thiocarbonyldiazoles in general are difficult to recrystallize (e.g., analytically pure 1 is obtained by sublimation in high vacuum[3b]), the synthesis via silylated precursors is to be preferred when pure products are needed. It is also our experience that the pure products are more "nonperishable" compared to compounds having a lesser purity.

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A New Tetrahydropyran Synthesis. Acid-Catalyzed Cyclization of δ-Substituted Aldehydes

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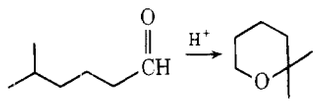
In preparing 1,1-diarylalkanes via acid-catalyzed condensation of aldehydes with alkylbenzenes, a novel rearrangement was discovered involving hydrogen exchange. While the scope of this rearrangement has not been defined, this reaction appears useful for a one-step synthesis of certain tetrahydropyran derivatives.[1] To function in this cyclization, the al-



(1)

dehydes must have at least seven carbon atoms and an alkyl substituent in the δ position.

Experiments were carried out using a C_8 aldehyde fraction, bp 148–150 °C, containing over 90% of 3,5-dimethylhexanal. This aldehyde was obtained from hydroformylation of mixed heptenes, bp 76–100 °C, synthesized in our laboratory by phosphoric acid dimerization of propylene with butenes. The novel cyclization product was isolated by distillation and characterized (Table I). Data were consistent for either 2,2,4-trimethyltetrahydropyran or 2-isopropyl-3-methyltetrahydrofuran, both unreported in the literature. For further elucidation, we prepared a simpler aldehyde, 5-methylhexanal, which on treatment with sulfuric acid gave 2,2-dimethyltetrahydropyran, a known compound.[2] Its structure was additionally verified by NMR.

Table I. Cyclization of 3,5-Dimethylhexanal[a]

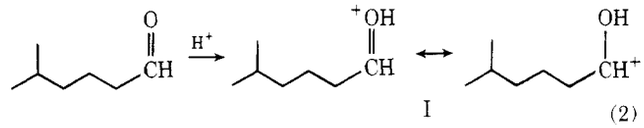
Run no.	Acid concn, wt %	Molar ratio, acid/RCHO	%yield of 2,2,4-trimethyl tetrahydropyran	Remarks
1	96% H_2SO_4	6:1	60	
2	96% H_2SO_4	9:1	74	
3	80% H_2SO_4	6:1	3	
4	100% H_2SO_4	6:1	65	
5	BF_3·H_2O	3:1	90	BF_3/H_2O ratio, 1:1
6	BF_3·H_2O	3:1	75	BF_3/H_2O ratio, 1:1.5
7	85% H_3PO_4	6:1	~0	Two-phase system.
8	100% H_3PO_4	6:1	25	
9	BF_3·H_2O·H_3PO_4	6:1	80	$BF_3/H_2O/H_3PO_4$, 1:0.23:1.27

[a] Reaction temperature 0 °C. [b] By distillation; bp 134–136 °C. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58; O, 12.48 (diff); $[M_R]_D$ 38.6 mL/mol. Found: C, 74.5; H, 12.4; O, 13.1 (diff). mol wt (*m/e*) 128; IR 1100 cm^{-1} (s, cyclic ether); sp gr (15°) 0.8493; n^{20}_D 1.4250; $[M_R]_D$ 38.6 mL/mol.

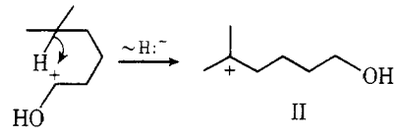
Cyclization competes with condensation and oxidation, but was favored by adding aldehyde slowly to acid. In cases where the addition sequence was reversed, cyclic ethers were not detected, and only resinous product was obtained.

The driving force for cyclization of δ-substituted aldehydes appears to be the generation of a relatively stable tertiary carbonium ion at the δ position when the hydride ion transfers. With *n*-hexanal and *n*-heptanal consequently, only condensation, but no cyclization, is observed as there is no incentive to form the less stable secondary carbonium ion. An attempt to prepare 2-phenyltetrahydropyran from 5-phenylpentanal failed, as intermolecular alkylation of the benzene ring was considerably faster than the expected benzylic carbonium ion formation.

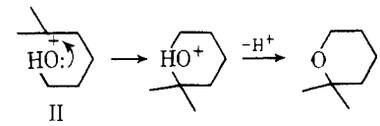
Products are rationalized by an ionic mechanism. In the first step, aldehyde is protonated to give carbonium ion I, which then undergoes intramolecular exchange to form carbonium ion II, followed by cyclization.



I (2)

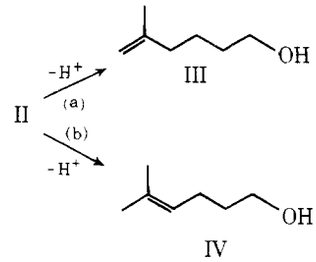


I II (3)



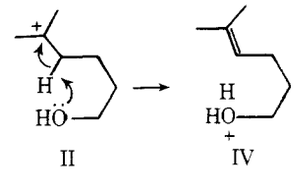
II (4)

In view of the similarity of products and also the reaction conditions between the present work and that of the Prins reaction,[3-5] it is also possible for the tetrahydropyran ring to form by a mechanism involving olefinic intermediates. Ion II can undergo deprotonation in two directions to give alcohols which are derivatives of vinylidene III or internal olefin IV, respectively.



III IV (5)

Since typical El elimination reactions afford the more highly substituted olefins as major products (Saytzeff rule),[6] the dominant pathway in our work would involve route b. Formation of IV can be assisted by a quasi-six-membered transition state. To form III, this process would require an eight-membered ring transition state which is energetically not fa-



II IV (6)

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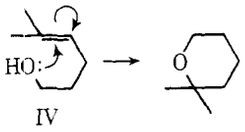
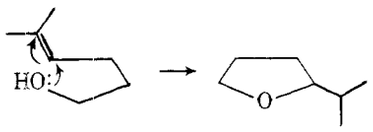
vored. The last step involves cyclization of IV to the tetrahydropyran ring.



(7)

IV

In fact, acid-catalyzed cyclizations of unsaturated alcohols to give either tetrahydropyrans[7,8] or tetrahydrofurans[8,9] are known, and in at least one case unsaturated alcohol has been isolated as an intermediate in the Prins reaction.[4] If unsaturated alcohols are involved, some cyclization is expected to



(8)

occur via a five-membered transition state to give tetrahydrofuran derivatives. The key compound in the case of 5-methylhexanal cyclization would be the presence of 2-isopropyltetrahydrofuran. We found no evidence for this ether among the reaction products. Cyclization appears therefore not to involve olefinic intermediates, and the reaction proceeds mostly via eq 4, analogous to acid-promoted cyclization of 1,5-pentanediol or pentamethylene chlorohydrin which form a tetrahydropyran ring via a cyclic oxonium ion intermediate.[10]

Experimental Section

Preparation of 5-Methylhexanal. About 100 g of 4-methyl-1-pentene (Phillips Petroleum) was carbonylated in benzene solvent (437 g) over 1.0 g of $RhH(CO)(Ph_3P)_3$ catalyst (100 °C, 60 atm, 30 min, $2H_2/CO$) to give 17 g of 5-methylhexanal: bp 80–85 °C (100 mm.Hg) (lit.[11] bp 84 °C at 100 mm); NMR (CCl_4, Me_4Si) 9.5 (s, 1 H, CHO), 2.3 (t, 2 H, CH_2CO, $J \approx 7$ Hz), 1.0–1.8 (m, 5 H, CH_2, CH), and 0.95 (d, 6 H, CH_3, $J \approx 7$ Hz) ppm. The spectrum, however, contained several peaks in the 9.5-ppm region, indicating a purity of only 70%. This is consistent with compositions carried out with $(Co_2(CO)_4)_2$ catalysts.[12,13]

Cyclization of 5-Methylhexanal. In a typical experiment, 9.0 g (0.08 mol) of the above aldehyde was added dropwise, while stirring, to 184 g of 96% sulfuric acid (1.8 mol), maintaining a temperature between 0 and −5 °C. After the addition was completed, the reaction mixture was stirred for 30 min and poured over 500 g of cracked ice. Extraction with ether, followed by washing with water, drying ($MgSO_4$), and distillation gave 3.5 g (39%) of 2,2-dimethyltetrahydropyran: bp 58–60 °C (100 mmHg), $n^{24.5}D$ 1.4245 [lit.[2] bp 119–120 °C (atm), $n^{18}D$ 1.4272]; NMR (CCl_4, Me_4Si) 3.5 (m, 2 H, CH_2O), 1.5 (m, 6 H, CH_2), and 1.1 (s, 6 H, CH_3) ppm, identical to the spectrum of the authentic sample. Aldehydes which did not have a methyl substituent in the δ position were converted to high-boiling resinous materials.

Acknowledgment. We thank Dr. R. C. Williamson for a gift of rhodium carbonylation catalyst.

Registry No.—3,5-Dimethylhexanal, 19796-88-4; 2,2,4-trimethyltetrahydropyran, 7379-08-0; 4-methyl-1-pentene, 691-37-2; 5-methylhexanal, 1860-39-5; 2,2-dimethyltetrahydropyran, 35270-87-2.

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Studies on Pyrazines. 2.[1] Structural Assignment of the Reaction of α-Amino-α-phenylacetonitrile with Chloral or Bromal to *N*-(2,2-Dihaloethenyl)-1-imino-1-phenylacetonitriles

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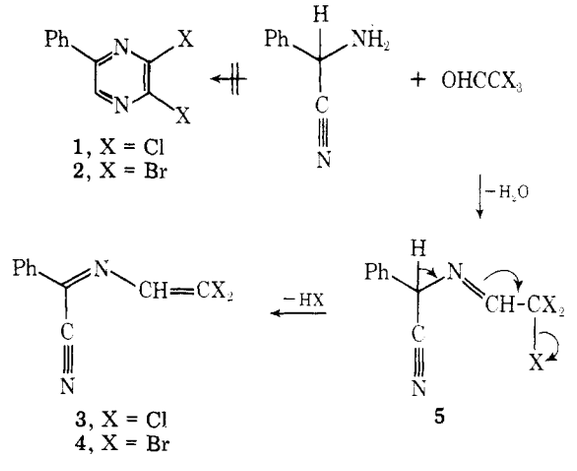
In a previous paper,[1] we reported a preparation of 2,3-dichloro-5-phenylpyrazine (1) by chlorination of 2,3-dihydroxy-5-phenylpyrazine with phosphoryl chloride. In 1915, Minovici and Bente[2] also described compound 1 and its bromo homologue 2 as reaction products of α-amino-α-phenylacetonitrile with chloral and bromal, respectively. We have now found that the dichloro product obtained in this reaction is entirely different (spectra, mixture melting point) from our earlier preparation and have assigned the structures of the Minovici–Bente products as *N*-(2,2-dihaloethenyl)-1-imino-1-phenylacetonitriles 3 and 4.

The NMR spectra contain 1 H singlets at δ 7.78 in 3 and 8.11 in 4. These signals can not be assigned to the ring protons of authentic 2,5-[3] and 2,6-dihalo-3-phenylpyrazines,[4] the latter of which were prepared by halogenation of 2-hydroxy-6-chloro-5-phenylpyrazine. The presence of a conjugated cyano group in the IR spectra at 2210 cm^{-1} in 3 and 2205 cm^{-1} in 4 indicates that 3 and 4 are not dihalopyrazines but acyclic compounds formed on dehydrohalogenation of Schiff base 5



1, X = Cl
2, X = Br

3, X = Cl
4, X = Br

5

prior to the cyclization of dihalopyrazines. The presence of a Ph–C–CN group in 3 and 4 was further confirmed by hydrolytic degradations with concentrated hydrochloric acid to give phenylglyoxalic acid (90–93%) and with 5% ethanolic potassium hydroxide to give benzoic acid (70–75%). Additional evidence for the structure of 3 and 4 was obtained from mass spectra, e.g., for the formation of β,β-dihaloethenium ion, *m/e* 95 and 183, respectively.

The formation of **5**, in contrast to the reaction of α-aminoacetonitrile and chloral which forms an adduct and not a Schiff base,[5] is clearly due to the phenyl group. Similarly,

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