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SYNTHESIS AND NONCHAIR CONFORMATIONS OF 2,2-DISUBSTITUTED 4,4-DIMETHYL-1,3-DIOXANES

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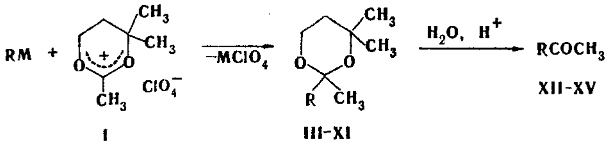
The fundamental possibility of the synthesis of 2-substituted 1,3-dioxanes by reaction of 1,3-dioxanium perchlorates with organometallic compounds is demonstrated. A method for the synthesis of acyl derivatives of heterocycles was developed on the basis of these compounds. The existence of 2,2,4,4-substituted 1,3-dioxanes in the twist conformation was shown by ^{1}H NMR spectroscopy; the twist conformation is explained by the effect of nonbonded 1,3-syn-axial interactions.

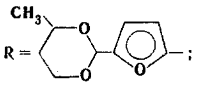
We have studied the synthesis and stereochemistry of new 1,3-dioxane systems that have not been previously described in the literature and have a gem-dimethyl grouping attached to the $C_{(4)}$ atom in all cases. The most convenient method for the synthesis of 1,3-dioxanes [1] is condensation of carbonyl compounds with 1,3-diols. However, it is difficult to prepare ketals by this method [2]. Having a convenient method for the synthesis of 1,2-dioxanium perchlorates [3] at our disposal, we deemed it expedient to use these salts for the preparation of new 1,3-dioxanes. 1,3-Dioxanium systems have an electrophilic center at the meso carbon atom of the $O{-}\overset{+}{C}{-}O$ fragment and can readily undergo nucleophilic attack [4-6].

Reactions of 2,4,4-trimethyl-1,3-dioxanium perchlorate (I) were first carried out with lithium aluminum hydride (LAH), a Grignard reagent, and Li derivatives of the heterocyclic series, as a result of which cyclic acetals and ketals that are difficult to obtain by other methods were obtained. The reduction of perchlorate I with LAH leads to 2,4,4-trimethyl-1,3-dioxane (II) in high yield (Table 1). 1,3-Dioxanes III-V were obtained by mixing the Grignard reagent with perchlorate I at room temperature and subsequent decomposition of the excess Grignard reagent with water.



M = MgBr, Li; III R = CH_3; IV R = C_2H_5; V R = n-C_3H_7; VI R = n-C_4H_9;

VII R = 1-methyl-2-benzimidazolyl; VIII, XII R =



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Krasnodar Polytechnic Institute, Krasnodar 350006. V. I. Ul'yanov-Lenin Kazan State University, Kazan 420008. Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1172-1179, September, 1978. Original article submitted November 11, 1976; revision submitted October 24, 1977.

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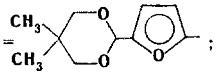
IX, XIII R=

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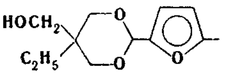
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XI, XV R=1-phenyl-2-imidazolyl; XIV R=5-formyl-2-furyl

A decrease in the yield of the dioxane, which is associated with side reactions, is observed as the length of hydrocarbon chain is increased (III-V). These side reactions include, first, cleavage of the C—O bond under the influence of organomagnesium compounds, as confirmed by the formation of a glycol monoester, and, second, hydrolysis of the resulting ketals. We were unable to isolate ketals when R = C_4H_9, C_6H_5; only their hydrolysis products were obtained, in agreement with [7]. However, we were able to synthesize 2-butyl-2,4,4-trimethyl-1,3-dioxane (VI) by means of butyllithium.

2-Hetaryl-substituted 1,3-dioxanes (VII-XI) were obtained from the corresponding hetaryllithium and perchlorate I at —78°C.

In acidic media all of the 1,3-dioxanes obtained are hydrolyzed to the corresponding ketones XII-XV. Their synthesis can be realized without isolation of the intermediate 1,3-dioxanes. In slightly alkaline media bis(1,3-dioxanyl)furans VIII and IX are hydrolyzed only at the ketal link to give methyl ketones XII and XIII; this once again confirms the lower hydrolytic stability of the ketal as compared with the acetal ring. Both dioxane rings are opened to give acetylfurfural XIV under more severe conditions (refluxing in 10% HCl). The preparation of XIV from bromofurfural acetals by means of Li and Cd organic derivatives has been previously described [8]. The use of perchlorate I simplifies the method considerably. Acyclic acetals can also be used preparatively in this case. We demonstrated the preparation of difficult-to-obtain ketones by this method in the case of N-substituted imidazoles and benzimidazoles. 1-Methyl-2-acetylbenzimidazole was identified in the form of the 2,4-dinitrophenylhydrazone, with mp 286°C.

The stereochemistry of the synthesized 1,3-dioxanes is of considerable interest from the point of view of the study of the effect of the nonbonded 1,3-syn-axial interactions. Several years ago it was demonstrated for diastereomeric 2,4,4,6-tetramethyl-1,3-dioxanes [9-11] that in the case of the trans isomer the conformational equilibrium is shifted

TABLE 1. 2-Substituted 2,4,4-Trimethyl-1,3-dioxanes

Compound	bp, °C (mm)	Found, %		Empirical formula	Calc., %		Absorption bands in the IR spectra, cm^{-1}	Yield, %
		C	H		C	H		
II	140	64,2	10,1	$C_7H_{14}O_2$	64,6	10,7	1460, 1430, 1400, 1340, 1250, 1210, 1160, 1110, 1040, 950, 820	87
III	45 (18)	67,0	11,5	$C_8H_{16}O_2$	64,4	11,1	1480, 1350, 1280, 1270, 1240, 1210, 1170, 1150, 1080, 1050, 1020, 980	70
IV	165	69,5	12,10	$C_9H_{18}O_2$	68,8	11,3	1460, 1340, 1280, 1270, 1240, 1190, 1180, 1150, 1070, 1040, 960, 800	52
V	68 (13)	70,2	11,2	$C_{10}H_{20}O_2$	69,7	11,6	1460, 1330, 1280, 1250, 1180, 1170, 1140, 1120, 1080, 1040	31
VI	85 (15)	72,2	11,6	$C_{11}H_{22}O_2$	72,7	11,1	1450, 1350, 1300, 1250, 1180, 1170, 1120, 1080, 1060, 1040, 960	60
VII	119—120[a]	69,3	7,8	$C_{15}H_{20}N_2O_2$[b]	69.2	7,7	3050, 3020, 1620, 1500, 1385, 1330, 1295, 1270, 1180, 1165, 1120, 1090, 1070, 1050, 1020	42
VIII	172 (15)[c]	65.3	8,2	$C_{16}H_{20}O_5$	64,6	8,4	3140, 1670, 1470, 1460, 1450, 1430, 1370, 1320, 1275, 1255, 1240, 1210, 1180, 1120, 1075, 1050, 1040, 1010, 810	52
IX	76—78[a]	66,8	7,5	$C_{17}H_{22}O_5$	66,6	7,1	3100, 1610, 1470, 1360, 1250, 1230, 1200, 1170, 1100, 1070, 1040, 970, 930, 800	40
X	165 (5)[d]	62,7	7,7	$C_{18}H_{28}O_6$	63,5	8,2	3490, 3120, 1610, 1520, 1480, 1320, 1250, 1210, 1160, 1110, 1070, 1050, 1030, 1020, 990, 930	45
XI	173 (10)	70,6	7,8	$C_{16}H_{20}N_2O_2$[e]	70,58	7,3	3120, 1610, 1520, 1470, 1430, 1410, 1380, 1320, 1270, 1250, 1200, 1190, 1170, 1150, 1110, 1065, 1010, 970	85

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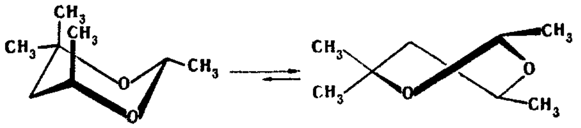
[a] Melting point. [b] Found: N 11.1%. Calculated: N 10.7%. [c] This compound had mp 57-59°C. [d] This compound had mp 65-67°C. [e] Found: N 10.9%. Calculated: N 10.2%.

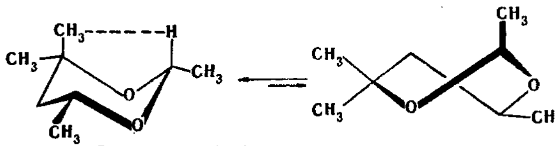
TABLE 2. Chemical Shifts and Spin–Spin Coupling Constants of 2-Substituted 2,4,4-Trimethyl-1,3-dioxanes

Compound	Solvent	δ, ppm					J, Hz						
		R	$2\text{-}CH_3$	$4\text{-}(CH_3)_2$	5-H	6-H	$^3J_{Aa}$	$^3J_{Ae}$	$^2J_{AB}$	$^3J_{Ba}$	$^3J_{Be}$	$^3J_{HCH_3}$	$^3J_{HH}$
II	C_6H_6	4,78 q (H_a)	1,34 d	1,03 s 1,15 s	0,82 m 1,68 m	3,53 m 3,69 m	11,0	2,6	−11,0	5,5	1,6	5,0	
	CCl_4	4,75 q (H_a)	1,21 d	1,18 s	—	—						5,0	
III	CCl_4	1,31 s (CH_3)	1,31 s	1,20 s	1,51 t	3,78 t							5,6
	C_6H_6	1,42 s (CH_3)	1,42 s	1,17 s	1,28 t	3,67 t							5,6
	$CHCl_3$	1,42 s (CH_3)	1,42 s	1,32 s	1,62 t	3,92 t							5,6
IV	CCl_4	1,58 q (CH_2), 0,88 t (CH_3)	1,25 s	1,20 s	—	3,78 m							
	C_6H_6	1,62 q (CH_2), 1,01 t (CH_3)	1,35 s	1,17 s	—	3,68 m							
V	CCl_4	2,24 t (α-CH_2), 1,64 q (β-CH_2), 0,9 t (CH_3)	2,06 s	1,23 s	1,32 q	3,76 m							
VII	C_6H_6	3,37 s (N—CH_3)	1,69 s	1,57 s 1,14 s	—	3,85 m 4,72 m	11,7	3,1	−11,7	5,2	3,1		
	CCl_4	7,18 s (C_6H_4), 3,95 s (N—CH_3)	1,64 s	0,80 s 1,30 s	1,30 m 1,86 m	3,86 m 4,66 m	11,7	3,1	−11,7	5,2	3,1		
VIII	C_6H_6	3,48 m, 3,88 m (6-H_{AB}, 6-H_B; $^2J_{AB}=-11{,}7$, $^3J_{Aa}=11{,}7$, $^3J_{Ae}=3{,}1$, $^3J_{Ba}=5{,}2$, $^3J_{Be}=1{,}6$ Hz); 1,10 d (4-CH_3, $^3J_{HCH_3}=6{,}0$ Hz)	1,69 s	0,96 s 1,22 s	—	3,60 m 4,05 m	11,7	3,1	−11,7	5,2	3,1		
	CCl_4	6,22 and 6,12 dd (3′-and 4′-H), 5,42 s (2-H), 1,25 d (4-CH_3, $^3J_{HCH_3}=6{,}0$ Hz)	1,47 s	0,88 s 1,24 s	—	3,72 m 4,14 m	11,7	3,1	−11,7	5,2	3,1		
XI	CCl_4	7,86, 7,78 dd (3′and4′-H); 7,32 s (C_6H_5)	1,72 s	0.78 s 1,38 s	—	3,84 m 4,20 m							

markedly to favor the 1,4-twist conformation (B), whereas in the case of the cis isomer the equilibrium is shifted to favor the chair conformation (C), in which the $4\text{-}CH_3\ldots H$ 1,3-syn-axial interaction (4.12 kcal/mole per interaction) [12] does not make a contribution sufficient to invert it to a "flexible" form (twist or boat). On the other hand, in the trans isomer the CH_3—CH_3 1,3-syn-axial interaction substantially increases the conformational energy (A), and the molecules take on the less strained 1,4-twist conformation (B).



A trans isomer B



C cis isomer D

The results of our study of 1,3-dioxanes II-XI are in complete agreement with these general concepts.

We established the three-dimensional structures of the synthesized 1,3-dioxanes by ^1H NMR spectroscopy. The principal spectral parameters of II-XI are summarized in Table 2.

A number of characteristic features in the PMR spectrum of 2,4,4-trimethyl-1,3-dioxane (Fig. 1) provide evidence that the II molecules exist primarily in the chair conformation. This is indicated, first, by the vicinal constants of spin–spin coupling of the 5-H and 6-H protons and, second, by the fact of inversion of the constants of nuclear magnetic shielding of the methylene 5-H protons. The latter is typical for 1,3-dioxane systems and similar complex cyclic ethers [13], in which case the molecules exist in a chair conformation.

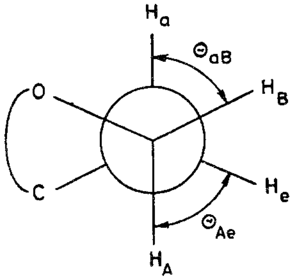
The methylene H_A and H_B protons attached to the $C_{(6)}$ atom give a typical multiplet, which is analyzed within a first-order approximation and is characterized by the vicinal constants $^3J_{Aa}$ = 11.0, $^3J_{Ba}$ = 5.5, $^3J_{Be}$ = 1.6, and $^3J_{Ae}$ = 2.6 Hz. The conformation of the ring is characterized by an "R factor" [14, 15] of 1.55, to which ring torsion angle ψ = 53° corresponds. This value of the ψ angle constitutes evidence for a certain amount of compression of the carbon side of the ring. The torsion angle can be more accurately estimated by the Forrest method [16] using Eqs. (1)-(3):

$$^{3}J_{HH'}{}^{calc}(60^\circ) = (4.1+0.63\Sigma\Delta X_i)\,(1-0.462\Delta X_1)\,(1-0.462\Delta X_2); \tag{1}$$

$$A = (^{3}J_{HH'}{}^{calc}+0.3)/\cos^2 60^\circ; \tag{2}$$

$$\cos\theta = [(^{3}J_{HH'}{}^{exp}+0.3)/A]^{1/2}, \tag{3}$$

where ΔX_i is the difference in the electronegativities (EN) of the i-th substituent in the ethane fragment under examination and hydrogen, and ΔX_1 and ΔX_2 are the differences in the EN of the substituents with an antiperiplanar orientation relative to the coupling protons. Substituting X_1 = 1.3 (oxygen) and X_2 = 0.4 (carbon) in Eq. (1), we obtain $^3J_{Ae}{}^{calc}$ = 2.0 and $^3J_{aB}{}^{calc} \cong$ 5.17 Hz and find that A = 9.2 and 17.2. Substituting $^3J_{HH'}{}^{exp}$ in Eq. (3), we find that $\theta = (\theta_{aB} + \theta_{Ae})/2 = (56^\circ + 54.5^\circ)/2 = 55^\circ 15'$, i.e., the carbon portion of the ring is actually compressed as compared with cyclohexane.



In the chair conformation the protons of the methyl groups should be nonequivalent, and this is actually observed (Δδ 0.125 ppm in benzene solution). As the temperature of the sample is raised to +120°C, the lines of the gem-dimethyl grouping almost merge because of averaging of their shifts due to the contribution of flexible forms. The shift of the resonance of the quartet of the H_a proton to weaker field as compared with 1,3-dioxanes, in which an axial methyl group is absent, also indicates the primary chair conformation with an axial orientation of one of the methyl groups.

2,2,4,4-Tetramethyl-1,3-dioxane (III) is of greatest interest from a stereochemical point of view. The ^{1}H NMR spectrum of this compound is presented in Fig. 2. It can be seen that the chemical shifts of the 5- and 6-H protons of the methylene groups are averaged here, as a result of which they resonate, to a first approximation, in the form of a degenerate triplet. Since the amplitude of the average lines of the triplets* is comparable to the amplitude of the two side lines, this indicates the existence of an unresolved structure of the average line; this is possible if the protons being analyzed belong to the A_2B_2 spin system. In this case the average line is the superimposition of five lines [17], and the distance between the two extreme lines is J + J' = 11.2 Hz, where $J = 1/2(^3J_{6e5a} + {}^3J_{6a5e})$ and $J' = 1/2(^3J_{6e5e} + {}^3J_{6a5a})$. In [17] the observed spectrum of the 6-CH_2 and 5-CH_2 methylene groups of 4,4-dimethyl-1,3-dioxane was explained by the existence of rapid exchange between the chair conformations, to which one can raise no objections. However, a study of the temperature dependence of the PMR spectrum (5% by volume solution in chloroform) in the case of dioxane III shows that neither the form of the spectrum nor the chemi-

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*The integral intensities of the lines of the triplet follow the 1:2:1 binomial ratio.

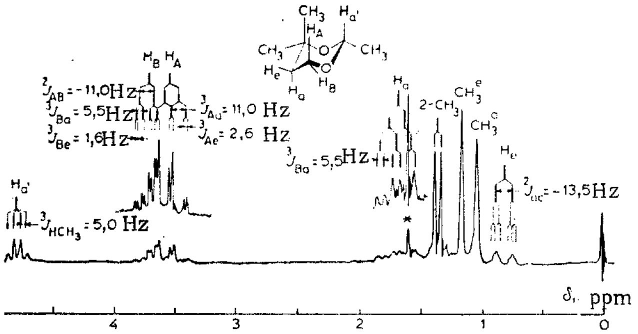


Fig. 1. PMR spectrum of 2,4,4-trimethyl-1,3-dioxane (II) (5% by volume solution in benzene at 29°C; the signal of an impurity is indicated by an asterisk).

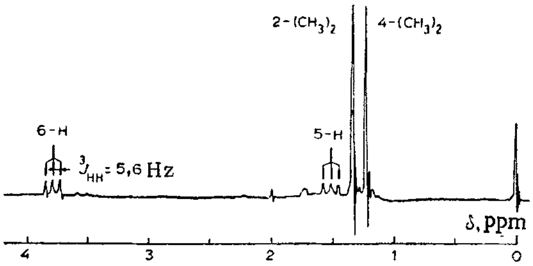


Fig. 2. PMR spectrum of 2,2,4,4-tetramethyl-1,3-dioxane (III) (5% by volume solution in CCl_4 at 29°C).

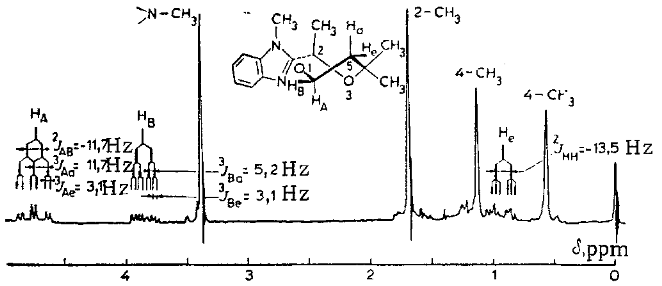
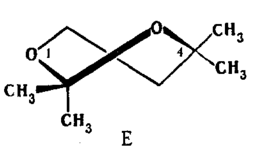
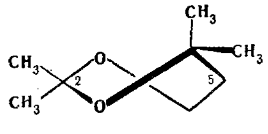


Fig. 3. High-field region of the PMR spectrum of 2-(1-methyl-2-benzimidazolyl)-2,4,4-trimethyl-1,3-dioxane (VII) (5% by volume solution in benzene at 29°C).

cal shifts change as the temperature is lowered to −60°C. This fact makes it possible to assume that in this case a homogeneous conformation of the 2,5-twist form (F) most likely is present [10], since a 1,3-syn-axial interaction of the 4-CH_3 group with the hydrogen atom is absent in it. More nearly complete averaging of the magnetic anisotropic environments of the methylene and methyl protons is likely in this conformation, considering the possibility of its pulsation because it has greater flexibility than the chair form. In any case, the experimental spectrum is indicative of this. On the other hand, a shift of the conformational equilibrium to favor twist form E with a pseudoaxial orientation of the 2-CH_3 group and a pseudoequatorial orientation of the large substituent, as in the case of VII (see below) is more likely in the case of other representatives of this series (IV, R = C_2H_5; V, R = C_3H_7). In this case the chirality of the $C_{(2)}$ atom in IV creates anisochronic character of the protons of the gem-dimethyl grouping attached to the $C_{(4)}$ atom, whereas in dioxane V the effect of the specific magnetic anisotropic environment is such that the protons of the gem-dimethyl grouping are isochronic, despite the realization of an apparently homogeneous 1,4-twist conformation.



E



F

2-(1-Methyl-2-benzimidazolyl)-2,4,4-trimethyl-1,3-dioxane (VII) has the most characteristic ^{1}H NMR spectrum; this makes it possible to assert that primarily 1,4-twist conformations are realized for VII-XI. The PMR spectrum of VII, which is presented in Fig. 3, can be compared only with the case in which the molecules of the substance have a conformation that differs from the chair form. This conclusion follows from an analysis of the fine structure of the two lines lying at δ 3.70-4.80 ppm, which can be assigned only to the methylene 6-H protons. It is apparent from Fig. 3 that inversion of the proton shielding constants occurs in this group; this inversion is manifested in the fact that the pseudoaxial H_A proton resonates at a substantially lower magnetic field than the pseudoequatorial H_B proton. In 1,3-dioxanes of the acetal series, in which the molecules have primarily a chair conformation, the protons of the endocyclic CH_2 groups in the 4 and 6 positions never have displayed inversion of the shielding constants [13, 18]. The fundamentally possible symmetrical and unsymmetrical boat conformations can be excluded in the first case for steric reasons and in the second case because of the atypical spin—spin coupling constants (see below).

A shift in the resonance of the H_A proton to lower field may occur in the 1,4-twist conformation under the influence of the magnetic anisotropy of the orbitals of the unshared pair of electrons of the $O_{(3)}$ atom; this twist conformation is substantially homogeneous, as indicated by the vicinal constants $^3J_{Aa}$ = 11.7 Hz, $^3J_{Ba}$ = 5.2 Hz, and $^3J_{Be}$ = 3.1 Hz. If the VII molecules existed in the chair conformation, the $^3J_{Be}$ constant would have a value of 1.3 Hz [19] rather than 3.1 Hz, the value actually observed.

The protons of the gem-dimethyl grouping display substantial nonequivalence ($\Delta\delta$ 0.6 ppm); this is evidently due to the chirality of the $C_{(2)}$ atom.

The 1,4-twist conformation is evidently not strained, as evidenced by the magnitude of the geminal constant ($^2J_{ae}$ = —13.5 Hz); evidence for this is also provided by the R factor (1.78), to which a ring torsion angle (ψ) of 55° corresponds, i.e., the twist form differs little from the ideal form.

Similar characteristic peculiarities in the NMR-spectral parameters are retained for VIII-XI. This makes it possible to conclude that they have three-dimensional structures similar to the structure of dioxane VII.

EXPERIMENTAL

The IR spectra of mineral oil suspensions and thin layers with LiF and NaCl (in the case of liquids) of the compounds were obtained with a UR-20 spectrometer. The UV spectra of ethanol solutions of the compounds were measured with a Specord spectrophotometer. The PMR spectra (Table 2) of solutions of the compounds in CCl_4, C_6H_6, and $CHCl_3$ were recorded with a Varian HA-100D spectrometer at 29°C with tetramethylsilane as the internal standard.

2,4,4-Trimethyl-1,3-dioxane (II). A solution of 0.38 g (0.01 mole) of lithium aluminum hydride (LAH) in absolute ether was added dropwise in the course of 30 min to a suspension of 4.56 g (0.02 mole) of 2,4,4-trimethyl-1,3-dioxanium perchlorate (I) in ether, during which an exothermic reaction developed. After 15 min, the solution was cooled to 0°C, and the excess LAH was decomposed with water. The ether layer was separated and dried with KOH, the solvent was removed by evaporation, and the residue was distilled.

2,2,4,4-Tetramethyl-1,3-dioxane (III). An 18.2-g (0.08 mole) sample of perchlorate I was added in portions to a Grignard reagent prepared from 2.6 g (0.11 mole) of magnesium, 9.5 g (0.1 mole) of methyl bromide, and 90 ml of absolute ether, and the mixture was stirred for 1 h. It was then cooled with ice and decomposed with 30 ml of water. The ether layer was separated, dried with KOH, and evaporated, and the residue was vacuum distilled. Dioxanes IV and V were similarly obtained.

2-Butyl-2,4,4-trimethyl-1,3-dioxane (VI). An 8.2-g (0.036 mole) sample of perchlorate I was added in the course of 15 min at —78°C to butyllithium obtained from 0.5 g (0.072 mole) of lithium and 5 g (0.036 mole) of butyl bromide in 30 ml of ether. After 1 h, 30 ml of water was added, and the ether layer was separated, dried with KOH, and evaporated. The residue was vacuum distilled.

2-(1-Methyl-2-benzimidazolyl)-2,4,4-trimethyl-1,3-dioxane (VII). An 8.2-g (0.036 mole) sample of perchlorate I was added in the course of 15 min at —78°C to 2-lithia-1-methylbenzimidazole [20]. After 1 h, the temperature was raised to room temperature, and 30 ml of water was added. The ether layer was separated and washed with 10% HCl. The aqueous solution was neutralized with 10% NaOH solution and extracted with ether. The solvent was removed by evaporation, and the residue was crystallized from heptane.

2-[5-(4-Methyl-1,3-dioxan-2-yl)-2-furyl]-2,4,4-trimethyl-1,3-dioxane (VIII). An 8.2-g (0.036 mole) sample of perchlorate I was added in the course of 15 min at —78°C to 2-(5-lithia-2-furyl)-4-methyl-1,3-dioxane [21]. After 1.5 h, the temperature was raised to room temperature, 30 ml of water was added, and the ether layer was separated. The aqueous layer was extracted with ether, and the ether extracts were dried with sodium sulfate and evaporated. The residue was vacuum distilled. A similar procedure was used to obtain 2-[5-(5,5-dimethyl-1,3-dioxan-2-yl)-2-furyl]- (IX) and 2-[5-(5-ethyl-5-hydroxymethyl-1,3-dioxan-2-yl)-2-furyl]-2,4,4-trimethyl-1,3-dioxane (X).

2-(1-Phenyl-2-imidazolyl)-2,4,4-trimethyl-1,3-dioxane (XI). A solution of 4.5 g (0.033 mole) of butyl bromide in 8 ml of ether was added in the course of 45 min at 0°C in a nitrogen atmosphere to a suspension of 0.45 g (0.065 mole) of ground lithium in 15 ml of ether, and the mixture was then refluxed for another 15 min. It was then cooled to −15°C, and a solution of 2.59 g (0.018 mole) of 1-phenylimidazole in 10 ml of ether was added in the course of 40 min. After 1 h, the mixture was cooled to −78°C, 7.5 g (0.033 mole) of perchlorate I was added, and the mixture was allowed to stand for 1 h. Water (30 ml) was then added at room temperature, and the ether layer was separated and dried with sodium sulfate. The solvent was removed by evaporation, and the residue was vacuum distilled.

2-(5-Acetyl-2-furyl)-4-methyl-1,3-dioxane (XII). The synthesis of XII was similar to the synthesis of dioxane VII. It differed only with respect to the addition of 20 ml of 10% HCl after decomposition of the lithium residues with water. The ether layer was then separated, and the aqueous layer was extracted with ether. The ether extracts were washed with water, combined, and dried with sodium sulfate. The solvent was removed by evaporation to give 1.1 g (52%) of XII with mp 81-82°C (from heptane). PMR spectrum, δ: 2.70 (s, CH_3CO), 6.22 and 6.12 (dd, 3'- and 4'-H), 1.26 (d, 4-CH_3), 4.05 and 3.60 (m, 4- and 6-H), and 5.42 ppm (s, 2-H). UV spectrum: λ_{max} 278 nm (ε 15,000). IR spectrum: 3120 and 1530 (furan); 1690 (C=O); 1170, 1150, 1110, and 1070 cm^{-1} (O—C—O). Found: C 62.4; H 6.9%. $C_{11}H_{14}O_4$. Calculated: C 62.8; H 6.7%.

2-(5-Acetyl-2-furyl)-5,5-dimethyl-1,3-dioxane (XIII). This compound, with mp 114-115°C (from heptane), was obtained in 60% yield by a procedure similar to that in the preceding experiment. PMR spectrum, δ: 0.74 (s, 5a-CH_3), 1.20 (s, 5e-CH_3), 2.40 (s, CH_3CO), 3.45 and 3.66 (dd, 4- and 6-H), 5.32 (s, 2-H), and 6.40 and 6.57 ppm (dd, 3'- and 4'-H). UV spectrum: λ_{max} 276 nm (ε 15,100). IR spectrum: 3080 and 1530 (furan); 1670 (C=O); 1200, 1110, and 1020 cm^{-1} (O—C—O). Found: C 64.2; H 7.7%. $C_{12}H_{10}O_4$. Calculated: C 64.4; H 7.2%.

5-Acetylfurfural (XIV). A) The synthesis was carried out in analogy with the preparation of ketone XII. The only difference was that the residue after evaporation of the ether was refluxed with activated charcoal in 10% HCl, after which the mixture was extracted with ether. The ether extracts were washed with sodium carbonate solution and dried with sodium sulfate. The ether was removed by evaporation, and the residue was crystallized from heptane to give XIV, with mp 85°C, in 50% yield. UV spectrum: λ_{max} 290 nm (ε 20,000). IR spectrum: 3140 and 3110 (furan); 1680 cm^{-1} (C=O).

B) A solution of 4.99 g (0.036 mole) of butyl bromide in 5 ml of ether was added in the course of 1.5 h at 0°C in a nitrogen atmosphere to 0.51 g (0.072 mole) of ground lithium in 20 ml of absolute ether, and the resulting solution of butyllithium was cooled to −10°C and treated in the course of 15 min with a solution of 3.04 g (0.01 mole) of bromofurfural dibutylacetal in 10 ml of ether. After 15 min at −78°C, 8.2 g (0.036 mole) of perchlorate I was added, and the mixture was allowed to stand for 1 h. Water (30 ml) and 20 ml of 10% HCl were then added. After 20 min, the ether layer was separated and evaporated, and the residue was worked up as in method A. The characteristics of acetylfurfural XIV obtained by methods A and B were in agreement with those described in [8].

2-Acetyl-1-phenylimidazole (XV). The synthesis was carried out as in the preparation of ketone XI. The only difference was that the ether layer was shaken with 50 ml of 10% HCl. The ether layer was separated, and the aqueous layer was neutralized with 10% NaOH solution and extracted with ether. The extract was dried with sodium sulfate, and the ether was removed by evaporation to give 2.5 g (75%) of colorless acicular crystals with mp 75°C (from hexane). PMR spectrum, δ: 2.65 (s, CH_3CO), 7.06 (s, 4-H), 7.12 (s, 5-H), and 7.36 ppm (s, C_6H_5). UV spectrum: λ_{max} 279 nm (ε 8600). IR spectrum: 3100 and 1610 (phenyl); 1700 cm^{-1} (C=O). Found: C 71.0; H 5.8; N 15.4%. $C_{11}H_{10}N_2O$. Calculated: C 70.9; H 5.4; N 15.0%.

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