7 (R = *p*-$CH_3C_6H_4$), 25677-27-4; **8** (R = Ph), 25726-00-5; **8** [R = *p*-$CH_3C_6H_4$ (picrate)], 25677-28-5; **9** [R = Ph (picrate)], 25677-29-6; **10** (R = Ph), 25677-30-9; **10** (R = *p*-$CH_3C_6H_4$), 25677-31-0; **10** [R = *p*-$CH_3C_6H_4$ (picrate)], 25677-32-1; **11** (R = *p*-$CH_3C_6H_4$), 25677-33-2; **12** (R = *p*-$CH_3C_6H_4$), 25676-99-7; **12** [R = *p*-$CH_3C_6H_4$ (picrate)], 25677-34-3; **14** (R = *p*-$CH_3C_6H_4$), 25677-35-4; **17** (R = *p*-$CH_3C_6H_4$), 25677-36-5; **18** (R = *p*-$CH_3C_6H_4$), 25677-37-6.

Acknowledgments. –The award of a grant from the National Science Foundation (NSF GP 6905) for the purchase of the mass spectrometer used in this study is gratefully acknowledged.

An Intramolecular Facilitated Acylation of a Tertiary Hydroxyl Group in a Perhydrobenzo[*b*]quinolizinetetrol[1,2]

JOHN H. BLOCK AND MATHEWS A. NUNES

Department of Pharmaceutical Chemistry, School of Pharmacy, Oregon State University, Corvallis, Oregon 97331

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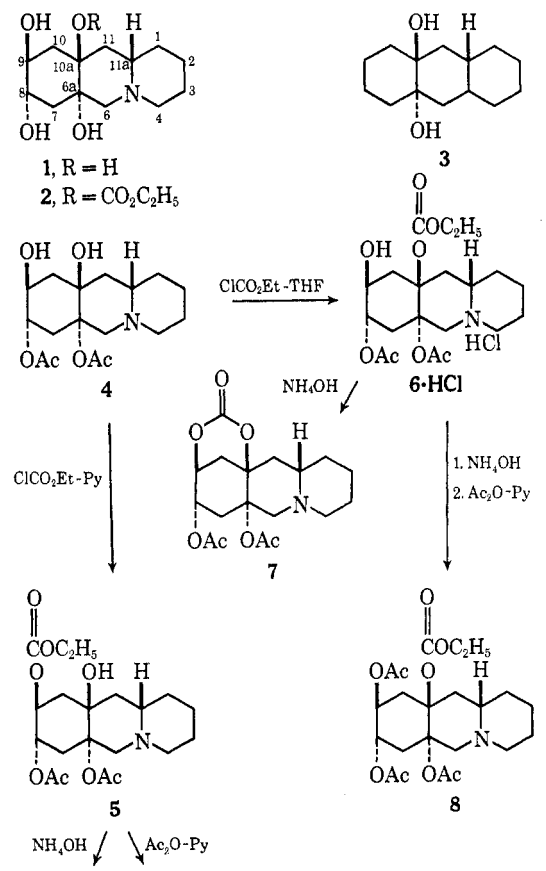
During the structure elucidation of 1,3,4,6,6a,7,8,9,10,10a,11,11a-dodecahydro-2H-benzo[*b*]quinolizine-6a,8,9-10a-tetrol (**1**), a selective acylation of the tertiary 10a-hydroxyl was observed. This reaction has been examined in more detail on the 6a,8-diacetate derivative **4**. It has been found that the acylation is solvent dependent. In pyridine, the secondary 9-hydroxyl is acylated with difficulty. In chloroform and tetrahydrofuran, the 10a-ethyl carbonate is obtained. Evidence is given for postulating that the acylation occurs directly by attack on the tertiary 10a-hydroxyl with an assist by the secondary *cis*-9-hydroxyl and by what appears to be a long-range field effect of the ring nitrogen.

In an earlier paper,[3] the novel facile acylation of a tertiary hydroxyl group bearing a 1,3-diaxial juxtaposition to both a secondary hydroxyl and a nitrogen lone pair of electrons was reported. The compound under investigation was 1,3,4,6,6a,7,8,9,10,10a,11,11a-dodecahydro-2H-benzo[*b*]quinolizine-6a,8,9,10a-tetrol (**1**), and the tertiary hydroxyl was located at position 6a.[4] During the stereochemical elucidation of the all-axial tetrol **1**, it was decided that one approach would be to form bridged structures of the two pairs of *cis*-1,3-diaxial hydroxyl groups. One method is to form a carbonate bridge using ethyl chloroformate.[5]

Treatment of tetrol **1** in tetrahydrofuran (THF) yielded the 10a-ethyl carbonate **2**.[3] Fieser has reported on the use of ethyl chloroformate as an alcohol protecting group. He called the reaction cathylation and the products cathylates. He also noted that no carbonates (cathylates) would form if the hydroxyl group was axial.[6] Thus here is ethyl chloroformate acylating an axial tertiary hydroxyl group. Because of the unusual nature of this acylation, it was decided to investigate this reaction further.

In studying the properties of this reaction in more detail, two items of information became apparent: (1) the C-9 secondary hydroxyl is necessary and (2) the reaction is solvent dependent. There was no reaction when diol **3** was the starting material.[3] Use of pyridine gave a mixture of products when **1** was the starting material, presumably owing to partial acylation of any of the four possible hydroxyls and in any combination. In order to eliminate two of the four possible hydroxyls, it was decided to use the known 6a,8-diacetate[3] (**4**) as the starting material.



Acylation of the 6a,8-diacetate (**4**) in tetrahydrofuran yielded the 6a,8-diacetate tertiary 10a-ethyl carbonate (**6**) in low yield. It was not possible to isolate

(1) This work was presented before the Medicinal Chemistry Section of the Academy of Pharmaceutical Sciences at the annual meeting of the American Pharmaceutical Association, Montreal, Quebec, May 1969, Abstracts, p 88.

(2) Financial support by the General Research Fund of the Oregon State University Graduate School is gratefully acknowledged.

(3) S. M. Kupchan, J. H. Block, and A. C. Isenberg, *J. Amer. Chem. Soc.* **89**, 1189 (1967).

(4) All asymmetric synthetic products described are racemic mixtures. Only one optical antipode for each is drawn for convenience of representation and discussion. In the representation of the quinolizidine derivatives the electron pair on nitrogen is understood to project downward, and a heavy bond to the 11a hydrogen indicates the *trans*-quinolizidine configuration.

(5) L. Hough, J. E. Priddle, and R. S. Theobold, *Advan. Carbohyd. Chem.*, **15**, 91 (1960).

(6) L. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y. 1959, pp 192, 217–219, 221, 241, 836.

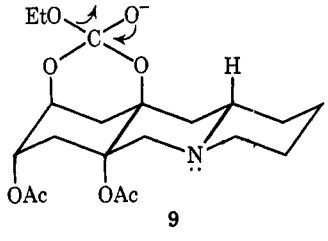
this compound as the thin layer chromatograms always indicated the presence of starting material. However, it was still possible to characterize the structure. The nmr spectrum showed the typical signals for an ethoxy moiety: quartet at δ 4.10 (J = 7 cps) and triplet at δ 1.28 (J = 7 cps). There was no downfield shift of the C-9 carbinol proton as would be expected had the C-9 hydroxyl been acylated.[7,8] Acetylation with acetic anhydride in pyridine yielded the already known 6a,8,9-triacetate 10a-ethyl carbonate (**8**). Treatment of **6** in mild base yielded the already known cyclic carbonate diacetate **7**.[3]

In contrast, acylation of the 6a,8-diacetate **4** with ethyl chloroformate in pyridine yielded the C-9 secondary carbonate **5**. This reaction went with difficulty requiring long periods of heating and 2–3 additions of ethyl chloroformate. This is consistent with previous observations reporting the difficulty of acylating an axial hydroxyl group with this reagent.[6] The carbonate's location on the secondary position is shown by the downfield shift of the C-9 equatorial carbinol proton[9] from δ 3.99 to the δ 5 region, failure to form a cyclic carbonate in mild base, and the lack of any hydroxyl groups capable of being acylated by acetic anhydride in pyridine.

No acylation occurred when the reaction solvent was *tert*-butyl alcohol or dioxane. Some product would form in chloroform. However, proper concentration of solvent is critical, and it may be that the concentrations, particularly of dioxane, were incorrect.

While it is not possible to postulate a definite mechanism, it is possible to reject some possibilities and speculate on others. It appears from the present evidence that the acylation is a direct attack on the C-10a tertiary hydroxyl. The tertiary position at both C-6a and 10a are hindered. The migration of an acetate from position 6a to a *cis*-hydroxyl at position 8 has been demonstrated[3] as has a similar migration from position 5 to position 3 in the cholestane series.[10] There is no reason to doubt that the hydroxyl at C-10a is any less hindered than that at C-6a.

The migration of an acetate presumably goes through an orthoacetate intermediate. In an analogous manner, the 10a-ethyl carbonate probably migrates to the secondary C-9 hydroxyl under basic conditions. In contrast with the migration of an acetate group, the ethyl carbonate contains the ethoxy leaving group (see intermediate **9**) resulting in a cyclic carbonate rather



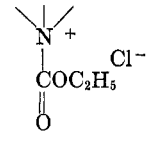
9

than the 9-ethyl carbonate **5**. The latter compound would not form the 9,10a-cyclic carbonate **7** when treated with mild base which is predicted as there is no driving force for a migration from the less hindered C-9 position to the more hindered C-10a position.

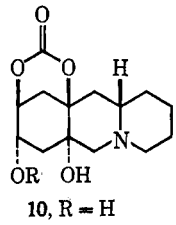
At first one might think that under the harsher conditions of the acylation in pyridine there might have been an acylation at the C-10a position followed by migration to the C-9 position. Refluxing of **6** in pyridine showed no changes in the infrared spectrum as compared to the starting material and no thin layer chromatogram (tlc) evidence for the presence of **5**. Tlc did show traces of the cyclic carbonate 6a,8-diacetate **7** which would be consistent if any migration were to occur from the C-10a position to C-9. Also refluxing the 10a-ethyl carbonate **2** in THF showed no further reaction. In addition, compound **5** does not react further with additional ethyl chloroformate in THF, dioxane, or pyridine.

Further evidence of the hindrance at position 10a is the nmr spectrum of the original 10a-ethyl carbonate **2** which shows the normal splitting pattern for an ethoxy group compared with that of the 6a,8,9-triacetate 10a-ethyl carbonate (**8**) in which the expected methylene quartet shows additional splitting.[3] This would indicate hindered rotation of the methylene group resulting in each methylene proton being in a nonequivalent environment.

A possible mechanism for the facilitated acylation would be the formation of an acylonium intermediate of the type involving the ring nitrogen which would then



acylate an alcoholic function. This intermediate would be consistent with the observation that lower yields of 10a-ethyl carbonate result when the pK_a of the ring nitrogen is decreased. However, it must still be kept in mind that only the C-10a alcohol is acylated even when tetrol **1** is the starting material. Thus the unique character of position 10a must always be considered when postulating a mechanism. In the case of the 9,10a-cyclic carbonate (**10**), no acylation of the C-6a or C-8 hydroxyl occurred with ethyl chloroformate in THF, while acylation did occur in pyridine producing 8-ethyl carbonate 9,10a-cyclic carbonate **11**.[3] Further, whenever triethylamine was present, all that was obtained was triethylamine hydrochloride and no acylated product.



10, R = H
11, R = COOEt

An alternative mechanism is based on the fact that the C-10a tertiary hydroxyl is in a unique position in that it is in a *trans*-1,4 relationship to the nitrogen lone pair of electrons. It appears that the ring nitrogen and the C-10a hydroxyl exert a long range field effect on

(7) R. U. Lemieux, R. K. Kullnig, W. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80** 6098 (1958).
(8) J. N. Schoolery and M. T. Roger, *ibid.*, **80**, 5121 (1958).
(9) See E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4249, (1962), and ref 7 for discussions of the use of W_H (width of the signal at one-half the peak height) in determining the conformation of carbinol protons.
(10) B. W. Sands and A. T. Rowland, *Steroids*, **4**, 175 (1964).

each other. Whenever there is an acyl group on the C-10a hydroxyl, the pK_a of the ring nitrogen decreases by at least 0.9 pK_a units.[3] Further, the yield of tertiary carbonate apparently decreases as the pK_a of the ring nitrogen decreases. Thus, the reaction of ethyl chloroformate in tetrahydrofuran with tetrol **1** (pK_a' = 8.14) produces yields of 50% **2** compared with no more than 9% **6** when the 6a,8-diacetate **4** (pK_a' = 6.98) is the starting material. Other long range field effects involving the ring nitrogen in the benzo[*a*]-quinolizine series have also been observed. In these compounds and appropriate model systems, the carbonyl frequency (infrared) of a ketone in a 1,4 relationship to a ring nitrogen would shift 15–25 cm^{-1} to higher wavenumbers whenever the ring nitrogen was protonated. Also the hydrates of some of these ketones were nearly as stable as chloral hydrate when the ring nitrogen was protonated.[11]

The role of the secondary C-9 hydroxyl is also essential as shown by the inability of the 6a,10a-diol **3** to be acylated by ethyl chloroformate in THF. In carbon tetrachloride, intramolecular hydrogen bonding between two *cis*-1,3-diaxial alcohols is quite pronounced.[12a,b] From infrared evidence, it was concluded that in *cis*-1,3-diols of certain bicyclononenes, hydrogen bonding between the hydrogen of the secondary hydroxyl and the oxygen of the tertiary hydroxyl was more favorable than the alternate possibility by a factor of two.[12a] In *cis*-3α,5α- and 3β,5β-cholestanediols, infrared and stereochemical evidence was given showing that hydrogen bonding of the tertiary 5-hydroxyl to the secondary 3-hydroxyl predominated. Since the perhydrobenzo[*b*]quinolizines are analogous to the cholestane-3α,5α-diol and hydrogen bonding of the secondary C-9 hydroxyl hydrogen to the oxygen of the C-10a tertiary hydroxyl would result in a steric repulsion between the C-10a hydroxyl hydrogen and the C-11a hydrogen (analogous to repulsion between the 5α-hydroxyl hydrogen and the 7α hydrogen in cholestane), it would appear probable that the C-10a hydroxyl hydrogen bonds to the C-9 hydroxyl oxygen.

It may be that the ring nitrogen has further weakened the O–H bond of the C-10a tertiary hydroxyl group permitting a direct acylation at the C-10a position. As the reaction proceeds, the generated hydrochloric acid protonates the ring nitrogen of the more basic unreacted starting material which, as the hydrochloride salt, is no longer susceptible to acylation. When the 6a,8-diacetate hydrochloride **4**·HCl was the starting material, there was no evidence of any acylation occurring. Pyridine may solvate both the C-9 and C-10a hydroxyls breaking the intramolecular hydrogen bonds with the result that acylation occurs at the C-9 secondary hydroxyl.

Intramolecular facilitated acylations have interest as potential enzyme models particularly for the esteratic enzymes where an acylated enzyme is an intermediate. It is plausible that at the enzyme's active site, there are long range effects due to the side chains of the amino acids being in a proper spatial relationship with each other. Rigid polyfunctional molecules of the benzo[*b*]quinolizine type provide a means of studying such potential long range actions.

(11) L. Novak, P. Sohar, and Cs. Szantay, *Acta Chim. Acad. Sci. Hung.*, **54**, 161 (1967).

(12) (a) R. West, J. J. Korst, and W. S. Johnson, *J. Org. Chem.*, **25**, 1976 (1960); (b) F. Dalton, J. I. McDougall, and G. D. Meakins, *J. Chem. Soc.*, 4068 (1963).

Experimental Section

Melting points were determined in unsealed capillaries on a Hoover–Thomas apparatus and are corrected. Infrared spectra were obtained on a Beckman Model IR-8 spectrophotometer in mineral oil. Nmr spectra were obtained on a Varian A-60 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard.[13] *Thin layer chromatograms prepared with silica gel G* (Brinkmann) were developed in a $CHCl_3$–CH_3OH (7:3) solvent system. Visualization was by iodine vapor. Skellysolve B refers to a petroleum ether fraction boiling at 60–68°. Microanalyses were performed by Dr. F. B. Strauss, Oxford, England.

1,3,4,6,6a,7,8,9,10,10a,11,11a-Dodecahydro-2H-benzo[*b*]-quinolizine-6a,8,9,10a-tetrol 6a,8-Diacetate 9-Ethyl Carbonate (5).—To a solution of 50 ml of pyridine and 0.5 g of **4** cooled in an ice bath was added slowly 10 ml of ethyl chloroformate. The mixture thickened and then liquified upon warming to room temperature. The solution was then refluxed for 4.5 hr and recooled, 7 ml of ethyl chloroformate added, and the solution allowed to come to room temperature again. Two hours later the solution was recooled, 5 ml of ethyl chloroformate added, and the solution let stand overnight at room temperature. After the second addition of ethyl chloroformate, a solid remained in the flask even after warming to room temperature. Also, there would be some effervescence occurring as the ethyl chloroformate was being added to the cooled mixture to the extent that the reaction flask should be only loosely stoppered while the reaction mixture stands. After standing overnight, the mixture was cooled in an ice bath and ice was added to the flask. Ammonium hydroxide (7 *N*) was added until pH 8–9 (pHydrion paper). The basic mixture was extracted with chloroform (three 30-ml portions.) The chloroform extracts were dried over anhydrous magnesium sulfate and removed under reduced pressure. The residue was treated with benzene and distilled under reduced pressure removing the pyridine as an azeotrope. Treatment of the semisolid residue with Skellysolve B caused solidification yielding 0.465 gm of one spot material. The crude material was dissolved in 30 ml of ethyl acetate and boiled with Norit; the mixture was filtered. The filtrate was concentrated to 15 ml and Skellysolve B added. Upon cooling, crystalline material totaling 0.3 g, mp 170–173° dec, was obtained. The infrared spectrum showed hydroxyl at 3460 cm^{-1} and carbonyl at 1735 and 1705 cm^{-1}. The nmr spectrum showed significant signals at δ 5.08 (W_H = 7 cps) and δ 4.86 (W_H = 7 cps) for a total of 2 H consistent for acylated equatorial carbinol protons, δ 4.16 q (J = 7 cps, 2 H) and δ 1.29 t (J = 7 cps) consistent for ethoxy, and loss of one proton at δ 3 when shaken with D_2O. It was characterized as the hydrochloride salt recrystallized from chloroform–ethyl acetate, mp 231–232° dec. The infrared spectrum of **5**·HCl shows hydroxyl at 3200 cm^{-1} and carbonyl at1738 cm^{-1}.

Anal. Calcd for $C_{20}H_{32}O_8NCl$: C, 53.39; H, 7.17; N, 3.11; Cl, 7.88. Found: C, 53.18; H, 6.97; N, 2.95; Cl, 7.56.

Treatment of 6a,8-Diacetate 9-Ethyl Carbonate (5) with Mild Base.—Compound **5** (0.077 g) was dissolved in 13 ml of methyl alcohol and 17 ml of water added. Ammonium hydroxide (7 *N*) was added to pH 8–9 (pHydrion paper) and the solution allowed to stand at room temperature for 15 min. The solution was then extracted with chloroform (three 10-ml portions). The chloroform extracts were dried over anhydrous magnesium sulfate and then removed under reduced pressure yielding 0.04 gm. The infrared spectrum showed no decrease in hydroxyl as would be predicted if the 6a,8-diacetate 9,10a-cyclic carbonate (**7**) was formed. Just the opposite was observed. The spectrum showed new hydroxyl at 3330 cm^{-1} and decrease of carbonyl at 1705 cm^{-1} pointing to a solvolysis of the 9-ethyl carbonate. The thin layer chromatogram was consistent for this conclusion.[14]

1,3,4,6,6a,7,8,9,10,10a,11,11a-Dodecahydro-2H-benzo[*b*]-quinolizine-6a,8,9,10a-tetrol 6a,8-Diacetate 10a-Ethyl Carbonate Hydrochloride (6·HCl).—A solution of 1040 ml of THF, 2.62 g of 6a,8-diacetate (**4**), and 104 ml of ethyl chloroformate was stirred for 2 hr and then allowed to stand overnight. A precipi-

(13) We thank Dr. Elliot Marvel of the Department of Chemistry, Oregon State University, for obtaining these nmr spectra.

(14) See ref 3 for a discussion of the intramolecular facilitated solvolysis of an acetate located at position 9.

tate appeared within 15 min after addition of the ethyl chloroformate. Filtration of the reaction mixture yielded 1.74 g of material characterized as 6a,8-diacetate hydrochloride **4**·HCl, mp 269.5–270° dec, by mixture melting point and comparison with the infrared spectrum of an authentic sample produced by adding diethyl ether saturated with hydrogen chloride gas to an ether solution of 6a,8-diacetate **4** and recrystallizing from ethyl alcohol–ethyl acetate. The infrared spectrum showed hydroxyl at 3340 and 3130 cm^{-1} and carbonyl at 1745 cm^{-1}.

Anal. Calcd for $C_{17}H_{28}O_6NCl$: C, 54.04; H, 7.47; N, 3.71; Cl, 9.47. Found: C, 54.14; H, 7.40; N, 3.65; Cl, 9.81.

The tetrahydrofuran filtrate was evaporated under reduced pressure and the residue suspended in ethyl acetate and filtered yielding 0.656 g, mp 202° dec.[15] The infrared spectrum showed hydroxyl at 3290 cm^{-1} and carbonyl at 1738 cm^{-1} and also indicated the product was a mixture containing about 50% 6a,8-diacetate hydrochloride **4**·HCl. Further characterization was done on the free amine.

1,3,4,6,6a,7,8,9,10,10a,11,11a-Dodecahydro-2H-benzo[*b*]quinolizine-6a,8,9,10a-tetrol 6a,8-Diacetate 10a-Ethyl Carbonate (6).—The mixture of hydrochloride salts of **4** and **6** (0.051 gm) was dissolved in 10 ml of water in a separatory funnel and ice added. Chloroform (10 ml) followed by 7 *N* ammonium hydroxide to pH 8–9 (pHydrion paper) was then added and the mixture strongly agitated. The chloroform phase was removed and the aqueous phase extracted twice more with chloroform (10 ml portions). The chloroform extracts were dried over anhydrous magnesium sulfate and then removed under reduced pressure. The viscous residue solidified upon treatment with Skellysolve B. The presence of 6a,8-diacetate **4** starting material was shown by thin layer chromatography. The infrared spectrum showed hydroxyl at 3490 cm^{-1} and carbonyl at 1760, 1735, and 1715 cm^{-1}. The nmr spectrum showed significant signals at δ 4.98 (W_H = 8 cps, C-8 equatorial carbinol proton) and δ 3.91 (W_H = 8 cps, C-9 equatorial carbinol proton). The latter partially blocked the quartet at δ 4.10 (J = 7 cps), but the triplet at δ 1.28 (J = 7cps) confirmed the presence of ethoxy.

Characterization of 6. A. Formation of 1,3,4,6,6a,7,8,9,10,10a,11,11a-Dodecahydro-2H-benzo[*b*]quinolizine-6a,8,9,10a-tetrol 6a,8,9-Triacetate 10a-Ethyl Carbonate (8).—Using reported procedures,[3] the mixture of compounds **4** and **6** was acetylated yielding a mixture of 6a,8,9-triacetate[3] and **8**. Several recrystallizations from Skellysolve B yielded an almost one spot material whose infrared spectrum was identical in all respects with that of the known material.[3]

B. Formation of 1,3,4,6,6a,7,8,9,10,10a,11,11a-Dodecahydro-2H-benzo[*b*]quinolizine-6a,8,9,10a-tetrol 6a,8-Diacetate 9,10a-Carbonate (7).—The mixture of compounds **4**·HCl and **6**·HCl (0.38 g) was dissolved in 10 ml of water and 7 *N* ammonium hydroxide added until pH 8–9 (pHydrion paper). The mixture became cloudy but cleared up again with the addition of more water. The solution was allowed to stand at room temperature for several minutes and then extracted with chloroform (three 10-ml portions). The chloroform extracts were dried over anhydrous magnesium sulfate and then removed under reduced pressure. The residue was chromatographed on silica gel (J. T. Baker). The desired cyclic carbonate diacetate was eluted with chloroform. Crystallization from Skellysolve B yielded 0.016 gm, mp 170°, of material whose infrared spectrum was identical with that of the known compound.[3] Further elution of the column with $CHCl_3$–CH_3OH (9:1) yielded the 6a,8-diacetate **4**.

Registry No.—**4**, 25683-77-6; **4**·HCl, 25683-78-7; **5**, 25683-79-8; **5**·HCl, 25683-80-1.

(15) The total yields do not add up to 100% of starting material. The proportions of each product reported here are similar in both large and small scale experiments. Addition of an ethereal solution of hydrogen chloride which should convert all basic nitrogenous material to hydrochloride salts had no effect on the yields. Since the starting material is a tertiary amine, there is probably decomposition of the type reported for tertiary amines in the presence of chloroformates. *Cf.* J. D. Hobson and J. G. McClusky, *J. Chem. Soc. C*, 2015 (1967).

Vinylpyrazoles

S. TROFIMENKO

Contribution No. 1684 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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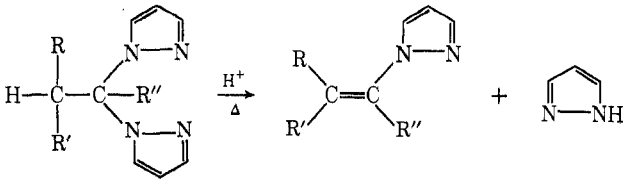
1-Vinylpyrazole and its vinyl-substituted analogs have been prepared by acid-catalyzed cracking of geminal bis(1-pyrazolyl)alkanes. 1-Vinylpyrazole polymerizes under free-radical initiation to a high polymer; the extent of polymerization diminishes with increasing substitution on the vinyl group. The various 1-vinylpyrazoles do not behave as enamines. Shielding effects of a 1-pyrazolyl substiuent on the gem, cis, and trans vinyl protons have been determined.

In the area of pyrazole chemistry there are few examples of 1-pyrazolyl olefins. Apart from the addition products of pyrazole to acetylenedicarboxylic ester,[1,2] and the 1-vinylpyrazoles obtained by the high-pressure reaction of acetylene with 3,5-dimethylpyrazole and 3-methyl-5-phenylpyrazole,[3] some 1-propenylpyrazoles have been synthesized by the pyrolysis of certain α,β-unsaturated azines.[4] A general synthesis of 1-pyrazolyl olefins has been lacking.[4a]

During our work with geminal poly(1-pyrazolyl)alkanes[5] which are available from the reaction of pyrazole with acetals or ketals, a convenient way was found for synthesizing the parent 1-vinylpyrazole and its analogs containing various alkyl substituents on the vinyl group. The method consists of heating geminal bis(1-pyrazolyl)alkanes which contain β hydrogens in the presence of a strong acid such as *p*-toluenesulfonic. Around 200° fragmentation to pyrazole and an olefin occurs. The pyrolysis products are removed as formed



by distillation at atmospheric or reduced pressure and they can be separated with ease.

The cyclic and acyclic 1-pyrazolyl olefins prepared by this method (Table I) are water-insoluble liquids possessing an "olefinic" odor. Their structure assignment rests, apart from the mode of formation and full

(1) E. Benary, H. Meyer, and K. Charisius, *Ber.*, **59**, 108 (1926).

(2) R. M. Acheson and P. W. Poulter, *J. Chem. Soc.*, 2138 (1960).

(3) N. O. Jones, British Patent 887,365 (1962); *Chem. Abstr.*, **57**, 1077*h* (1962).

(4) R. L. Stern and J. G. Krause, *J. Org. Chem.*, **33**, 212 (1968).

(4a) NOTE ADDED IN PROOF.—The synthesis of 1-vinylpyrazole from 1-(2-hydroxyethyl)pyrazole has also been reported: I. I. Grandberg and G. J. Sharova, *Khim. Geterotsikl. Soedin.*, **2**, 325 (1968); *Chem. Abstr.*, **69**, 96564*k* (1968).

(5) S. Trofimenko, *J. Amer. Chem. Soc.*, **92**, 5118 (1970).