carbonyl absorption for all of the 4-acylpyrazoles prepared was in the range of 1640–1655 cm^{-1}, comparing well with the values reported for 4-acylisoxazoles.[5]

This new route to 4-acylpyrazoles requires readily available starting materials, is easily and readily carried out, and products are easily purified.

Experimental Section

All combustion analyses were performed by Robertson Laboratory, Florham Park, N.J., and by M-H-W Laboratories, Garden City, Mich. Infrared spectra were obtained from a Perkin-Elmer 700 infrared spectrometer (0.1 mm, chloroform solvent). Melting points were taken in a Thomas-Hoover melting point apparatus in open tubes and are uncorrected. The *n*-butyllithium was obtained from the Lithium Corporation of America, Bessemer City, N.C. The tetrahydrofuran was obtained from Matheson Coleman and Bell and was used as supplied. The phenylhydrazones were prepared by a standard method,[6] recrystallized from ethanol, and used immediately.

General Procedure for the Preparation of 4-Acylpyrazoles. To a stirred solution of 0.02 mol of phenylhydrazone dissolved in 100 ml of dry THF, which was blanketed by nitrogen and cooled to 0°, was added 0.042 mol of *n*-butyllithium during 5 min. After stirring the resulting mixture for 30 min, 0.022 mol of acid chloride dissolved in 100 ml of THF was added during 5–10 min. The resulting mixture was stirred for 30 min and neutralized with 100 ml of 3 *N* HCl. The entire mixture was stirred and heated under reflux for 1 hr and cooled. The mixture was placed in a large flask and approximately 100 ml of ether was added, and this was followed by careful neutralization with sodium bicarbonate. The layers were separated, and the aqueous layer was extracted with two 50-ml portions of ether. The organic layers were combined, dried (Na_2SO_4), filtered, and concentrated, and the resulting oil or residue was immediately crystallized and/or recrystallized from hot 95% ethanol.

Preparation of 3-(*p*-Methoxyphenyl)-5-(*p*-tolyl)pyrazole. Dianion (0.025 mol) was prepared by the treatment of 0.025 mol of 4-methylacetophenone phenylhydrazone with 0.055 mol of *n*-butyllithium (see above). This dianion was condensed with 0.05 mol (twofold excess) of *p*-anisoyl chloride dissolved in 100 ml of THF. After acid cyclization and isolation of product, 5.00 g (59%) of 3-(*p*-methoxyphenyl)-5-(*p*-tolyl)pyrazole was obtained: nmr ($CDCl_3$) δ 2.38 (s, 3 H, CH_3), 3.78 (s, 3 H, CH_3O), 6.72 (s, 1 H, C_4H), and 6.88–7.88 (m, 13 H, ArH). *Anal.* Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 80.98; H, 5.92; N, 8.09.

Acknowledgment. This work was supported at Newberry College by grants from the Petroleum Research Fund, which is administered by the American Chemical Society, and the South Carolina Heart Association, Inc. The Public Health Service, Research Grant CA-04455, supported the work at Duke University. The use of the A-60 nmr spectrometer and the cooperation of Dr. R. Cargill, at the University of South Carolina, are gratefully acknowledged.

Registry No.—**1a** dianion, 13636-57-2; **1d** dianion, 53608-33-6; **1f** dianion, 53608-34-7; **1g** dianion, 53608-35-8; **1j** dianion, 53608-36-9; **2a**, 53608-37-0; **2b**, 53608-38-1; **2c**, 53608-39-2; **2d**, 53608-40-5; **2e**, 53608-41-6; **2f**, 53608-42-7; **2g**, 53608-43-8; **2h**, 53608-44-9; **2i**, 53608-45-0; **2j**, 53608-46-1; benzoyl chloride, 98-88-4; *p*-chlorobenzoyl chloride, 122-01-0; *p*-toluoyl chloride, 874-60-2; *p*-anisoyl chloride, 100-07-2; 5-(*p*-anisyl)-3-(*p*-tolyl)pyrazole, 53608-47-2.

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Acid-Catalyzed Rearrangement of 20-Vinylpregn-5-ene-3β,20-diol 3-Acetate[1]

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There are many reports that C-20 tertiary carbinol steroids may undergo dehydration,[2] rearrangement,[3] or both[4] under certain conditions.

A recent report by Narwid, Cooney, and Uskoković[5] on the Carroll rearrangement of (20*S*)-20-vinylpregn-5-ene-3β,20-diol 3-acetate (**2a**) prompts us to publish our results on the acid-catalyzed rearrangement of that compound. This work was undertaken in order to compare the behavior of the 20-vinyl- with the behavior of the 2-methyl-[3] and 20-ethynylcarbinols[4] under similar conditions.

The synthesis of 20-vinylpregn-5-ene-3β,20-diol 3-acetate (20-isomeric mixture) (**2a,b**) was achieved by treating 3β-hydroxypregn-5-en-20-one acetate (**1**) with vinylmagnesium bromide, followed by reacetylation[6] of the 3β-hydroxyl. The epimers **2a** and **2b** were isolated in an 11:1 ratio. The 20*S* configuration was assigned to the major product **2a** (77%) for the following reasons. (1) In a recent publication,[7] we have shown that the stereochemistries of nucleophilic additions of 20-keto steroids are in agreement with Cram's rule. (2) The (20*S*)-20-ethynylpregn-5-ene-3β,20-diol 3-acetate (**5**),[4,8] when selectively reduced with Lindlar catalyst,[9] gave a product identical in all respects with the vinylcarbinol **2a**.

The present study is concerned solely with acid-catalyzed reactions of the vinylcarbinol **2a**. The compounds isolated were those arising from dehydration and allylic rearrangement; no D-homoannulation was observed (Scheme I). Table I summarizes the results of this investigation.

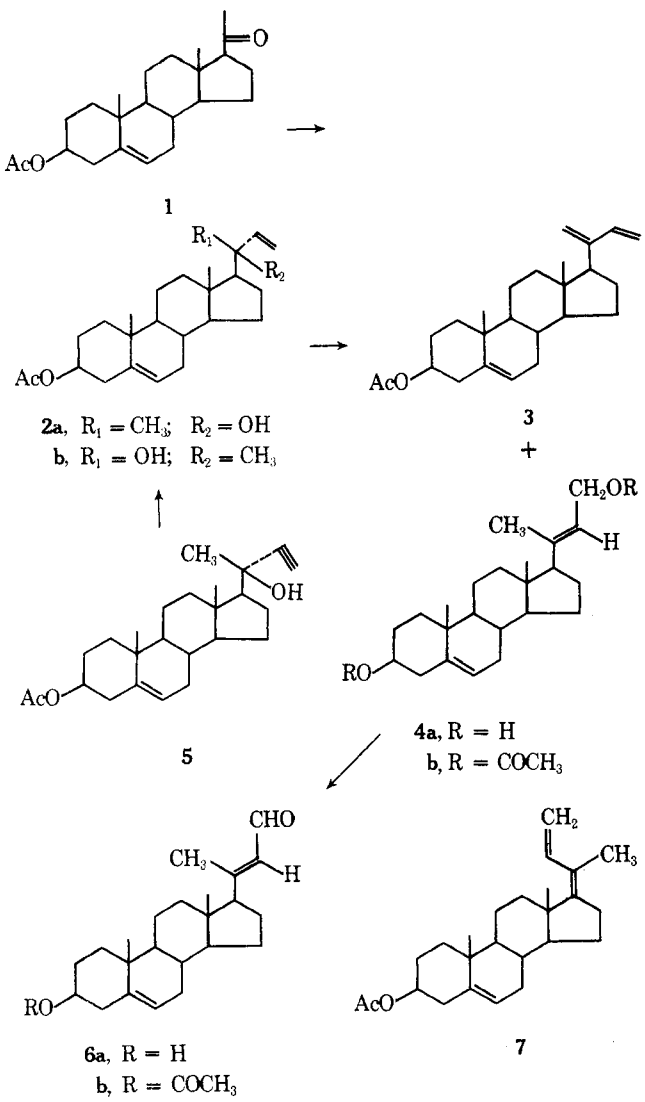
Table I
Reaction of Carbinol 2a

Reagents, conditions	Products in % yield		
	3	4b	7
AcOH–*p*-TsOH, 25°, 72 hr	20	50	
AcOH–I_2, 100°, 0.5 hr	10	50	
$POCl_3$–Py, 100°, 3 hr	30		
H_2SO_4–dioxane, 100°, 1 hr	80		
AcOH–*p*-TsOH, 100°, 0.25 hr		30	60
Benzene–PBr_3, 25°, 20 hr		70	

Structure of Triene 3. The elemental analysis of **3** showed that the compound was derived by loss of one molecule of water from the vinylcarbinol **2a** and the infrared spectrum showed the absence of any hydroxyl group. The ultraviolet absorption maximum was at 228 nm (ε 11,500), characteristic of a monosubstituted conjugated diene,[10,11] although higher than predicted according to Woodward's[12] rules. The proton magnetic resonance spectrum showed the presence of six vinylic protons and the absence of a methyl group on an unsaturated carbon, consistent with the structure **3**.

Structure of Diacetate 4b. The elemental analysis of **4b** indicated a formula derived from the starting material **2a** by acetylation of the alcoholic function. This was confirmed by the absence of any hydroxyl band in its infrared

Scheme I

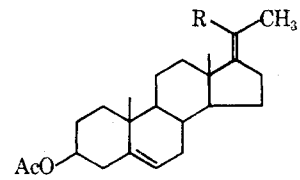


spectrum and the presence of two acetate peaks at δ 2.08 and 2.06 in its nmr spectrum. The absence of a terminal vinylic band in the infrared spectrum ruled out the possibility of the 20-acetate of compound **2a.** Furthermore, the nmr spectrum showed a peak at 1.74, assignable to a methyl group on an unsaturated carbon, which would fit the C-21 methyl in formula **4b.**

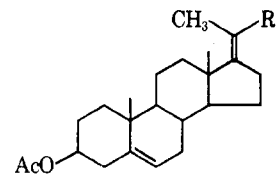
Stereochemistry of 4b. In order to determine the stereochemistry of the 20(22) double bond of **4b,** this compound was first hydrolyzed to the diol **4a** which was then oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone. The C-23 aldehyde **6a** was characterized by a strong infrared band at 1642 cm^{-1}, a uv absorption maximum at 247 nm, and a nmr peak at δ 10.1. The nmr signal of the C-21 methyl protons of **6a** appeared at δ 2.2. This indicated a cis configuration (with respect to the CH_3 and CHO groups) of the 20(22) double bond of **6a** and hence of **4b.** Faulkner[13] has shown that the average position of the nmr signals of the methyl protons of *E* olefins is at δ 2.15, and that of the *Z* olefins at δ 1.96. Recently we[14] have confirmed this stereochemical assignment of **6a** by converting it to the known (*E*)-cholesta-5,20(22)-dien-3β-ol.[5,15]

Structure of Triene 7. The infrared spectrum of norchola-5,17(20),22-trien-3β-ol acetate (**7**) displayed a conjugated diene band at 1580 cm^{-1} and a tetrasubstituted double bond at 1670 cm^{-1}. The uv absorption spectrum of **7** showed a maximum at 240 nm (ϵ 13,000) in agreement with the calculated value of 238 nm.[16]

The *Z* configuration about the 17(20)-double bond was determined by the position of the C-21 methyl peak in the nmr spectrum, as already described[8] for the following pairs:



7a, R = C≡N
b, R = C≡CH
c, R = $COOCH_3$



8a, R = C≡N
b, R = C≡CH
c, R = $COOCH_3$

7a and **8a, 7b** and **8b,** and **7c** and **8c.** Table II gives the positions of the nmr peaks for the above-mentioned pairs.

Table II

	(*Z*)-7	(*Z*)-7a	(*Z*)-7b	(*Z*)-7c	(*E*)-8a	(*E*)-8b	(*E*)-8c
21-CH_3	1.76[a]	1.8[a]	1.76[a]	1.75[a]	1.92[b]	1.98[b]	1.90[b]

[a] Broad. [b] Triplet, J = 1.5–1.6 Hz.

Experimental Section

Melting points are not corrected. The rotations were measured in chloroform solution and the ultraviolet spectra were recorded on a methanol solution with a Cary spectrophotometer Model 11 MS. Nmr spectra were obtained in deuteriochloroform solution on a 60-MHz Varian Associates DA-60 spectrometer using tetramethylsilane as an internal reference and the positions of the proton signals are expressed in parts per million downfield from tetramethylsilane signals. The microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

(20*S*)-20-Vinylpregn-5-ene-3β,20-diol 3β-Acetate (2a) from 1. To a cooled and stirred Grignard solution, prepared from 5 g of magnesium turnings and 15 ml of vinyl bromide in 60 ml of tetrahydrofuran, was added dropwise a solution of 15 g of **1** in 100 ml of tetrahydrofuran. The reaction mixture was refluxed overnight, then hydrolyzed with a saturated solution of ammonium chloride. The organic material was extracted with ethyl acetate, which was washed with water, dried over sodium sulfate, and evaporated to yield 13.4 g (89%) of crystalline residue. The infrared spectrum showed an intense hydroxyl peak (3,20-diol) at 3333 cm^{-1} and no absorption in the carbonyl region. The crude reaction product was acetylated with 40 ml of acetic anhydride and 80 ml of pyridine at 23° for 24 hr. The reaction mixture was then poured into a large excess of water. The crystalline precipitate was filtered off, washed with water until all pyridine was removed, and finally dried at 45°. Recrystallization from methanol gave **2a:** mp 163–164°; $[\alpha]^{22}D$ −67° (*c* 1.10). The ir spectrum showed bands at 3500 (hydroxyl), 1712 and 1250 (acetate), and 916 cm^{-1} (vinyl group); nmr δ 0.86 (18-CH_3), 1.04 (19-CH_3), 1.40 (21-CH_3), 6.05 (22-H) d of d (J_{cis} = 10.5 Hz and J_{trans} = 17.5 Hz), multiplet between 5.5 and 4.8 Hz (3 H, 2 H_{23} + 1 H_6).

Anal. Calcd for $C_{25}H_{38}O_3$: C, 77.67; H, 9.91. Found: C, 77.87; H, 10.12.

(20*R*)-20-Vinylpregn-5-ene-3β,20-diol 3β-Acetate (2b) from 1. The mother liquors of **2a** were combined and after chromatography on thick layer plates and several recrystallizations from benzene there was obtained 1.03 g (7%) of **2b:** mp 200–202°; $[\alpha]^{22}D$ −23° (*c* 0.70). The ir spectrum was very similar to the spectrum of its 20 epimer; nmr δ 0.80 (18-CH_3), 1.04 (19-CH_3), 1.24 (21-CH_3), 6.07 d of d (22-H).

Anal. Calcd for $C_{25}H_{38}O_3$: C, 77.67; H, 9.91. Found: C, 77.37; H, 9.99.

Reduction of (20*S*)-20-Ethynylpregn-5-ene-3β,20-diol 3β-Acetate (5) to (20*S*)-20-Vinylpregn-5-ene-3β,20-diol 3β-Acetate (2a). A solution of 500 mg of **5** in 40 ml of ethyl acetate was added to 100 mg of Lindlar catalyst. The mixture was hydrogenat-

ed under 40 psi for 1 hr. The reduction mixture was filtered through Celite and the filtrate concentrated to give **2a**. After recrystallization from methanol the product melted at 163–164°, $[\alpha]^{20}D$ −65° (*c* 0.35), and was in all respects identical with the material obtained from **1**.

Rearrangement of 2a in Acetic Acid and *p*-Toluenesulfonic Acid at Room Temperature. A solution of 1.3 g of **2a** in 50 ml of glacial acetic acid was gently warmed to effect solution. Then 17 mg of *p*-toluenesulfonic acid was added, and the reaction mixture was stirred at room temperature for 3 days. The solution was poured into 500 ml of cold 2 *N* sodium hydroxide and extracted with ether. The ether extracts were washed with saturated sodium bicarbonate, then water, dried over anhydrous sodium sulfate, and finally evaporated to give a yellow oil. Chromatography on activated alumina (Alcoa F-20) with benzene afforded two products: 256 mg (20% yield) of **3** and 700 mg (53% yield) of **4b.** Recrystallization of the latter from methanol gave pure **4b:** mp 134–135°; $[\alpha]^{20}D$ −52° (*c* 0.715); the ir spectrum showed bands at 1742 and 1247 (acetate), 805 cm^{-1} (trisubstituted double bond); nmr δ 0.57 (18-CH_3), 1.03 (19-CH_3), 1.74 (21-CH_3), 4.64 d (23-H), 5.40 m (6-H + 22-H).

Anal. Calcd for $C_{27}H_{40}O_4$: C, 75.66; H, 9.41. Found: C, 75.68; H, 9.32.

Compound **3** melted at 124–125°: $[\alpha]^{22}D$ −47° (*c* 1.60); λ_{max} 228 nm (ϵ 11,500). The ir spectrum showed bands at 1730 and 1250 (acetate), 1590 (conjugated diene), 898 cm^{-1} (terminal vinyl group); nmr δ 0.58 (18-CH_3), 1.04 (19-CH_3), 6.44 (22-H) d of d (J_{trans} = 17.5 Hz, J_{cis} = 11 Hz.

Anal. Calcd for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85. Found: C, 81.45; H, 9.89.

Rearrangement of 2a in Glacial Acetic Acid with a Catalytic Amount of Iodine. A solution of 100 ml of acetic acid, containing 400 mg of **2a** and 8 mg of iodine, was warmed on a steam bath for 30 min. It was then cooled and worked up as described above. Chromatography on a column of neutral alumina (Woelm grade III) gave **3** and **4b** in a ratio of 1:5.

Dehydration of 2a with Phosphorus Oxychloride. To a solution of 400 mg of **2a** in 6 ml of pyridine was added dropwise 13 ml of phosphorus oxychloride in 7 ml of pyridine. The reaction mixture was heated at reflux under nitrogen on a steam bath. After cooling, the solution was poured onto ice and extracted with ether. The ether extracts were combined, washed with 2 *N* aqueous sulfuric acid, sodium bicarbonate solution, water, and finally evaporated to give 100 mg of **3** (25% yield). After recrystallization, the uv exhibited λ_{max} 228 nm (ϵ 11,500).

Formation of 3 from 2a by the Action of Sulfuric Acid in Dioxane. A solution of 480 mg of **2a** in 100 ml of dioxane containing 0.2 ml of sulfuric acid was heated at reflux for 1 hr. After cooling, the solution was extracted with ether. The ether extracts were then washed with sodium bicarbonate and water and finally evaporated. Chromatography on silica gel furnished 345 mg of **3** in a yield of 72%, identical in all respects with a sample obtained previously.

Rearrangement of 2a in Glacial Acetic Acid and *p*-Toluenesulfonic Acid at Steam Bath Temperature. A solution of 3.4 g of **2a** in 120 ml of glacial acetic acid containing 42 mg of *p*-toluenesulfonic acid was refluxed on a steam bath for 15 min. Two products were isolated as described earlier for the rearrangement performed at room temperature. Chromatographic separation on alumina furnished 1.11 g (32% yield) of **4b** and 1.97 g (58% yield) of **7.**

Compound **7,** after recrystallization from methanol, had uv λ_{max} at 240 nm (ϵ 13,000); mp 138–139.5°; $[\alpha]^{20}D$ −62° (*c* 0.55). The ir spectrum had bands at 1580 (conjugated diene), 910 (vinyl), and 1670 cm^{-1} (tetrasubstituted double bond).

Anal. Calcd for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85. Found: C, 81.46; H, 9.93.

3α,23-Diacetate 4b from 2a by Treatment with Phosphorus Tribromide and Potassium Acetate. To 1 ml of benzene containing 4 drops of phosphorus tribromide was added 340 mg of **2a** in 9 ml of benzene. The reaction was stirred at room temperature overnight, methanol added, the solution washed with sodium bicarbonate and water, and finally the benzene layer was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was immediately dissolved in 30 ml of redistilled acetone, 1 g of anhydrous potassium acetate was added, and the reaction mixture was refluxed for 5 hr. The potassium salts were filtered and the acetone evaporated *in vacuo*. The residue was dissolved in ether, washed with dilute potassium carbonate and water, and dried over anhydrous sodium sulfate. Finally, the ether extract was evaporated and the crude product upon chromatography on Alcoa F-20 with benzene gave a small amount of an unidentified compound, which is believed to be the 20-vinyl acetate. Continued elution gave the major product, 225 mg (66% yield), which was identified as the 3β,23-diacetate **4b.**

Hydrolysis of 4b. A solution of 400 mg of **4b** in 20 ml of methanolic potassium hydroxide was boiled for 30 min. The solution was then diluted with water and extracted with ethyl acetate. The extract was washed with water to neutrality, dried over sodium sulfate, and evaporated *in vacuo* to give 300 mg of **4a.** Recrystallization from benzene furnished the pure **4a:** mp 197–198°; $[\alpha]^{20}D$ −51° (*c* 0.9) (lit.[17] gives 159–161°). The ir spectrum showed bands at 3400 and 1650 (allylic alcohol) and at 800 cm^{-1} (trisubstituted double bond); nmr δ 0.58 (18-CH_3), 1.00 (19-CH_3), 1.70 (21-CH_3), 4.17 (d, 2 H_{23}, J = 7 Hz).

Anal. Calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.12; H, 10.30.

Oxidation of 4a to 6a. A solution of 240 mg of the 3β,23-diol **4a** and 300 mg of 2,3-dichloro-5,6-dicyanobenzoquinone in 12 ml of dioxane was allowed to react in the dark at room temperature for 36 hr. The precipitate was collected and washed with dioxane, and the combined filtrate and washings were evaporated to give an oily residue which was chromatographed on neutral alumina (Woelm grade III). The eluates with 5% ethyl acetate in benzene gave 120 mg (50% yield) of the 23-aldehyde **6a.** Recrystallization from methylene chloride–cyclohexane yielded pure **6a:** mp 187–188°; $[\alpha]^{20}D$ −45° (*c* 0.215); uv absorption λ_{max} 247 nm (ϵ 12,600). The ir spectrum showed bands at 3448 (hydroxyl group) and at 1642 cm^{-1} (conjugated aldehyde); nmr δ 0.63 (18-CH_3), 1.02 (19-CH_3), 2.20 (21-CH_3), 5.4 (6-H), 6.0 (d, 22-H, J = 8 Hz), 10.1 (d, 23-H, J = 8 Hz).

Anal. Calcd for $C_{23}H_{34}O_2$: C, 80.65; H, 10.01. Found: C, 80.52; H, 9.96.

3β-Acetoxy-24-norchola-5,20(22)-dien-23-al (6b)[17] from 6a. The solution of 1.0 g of **6a** in 10 ml of pyridine and 1.2 ml of acetic anhydride was stirred at 25° for 20 hr. The mixture was poured on ice, and the precipitate was filtered, washed with water, and air dried. Recrystallization from acetone gave 981 mg (87%), mp 140–141°.

Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44. Found: C, 77.98; H, 9.56.

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Registry No.—**1,** 1778-02-5; **2a,** 53139-43-8; **2b,** 53495-20-8; **3,** 53432-00-1; **4a,** 53495-21-9; **4b,** 53432-01-2; **5,** 3091-94-9; **6a,** 53432-02-3; **6b,** 53495-22-0; **7,** 53432-03-4; vinyl bromide, 593-60-2.

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