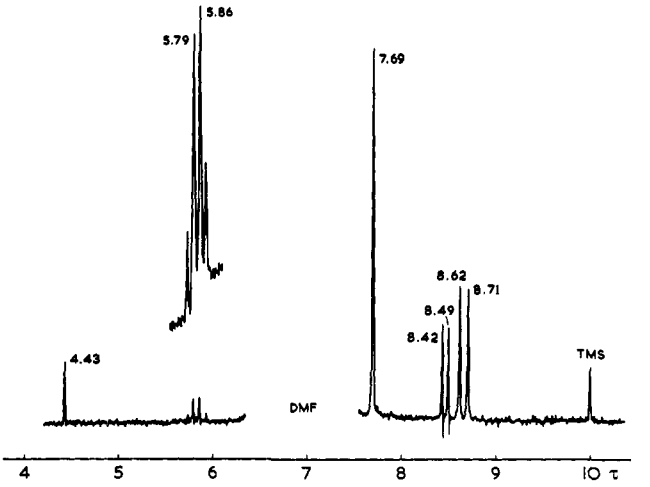


Figure 1. Nmr spectrum of **7** in DMF.

Experimental Section

Preparation of α,α'-Dibromo Ketones. The bromination of 2,4-dimethyl-3-pentanone[3c] may serve as an example for a large-scale preparation which was carried out without using any solvent. A three-necked 250-ml flask cooled in an ice bath was equipped with a dropping funnel and a water-cooled condenser, which were both protected by $CaCl_2$ drying tubes. 2,4-Dimethyl-3-pentanone (59 g, 0.52 mol) and PBr_3 (1 ml) were placed into the flask, and bromine (160 g, 1 mol) was added dropwise with magnetic stirring to the ketone over a period of *ca.* 45 min. After completed addition the reaction solution was allowed to warm to room temperature, when it decolorized slowly but completely. After HBr had been removed by blowing a stream of nitrogen through the reaction mixture, the condenser was replaced by a 30-cm Vigreux column and $CaCl_2$ granules were introduced into the flask. Distillation at 87–89° (10 mm) gave pure 2,4-dibromo-2,4-dimethyl-3-pentanone (**2**)[3c] (66% yield).

2,4-Dibromo-2-methyl-3-pentanone (3). This compound, which apparently has not been described in the literature, had bp 80–81° (13 mm); nmr τ 8.20 (d, 3 H, J = 6.9 Hz), 8.15 (s, 3 H), 7.95 (s, 3 H), 4.80 (q, 1 H, J = 6.9 Hz). Note that the geminal methyl groups are diastereotopic and give rise to two signals in the nmr.

1,3-Dibromo-3-methyl-2-butanone (**4a**)[3c] and 2,4-dibromo-3-pentanone (**5**)[3c] were obtained similarly; **5** proved to be a mixture of diastereoisomers formed in a ratio of 5:1.

3-Bromo-1-iodo-3-methyl-2-butanone (4b). **4a** was treated with an equimolar solution of NaI in acetone for 15 min at room temperature, NaBr being precipitated instantaneously. Distillation at 52–54° (0.2 mm) gave 3-bromo-1-iodo-3-methyl-2-butanone (**4b**) in quantitative yield; nmr τ 8.04 (s, 6 H), 5.73 (s, 2 H). The mass spectrum showed a molecular ion *m/e* 292.290.

1,3-Diiodoacetone. 1,3-Dichloroacetone was warmed with NaI using acetone instead of water[12] as the solvent. 1,3-Diiodoacetone was formed in >90% yield, nmr τ 5.95 (s).

The preparation of 1,3-dibromo-2-butanone has been described.[13]

Synthesis of 2-Dimethylamino-4-methylene-1,3-dioxolanes. The combined reaction and extraction apparatus (Figure 2) was devised in order to allow dehalogenation of the dihalo ketones and the isolation of the cycloadducts to proceed at low temperature. The following preparation of **4-ethylidene-5,5-dimethyl-2-dimethylamino-1,3-dioxolane** (**7**) may serve as an example of our procedure. The reaction vessel A was charged with a suspension of 3.7 g (0.06 mol) of a zinc–copper couple[6] in 25 ml of dimethylformamide and flushed with thoroughly dry and deoxygenated nitrogen. 2,4-Dibromo-2-methyl-3-pentanone (**3**) (5 g, 0.02 mol) was dissolved in

(9) W. E. Willy, G. Binsch, and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 5394 (1970).

(10) It is noteworthy that base-catalyzed isomerization of allyl ethers under conditions of kinetic control affords cis vinyl ethers at least preferentially, if not exclusively. See T. J. Prosser, *ibid.*, **83**, 1701 (1961); C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); C. D. Broaddus, *ibid.*, **87**, 3706 (1965); H. Kloosterziel and J. A. A. Van Drunen, *Recl. Trav. Chim. Pays-Bas*, **89**, 32 (1970); see also H. M. R. Hoffmann, *Annu. Rep. Progr. Chem.*, **62**, 242 (1965).

(11) H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Amer. Chem. Soc.*, in press.

(12) O. Völker, *Justus Liebigs Ann. Chem.*, **192**, 95 (1878).

(13) C. Rappe, *Ark. Kemi*, **21**, 503 (1964).

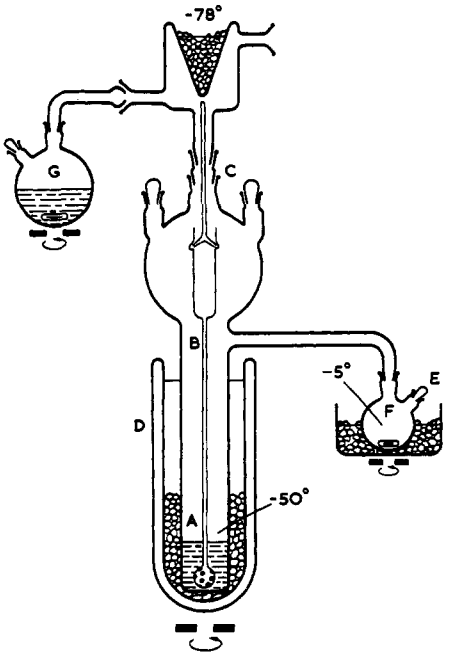


Figure 2. (A) Reaction vessel, (B) extraction tube with funnel, (C) opening for screw-cap adapter and/or Dry Ice condenser, (D) dewar flask, (E) opening for dropping funnel, (F) 100-ml flask, and (G) reservoir.

10 ml of dimethylformamide, placed into a dropping funnel, and stirred into the suspension of the metal at a rate of *ca.* 1 drop/5 sec at −35°. After complete addition the reaction mixture was stirred for a further 10 min at −35° and then worked up without delay by starting the extraction cycle. To this end the extraction tube B was lowered from its original position of about 4–5 cm above the stirring bar to the bottom of the vessel and the screw-adapter holding the tube was replaced at C by a Dry Ice condenser which was maintained at −78° and connected to a vacuum line. The nitrogen flow was switched off and *ca.* 250 ml of isopentane was distilled either from F or from a reservoir at G under reduced pressure into the extractor *via* funnel B. When the extractor A was filled to overflow, a further 25 ml of isopentane was introduced into the distillation flask F which was maintained at −5°. Throughout the extraction the solution in A was cooled to −50° and the vacuum was regulated so as to preclude bumping. Provided that the system is vacuum tight, further pumping is not required, the extraction being sustained by the temperature gradient from flask F to the Dry Ice condenser. After 2–3 hr the extraction into F was generally complete and isopentane could be removed from F without changing flasks by freezing out the solvent in A and distilling isopentane into the upper cylinder of the extraction tube leaving 4-ethylidene-5,5-dimethyl-2-dimethylamino-1,3-dioxolane (**7**, *ca.* 50%).

4-Isopropylidene-5,5-dimethyl-2-dimethylamino-1,3-dioxolane (**6**) was obtained similarly and in comparable yield. Because of its chemical reactions, its nmr spectrum which changes when **6** is present in dilute dimethylformamide solution showing three singlets in a ratio of 6:3:3, and its intense mass spectral peak at 112 (m − DMF), this compound was erroneously assumed to be 3-isopropylidene-2,2-dimethyloxirane in a preliminary note.[14] Metastable defocusing showed that the mass peak of 112 (calcd for $C_7H_{12}O$, 112.0888; found, 112.0888) was within experimental error, the daughter ion of the low intensity peak at 185 (calcd for $C_{10}H_{19}NO_2$, 185.1416; found, 185.1433) and no $C_7H_{12}O$ parent ion. This result was confirmed by determining the molecular weight of **6** using vapor pressure osmosis.

(14) H. M. R. Hoffmann and R. H. Smithers, *Angew. Chem.*, **82**, 43 (1970).

4-Ethylidene-5-methyl-2-dimethylamino-1,3-dioxolane was obtained on debromination of **5** as a diastereoisomeric mixture (*ca.* 15%), the major isomer predominating by a factor of 5:3 in several experiments. The structural assignment of this isomer to **9a** and that of the minor one to **9b** have been discussed above.

4,4-Dimethyl-2-dimethylamino-5-methylene-1,3-dioxolane (**8**) was obtained in relatively low yield only (5.2% from **4a**, but 11% from **4b**.)

The heterocyclics so obtained contained *ca.* 25% free dimethylformamide, which was introduced during the extraction and the amount of which could be minimized by extracting at low temperature. Otherwise, the compounds were remarkably pure, *i.e.*, at least 95% as judged by high resolution nmr. The compounds were stored below 0°, preferably in the presence of a stabilizer such as 2,6-lutidine and in the absence of oxygen. Attempts to prepare dimethylformamide adducts by dehalogenation of 1,3-diiodoacetone and 1,3-dibromo-2-butanone were not successful.

Dimethylacetamide Adducts. 4-Isopropylidene-2,5,5-trimethyl-2-dimethylamino-1,3-dioxolane (**10**). 2,4-Dimethyl-2,4-dibromo-3-pentanone (**2**, 5 g) in 7 ml of dimethylacetamide was stirred into a suspension of 3.6 g of zinc–copper couple[6] in 25 ml of dimethylacetamide at −15° over a period of 45 min. After a further 10 min the reaction mixture was extracted with isopentane which in turn was evaporated leaving a 4:1 mixture of dimethylacetamide and 4-isopropylidene-2,5,5-trimethyl-2-dimethylamino-1,3-dioxolane (**10**), *ca.* 20–30% yield, nmr (*cf.* Table I), mass spectrum *m/e* 199.1571 (calcd for $C_{11}H_{21}NO_2$, 199.1572). The relation to the supposed daughter ion at 112 (loss of dimethylacetamide) could not be established, presumably owing to the instability of the compound. A second minor product (*ca.* 10% of **10**) was 2,4,4,5,5,7-hexamethyl-3,6-octanedione:[15] nmr τ 6.90 (sept, 1 H), 8.81 (s, 6 H), 9.01 (d, 6 H); mass spectrum: *m/e* 226.1936 (calcd for $C_{14}H_{26}O$, 226.1932); ir 1690–1720 cm^{-1} ($\nu_{C=O}$ strong).

2,4,4-Trimethyl-2-dimethylamino-5-methylene-1,3-dioxolane (**11**) was similarly obtained as a highly reactive compound together with some unidentified material.

Table II. Selected Ir Peaks of 2-Dimethylamino-4-methylene-1,3-dioxolanes

6	7	8	9a + 9b	Assignment
2860	2870	2880	2870	NMe_2
2770	2790	2795	2790	
1700	1710	1710	1715	=C—O
	1388	1390		*gem*-Dimethyl
	1368	1370		
	1170	Obscure	1180	C—O
	1150	Obscure	1160	

Table III. Characteristic Mass Spectral Peaks of 2-Dimethylamino-4-methylene-1,3-dioxolanes[a]

6	*m/e* 185, 112, 86, 85, 84, 83, 82, 81, 74, 73, 69, 44, 43, 42, 41
7	*m/e* 171, 98, 74, 73, 72, 71, 70, 69, 44, 43, 42, 41
8	*m/e* 157, 84, 74, 73, 59, 58, 57, 56, 55, 44, 43, 42, 41
9a + 9b	*m/e* 157, 85, 84, 74, 73, 58, 57, 56, 55, 44, 43, 42, 41

[a] The dimethylacetamide adduct **11** was not stable enough for recording a mass spectrum; for compound **10** a molecular ion could be detected (*cf.* Experimental Section).

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(15) See also M. F. Ansell, W. J. Hickinbottom, and P. G. Holton, *J. Chem. Soc.*, 349 (1955).