H_2 (1170 ml) had ceased. The catalyst was removed by filtration (Filter-Cel) and washed with fresh ethanol. The combined filtrates were cautiously neutralized with saturated $NaHCO_3$ and concentrated at reduced pressure to *ca.* 200 ml. This residue was diluted with benzene, washed with H_2O, and dried (Na_2SO_4). Solvent removal gave a light yellow solid which was filtered through silica gel with 7:3 benzene–ether to give 15.4 g of light tan solid. Crystallization from CH_2Cl_2–ether gave 11.72 g (71.3%) of dione **2b** as fine white needles, sintered at 171°, mp 173–175°. The analytical sample was prepared by a second crystallization from CH_2Cl_2–ether of similarly prepared material: mp 170.5–174°; uv max (C_2H_5OH) 222 nm (ϵ 4750); ir ($CHCl_3$) 1740 (C-17 C=O), 1714 (C-5 C=O), and 1638 cm^{-1} (isoxazole); $[\alpha]^{25}D$ +122.0° (*c* 0.895, $CHCl_3$); mass spectrum (70 eV) *m/e* 329 (M^+) and 110 (base peak); nmr ($CDCl_3$) δ 0.99 (s, 3, C-18 CH_3), 2.20 (s, 3), and 2.37 ppm (s, 3, 2 isoxazole CH_3); ORD (dioxane) $[\alpha]_{230}$ +560°, $[\alpha]_{232}$ ±0°, $[\alpha]_{244}$ −938° (sh), $[\alpha]_{276}$ −2276° (min), $[\alpha]_{295}$ ±0°, and $[\alpha]_{317}$ +2926° (max).

Anal. Calcd for $C_{20}H_{27}O_3N$: C, 72.96; H, 8.26; N, 4.25. Found: C, 72.80; H, 8.40; N, 4.14.

Following similar procedures, we prepared these respective compounds.

(±)-19-(3,5-Dimethyl-4-isoxazolyl)-de-*A*-9β-androstane-5,17-dione (2a).—Very fine white needles were obtained by crystallization from CH_2Cl_2–ether: mp 176–178.5°; nmr, ir, uv, and mass spectrum identical with those of (+) enantiomer **2b**.

Anal. Calcd for $C_{20}H_{27}O_3N$: C, 72.96; H, 8.26; N, 4.25. Found: C, 72.57; H, 8.26; N, 4.13.

(±)-19-(3,5-Dimethyl-4-isoxazolyl)-18-methyl-de-*A*-9β-androstane-5,17-dione (2c).—Fine white needles were obtained by crystallization from CH_2Cl_2–ether: sintered at 159–163°, mp 174–176°; uv max (C_2H_5OH) 221 nm (ϵ 4850); ir ($CHCl_3$) 1730 (C-17 C=O), 1707 (C-5 C=O), and 1634 cm^{-1} (isoxazole); mass spectrum (70 eV) *m/e* 343 (M^+) and 110 (base peak); nmr ($CDCl_3$) δ 0.83 (t, 3, J = 7 Hz, C-18 CH_3), 2.21 (s, 3), and 2.38 ppm (s, 3, 2 isoxazole CH_3).

Anal. Calcd for $C_{21}H_{29}O_3N$: C, 73.43; H, 8.51; N, 4.08. Found: C, 73.36; H, 8.52; N, 4.05.

19-Nor-9β,10α-androst-4-ene-3,17-diones (3).—The procedure previously described[10,16] for the conversion of an isoxazole group to the steroid ring A was employed. We obtained the following compounds.

(±)-9β,10α-Estr-4-ene-3,17-dione (3a).—Small white prisms from CH_2Cl_2–ether: mp 149.5–152° and 159–162° (lit.[6] mp 150–151° and 156–157°)[18]; uv max (C_2H_5OH) 241 nm (ϵ 16,800); ir ($CHCl_3$) 1740 (C-17 C=O), 1669 (C-3 C=O), and 1619 cm^{-1} (conjugated C=C); mass spectrum (70 eV) *m/e* 272 (M^+); nmr ($CDCl_3$) δ 0.97 (s, 3, C-18 CH_3) and 5.84 ppm (broad s, 1, C-4 *H*).

(−)-9β,10α-Estr-4-ene-3,17-dione (3b).—Fine white needles from acetone–isopropyl ether: mp 132–135.5° (lit.[19] mp 135°); ir, uv, mass spectrum, and nmr are identical with those of racemic material; $[\alpha]^{25}D$ −23.9° (*c* 1.055, $CHCl_3$).

(±)-13β-Ethyl-9β,10α-gon-4-ene-3,17-dione (3c).—Small colorless prisms from acetone: mp 203.5–207°; uv max (C_2H_5OH) 240 nm (ϵ 17,900); ir ($CHCl_3$) 1730 (C-17 C=O), 1662 (C-3 C=O), and 1615 cm^{-1} (conjugated C=C); mass spectrum (70 eV) *m/e* 286 (M^+) and 110 (base peak); nmr ($CDCl_3$) δ 0.81 (t, 3, J = 7 Hz, C-18 CH_3) and 5.89 ppm (broad s, 1, C-4 *H*).

Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.64; H, 9.12.

Registry No.—**2a**, 35085-36-0; **2b**, 35085-37-1; **2c**, 35085-38-2; **3a**, 35085-39-3; **3b**, 2645-92-3; **3c**, 35085-41-7.

Acknowledgments.—We would like to thank the members of our Physical Chemistry Section for their assistance during the course of this work.

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[18] In many preparations this compound exhibited only a single mp of 149.5–152°.

[19] Roussel-Uclaf S.A., French Patent 1,453,221 (1966).

Tautomerism of Acid Derivatives[1a]

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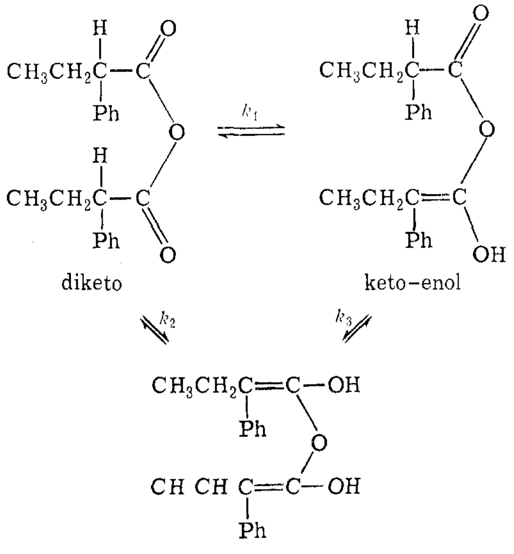
Optically active 2-phenylbutyric acid anhydride has been observed to undergo racemization on vacuum distillation[2,3] and to be thermochromic.[4,5,12] Distillation of the pure 2-phenylbutyric acid anhydride yields a distillate which is bright yellow. After a period of several hours, the yellow color of the distillate disappears. Repeated distillations of a sample of the anhydride give the same result. Nuclear magnetic resonance and infrared spectral studies of the freshly distilled anhydride indicate that diketo, keto–enol, and dienol forms are present.



An equilibrium between diketo and dienol tautomers can be established and maintained in carbon tetrachloride at room temperature. The dienol tautomer is believed to be responsible for the yellow color.

Thermochromism and tautomerism have also been observed during distillations of other acid derivatives

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[1] (a) Supported in part by the Committee on Institutional Studies and Research, Murray State University, Murray, Ky. Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Nashville, Tenn., Nov 1971. (b) Abstracted from the M.S. thesis of J. E. Hendon, Murray State University, 1971.

[2] A. Horeau, *Tetrahedron Lett.*, **No. 21**, 965 (1962).

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[5] A variety of organic compounds change color when heated and revert to the original color on cooling. This *reversible dependence of color on temperature* is known as thermochromism.[6] Thermochromism due to keto–enol equilibria has been observed for chromones, their derivatives, and chromone dimers.[7-9] Thermochromism of bindone has been explained on the basis of keto–enol tautomerism,[10] and the enolization of 1,3-diketo-2-phenyl-5-bromoindan has been used to explain its thermochromism.[11]

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[7] A. Schoenberg, E. Singer, and M. M. Sidky, *Chem. Ber.*, **94**, 660 (1961).

[8] A. Schoenberg and E. Singer, *ibid.* **94**, 248 (1961).

[9] A. Schoenberg and E. Singer, *ibid.* **94**, 254 (1961).

[10] A. Schoenberg, A. Mustafa, and W. Asher, *J. Amer. Chem. Soc.*, **75**, 4645 (1953).

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[12] A. W. Gordon, Ph.D. Dissertation, Vanderbilt University 1968.

such as 2-phenylpropionic and 2-phenylacetic acid anhydrides and 2-*p*-nitrophenylbutyric acid chloride.

Nmr Spectra.—The nmr spectrum of the colorless 2-phenylbutyric acid anhydride (diketo tautomer) gives the expected results: δ 7.05 (s, 10 H, phenyl), 3.3 (t, 2 H, methinyl), 1.8 (o, 4 H, methylene), 0.8 (t, 6 H, methyl). The results of the nmr spectra show that the rates of exchange among the tautomers were slow enough to observe each tautomer.

Spectra taken as a function of time indicate that the ratios of tautomers also change with time when the sample is maintained at the temperature of the instrument magnet (36°). If the freshly distilled anhydride is maintained at −80°, no change in tautomer composition is observed for at least 6 months, perhaps longer. Vacuum distillation of the anhydride and direct collection into an nmr tube containing carbon tetrachloride at −80° followed by warming and observing the nmr spectrum permitted the establishment of an equilibrium of approximately half and half diketo and dienol tautomers.

Chemical shift values for the various types of protons present in each tautomer are given in Table I.

TABLE I

CHEMICAL SHIFTS FOR 2-PHENYLBUTYRIC ACID ANHYDRIDE

	Type of proton (in CCl_4, ppm)			
Tautomer	Methyl	Methylene	Methinyl	Enol OH
Diketo	0.8	1.8	3.3	
Keto half of keto–enol	0.9	1.9	3.4	
Enol half of keto–enol	1.2	2.3		11.5
Dienol	1.2	2.3		11.5

Infrared Spectra.—In addition to the normal peaks observed in the infrared for the anhydride, the peaks described below underwent changes with time. Observations of infrared spectra of the freshly distilled anhydride as a function of time showed a broad peak at 3000 cm^{-1} that disappeared rapidly, a peak at 1700 cm^{-1} that disappeared more slowly than the one at 3000 cm^{-1}, and a strong, sharp peak at 2100 cm^{-1} that disappeared at the same rate as the one at 1700 cm^{-1}. The peak at 1700 cm^{-1} is due to the carbonyl in the keto half of the keto–enol tautomer. The broad peak at approximately 3000 cm^{-1} suggests intermolecular hydrogen bonding between dienol and diketo molecules. Perhaps the most interesting peak is the one at 2100 cm^{-1} because of its relative strength and position within the spectral region. At the present time no specific assignment can be made for this peak.

Experimental Section[13]

2-Phenylbutyric acid anhydride was prepared from the reaction of the sodium salt of 2-phenylbutyric acid with 2-phenylbutyryl chloride according to accepted procedures. Vacuum distillation [70° (0.02 mm)] of the anhydride was accomplished using a Nester-Faust Annular Teflon spinning band column. The collection apparatus permitted immediate sampling of the distillate and subsequent recording of nmr and ir spectra In some cases, collection was made directly into nmr tubes onto the solid solvent at −80°.

Registry No.—2-Phenylbutyric acid anhydride (diketo), 1519-21-7; 2-phenylbutyric acid anhydride (keto–enol), 35046-01-6; 2-phenylbutyric acid anhydride (dienol), 35046-02-7.

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[13] Nmr spectra were taken on a Varian A-60A spectrometer in carbon tetrachloride with TMS as an internal standard. Infrared spectra were taken on Beckman IR-10 and Perkin-Elmer 137B spectrophotomers.

Magnetic Shielding of Acetylenic Protons in Ethynylarenes

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A number of studies of the nuclear magnetic resonance spectra of monosubstituted acetylenes, with particular emphasis on chemical shifts, have been reported in the literature.[1-4] These investigations mainly dealt with the effects of substituents,[1] the intermolecular interactions, and solvent anisotropy on the chemical shifts of acetylenic protons.[2,3] In general, alkyl substituents increase the shielding of the acetylenic protons while phenyl group largely decreases the shielding.[1] The decrease in shielding is attributed to the distortion of the π system of the acetylenic bond by the inductive effect,[4] or accounted for by the counteracting effect of the ring current by the phenyl moiety on the diamagnetic shielding of the cylindrical π-electron cloud of the triple bond.[5]

In the course of study on another problem, we have had occasion to prepare several ethynylarenes. In order to investigate further the effects of the aromatic nuclei on the diamagnetic shielding of the acetylenic proton, we have studied the nmr spectra of the acetylenic protons in ethynylarenes. The chemical shifts of the acetylenic protons of ethynylarenes are listed in Table I. These values were determined at a concentration of 0.015–0.020 mol fraction solute in CCl_4. The chemical shifts are reported in hertz and τ below TMS.

TABLE I

CHEMICAL SHIFTS OF THE ACETYLENIC PROTONS OF ETHYNYLARENES

		Chemical shift			
No.	Compd	Hz	τ	ΣR^{-3}	ΣIR^{-3}
1	Phenyl	183	6.95	0.02567	0.02567
2	2-Naphthyl	190	6.83	0.03144	0.03426
3	1-Naphthyl	201	6.65	0.03939	0.04293
4	1-Pyrenyl	214	6.43	0.04733	0.05612
5	9-Anthryl	220	6.32	0.05221	0.06157

The effects of substituents on the chemical shift of the acetylenic proton in phenylacetylene have been extensively investigated, and correlations between the

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