(*E*)-**O-Methyl 4-Pyridineglyoxylamide Oxime** (**7**).—A 0.80-g (5.0×10^{-3} mol) portion of **3** was dissolved in 5.0 ml of methanol. To this was added 5.0 ml of water containing 0.56 g (1.0×10^{-2} mol) of potassium hydroxide. The mixture was heated in a water bath for 90 min at 60°, cooled, and neutralized to pH 7 with glacial acetic acid. Cooling in an ice bath yielded a white solid which was recrystallized from 10 ml of water to give 0.25 g (25%) of fine white needles: mp 149–152° (softening at 100°); ir (KBr) 3.01 and 3.16 (s, NH_2), 5.98 (s, C=O), 6.27 μ (m, pyridine).

Anal. Calcd for $C_8H_9N_3O_2 \cdot H_2O$: C, 48.7; H, 5.6; N, 21.3; O, 24.3; H_2O, 9.1; CH_3O, 15.7. Found: C, 48.6; H, 5.7; N, 21.6; O, 24.1; H_2O, 9.3; CH_3O, 15.3.[17]

(*E*)-**O-Benzyl 4-Pyridineglyoxylamide Oxime** (**8**).—Compound **4** (5.0 g, 0.02 mol) was dissolved in 100 ml of methanol. Water was added to the point of cloudiness; then 5.0 g of potassium hydroxide was added. The solution was heated on a steam bath for 15 min. Water was added to precipitate 5.5 g (96%) of **8** hydrate, cream-colored crystals. These were dissolved in a minimum amount of methanol and the solution was treated with charcoal. Addition of water gave 4.2 g (73.5%) of colorless crystals, mp 140–142° (softening at 100°).

Anal. Calcd for $C_{14}H_{13}N_3O_2 \cdot H_2O$: C, 61.5; H, 5.5; N, 15.4; O, 17.6; H_2O, 6.6. Found: C, 61.7; H, 5.6; N, 15.6; O, 16.8; H_2O, 6.9.[17]

A 0.5110-g sample of **8** hydrate was heated at 100° for 1 day under vacuum. The weight loss, 0.0367 g, corresponded to 7.2% water content (calcd, 6.6%). The resulting compound, mp 142–144°, gave an ir spectrum very similar to that of **8** hydrate: ir 2.99 and 3.19 (m, NH_2), 5.97 (s, C=O), 6.13 (m), 6.22 (m, pyridine).

Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.9; H, 5.1; N, 16.5; O, 12.54. Found: C, 65.8; H, 5.3; N, 16.4; O, 12.5.

8 Methyl Iodide (**12**).—This compound was prepared by reaction of methyl iodide with **8** in acetone–water (2.5:1): mp 82–85°.

Anal. Calcd for $C_{15}H_{16}IN_3O_2 \cdot H_2O$: C, 43.4; H, 4.4; I, 30.6; N, 10.1; O, 11.6. Found: C, 43.3; H, 4.6; I, 30.6; N, 9.7; O, 12.4.

(*Z*)-**O-Benzyl 4-Pyridineglyoxylamide Oxime** (**9**).—To a 1.5-g (5.6×10^{-3} mol) portion of **5** in 25 ml of methanol was added 25 ml of concentrated ammonium hydroxide. The solution was boiled 10 min and then cooled. Addition of water precipitated 1.0 g (62%) of colorless microcrystalline material: mp 166–167°; ir 2.99 and 3.16 (m, NH), 5.91 (s, C=O), 6.28 μ (m, pyridine).

Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.9; H, 5.1; N, 16.5; O, 12.5. Found: C, 66.1; H, 5.2; N, 16.2; O, 12.4.

9 Methyl Iodide (**13**).—This compound was obtained as pale yellow crystals, mp 218–219° dec.

Anal. Calcd for $C_{15}H_{16}I_1N_3O_2$: C, 45.5; H, 4.1; N, 10.6; O, 8.1. Found: C, 45.5; H, 4.1; N, 10.3; O, 8.4.

(*Z*)-**O-Methyl 4-Pyridineglyoxylamide Oxime** (**10**).—A 0.58-g (3.8×10^{-3} mol) portion of **6** was heated in 10 ml of concentrated ammonium hydroxide. A clear solution was obtained momentarily; then product began to precipitate. On cooling 0.46 g (71%) of colorless solid, mp 170°, was obtained: ir 3.01 and 3.15 (m, NH), 5.89 (s, C=O), 6.27 μ (m, pyridine).

Anal. Calcd for $C_8H_9N_3O_2$: C, 53.6; H, 5.1; N, 23.5; O, 17.9. Found: C, 53.9; H, 5.3; N, 23.3; O, 17.8.

When the product was allowed to stand for 6 months, hydration occurred.

Anal. Calcd for $C_8H_9N_3O_2 \cdot H_2O$: C, 48.7; H, 5.6; N, 21.3; O, 24.3; CH_3O, 15.7. Found: C, 49.3; H, 5.2; N, 23.0; O, 23.0; CH_3O, 16.2.

Isomerization of 8 to 9.—A 0.65-g sample of **8** was dissolved in 50 ml of 50% H_2SO_4 and allowed to stand overnight. A tan solid (0.45 g) precipitated when the solution was neutralized with sodium bicarbonate. The product was dissolved in methanol, treated with charcoal, and filtered. Addition of water precipitated 0.1 g of colorless solid, mp 150–160°, the ir spectrum of which corresponded exactly to that of **9**.

Registry No.—**1**, 21372-44-1; **2**, 21372-45-2; **2** hydrochloride, 21372-46-3; **2** methyl iodide, 21372-47-4; **3**, 21372-48-5; **4**, 21372-49-6; **4** perchlorate, 21372-50-9; **4** methyl iodide, 21449-74-1; **5**, 21449-75-2; **6**, 21449-76-3; **7**, 21449-77-4; **8**, 21449-78-5; **8** methyl iodide, 21449-79-6; **9**, 21449-80-9; **9** methyl iodide, 21449-81-0; **10**, 21449-82-1.

Acknowledgment.—The elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratories Edgewood Arsenal, Md.

(17) The Karl Fischer procedure was used for the H_2O analysis.

Ionization State of *p*-Toluenesulfonic Acid in Acetic Acid

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Received January 6, 1969

Recently, Goering and Fickes,[2] because of very accurate experimental data, were able to detect the upward drift of the acetolysis rate of a *p*-toluenesulfonate ester, and they ascribed this to a *p*-toluenesulfonic acid salt effect; such salt effects had been reported previously.[3] However, Bruckenstein and Kolthoff[4] had estimated a dissociation constant of $10^{-8.5}$ for *p*-toluenesulfonic acid in glacial acetic acid on the basis of emf measurements. This result means that either the substrate is not ionized in this solvent, or that if it is, the ionized form exists very largely as ion pairs. To distinguish between these two possibilities, a uv spectroscopic investigation was made of *p*-toluenesulfonic acid derivatives in acetic acid.

Spectra were examined in acetic acid 0.1% (v/v) in water and 2.5% (v/v) in acetic anhydride. In the former solvent, the spectrum of *p*-toluenesulfonic acid qualitatively resembled that of its methyl ester and was unchanged in 3.5×10^{-2} *M* perchloric acid, but was qualitatively and quantitatively changed in 4.2×10^{-2} *M* potassium acetate. Of special interest was the longest wavelength vibrational sub-band (Table I).

TABLE I
LONGEST WAVELENGTH VIBRATIONAL SUB-BAND IN ACETIC ACID 0.1% IN WATER

Solute at 1.49×10^{-2} *M*	λ_{max}, mμ	$\epsilon \times 10^2$	Other solute
MeOTs	273.1	5.0	...
HOTs	272.6	3.3	...
HOTs	272.6	3.3	3.5×10^{-2} *M* $HClO_4$
HOTs	272.2	1.7	4.2×10^{-2} *M* KOAc

A similar situation held with spectra examined in acetic acid 2.5% in acetic anhydride, except that addition of perchloric acid caused a marked change in the spectrum, possibly due to its catalysis of mixed anhydride formation (Table II).

In the more polar, more basic of the two solvents examined (0.1% in water), the addition of the very

(1) The author thanks Professor M. O. Whiting and Dr. D. J. MacGregor for their advice, and the Science Research Council of Great Britain for a maintenance grant.

(2) H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, **90**, 2848 (1968).

(3) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956).

(4) S. Bruckenstein and T. M. Kolthoff, *ibid.*, **78**, 2974 (1956).

TABLE II
LONGEST WAVELENGTH VIBRATIONAL SUB-BAND IN ACETIC ACID 2.5% IN ACETIC ANHYDRIDE

Solute at 1.75×10^{-2} M	λ_{max}, mμ	$\epsilon \times 10^2$	Other solute
MeOTs	273.1	5.1	...
HOTs	272.7	3.5	...
HOTs	272.7	3.3	4.7×10^{-2} M $HClO_4$
HOTs	272.2	1.6	4.0×10^{-2} M KOAc

strong acid perchloric acid did not change the extinction coefficient of the substrate by more than *ca.* 1.5%. If the absorption of the *p*-toluenesulfonate anion is taken into account, this places an upper limit of *ca.* 3% on the degree of ionization of *p*-toluenesulfonic acid. It could be argued that the observed rate enhancements are indeed salt effects caused by a small (<3%) proportion of the *p*-toluenesulfonic acid which is ionized but not dissociated, but to account for the rate enhancements observed for Goering and Fickes,[2] *b* values of *ca.* 100–300 would be required, well above the normal range of such values.

The observed rate enhancements may therefore be acid catalytic rather than salt effects. This interpretation is supported by the suppression of the phenomenon by the addition of sodium acetate.[2]

The data in the tables emphasize that the acetolyses of *p*-toluenesulfonic acid esters can be followed conveniently by uv spectroscopy either in the presence or absence of excess acetate ion. Ultraviolet spectroscopic methods have been described for kinetic measurements on the hydrolyses and methanolyses of *p*-toluenesulfonic acid esters[5] and on the formolyses of *p*-nitrobenzenesulfonic acid esters,[6] but the former method was based on the differential absorption of covalent ester and acid anion (rather than free acid), and the latter on uv assay of an ethereal–alcoholic solution of unreacted ester after *p*-nitrobenzenesulfonic and formic acids had been removed with base. In general, uv spectrophotometry requires lower concentrations of substrate than titrimetry, which is often experimentally tedious and profligate of hard-won material.

Experimental Section

Distillation of commercial (B. D. H.) glacial acetic acid gave a material 0.1% (v/v) in water (Karl Fischer titration), and distillation of a 10% (v/v) solution of acetic anhydride in the same commercial acid through a 30-cm Dufton column gave a material 2.5% (v/v) in acetic anhydride (uv absorbance). The following operations were performed with both distillates; the first of two quantities always refer to the wet acetic acid.

Methyl *p*-toluenesulfonate [bp 159° (15 mm), 146.2 and 171.7 mg] was dissolved in acetic acid (50.0 ml), and a sample was heated for 3 hr (>10 half-lives) at 157° in a sealed tube. Specimens were used to make up solutions of freshly fused anhydrous potassium acetate (40.7 and 39.2 mg/10 ml) and "AnalaR" 60.0% aqueous perchloric acid (62.4 and 80.7 mg/10 ml). The uv spectra of the resulting four samples were measured between 250 and 280 mμ in 1-mm path-length cuvettes (to minimize solvent absorption) in a Cary 14M spectrophotometer. Automatically programmed slit widths varied from 0.04 mm at 280 mμ through 0.05 mm at 273 mμ and 0.1 mm at 260 mμ to 0.3 mm at 250 mμ.

Registry No.—*p*-Toluenesulfonic acid, 104-15-4; acetic acid, 64-19-7; methyl *p*-toluenesulfonate, 80-48-8.

(5) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).
(6) W. S. Johnson, D. Bailey, R. Owyang, R. Bell, B. Jacques, and J. Crandall, *J. Amer. Chem. Soc.*, **86**, 1959 (1964).

Heterocyclic Studies. XXX. Photochemical Reactions of Diazabicyclo[3.2.0]-6-heptanones[1]

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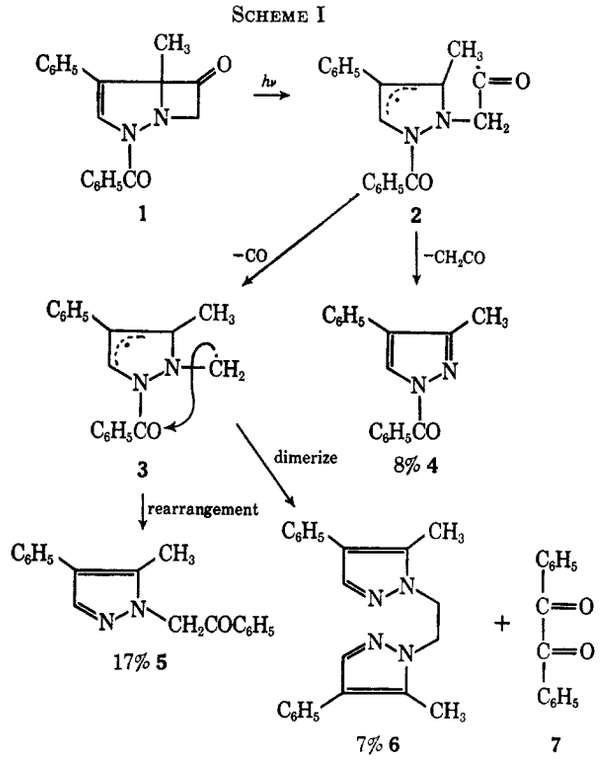
Received October 28, 1968

2-Acyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-ones (*e.g.*, **1**) undergo several novel rearrangements under mild solvolytic and thermal conditions.[2] We now report briefly on the photochemical behavior of **1** and some related compounds.

In benzene solution, irradiation of **1** gave four products, **4**–**7**, in the yields indicated (Scheme I). The product distribution was determined by the areas of methyl peaks in the nmr spectrum of the total product mixture. Structures **4** and **5** were inferred from the composition and spectral properties and confirmed by comparison of the photo products with synthetic samples. The phenacylpyrazole **5** was prepared by condensation of 5-methyl-4-phenylpyrazole-1-acetic acid[3] with phenyllithium according to a standard method.[4] Benzoylation of the

SCHEME I



parent 3-methyl-4-phenylpyrazole gave a sample of **4**.[5] The third product was dimeric; the symmetrical structure **6** is assigned entirely from spectral evidence. The uv maximum at 241 mμ is consistent for a 1-alkyl-

(1) Supported by Grant GP-5219 from the National Science Foundation.
(2) (a) J. A. Moore, R. L. Wineholt, F. J. Marascia, R. W. Medeiros, and F. J. Creegan, *J. Org. Chem.*, **32**, 1353 (1967); (b) J. M. Eby and J. A. Moore, *ibid.*, **32**, 1346 (1967).
(3) J. A. Moore and C. L. Habraken, *ibid.*, **30**, 1889 (1965).
(4) H. Gilman and P. R. van Ess, *J. Amer. Chem. Soc.*, **55**, 1258 (1933).
(5) The position of acylation in a 3-alkylpyrazole is presumably controlled mainly by steric effects, and **4** is expected to be the major product. This synthesis, however, does not unambiguously establish the position of the benzoyl group in **4**.