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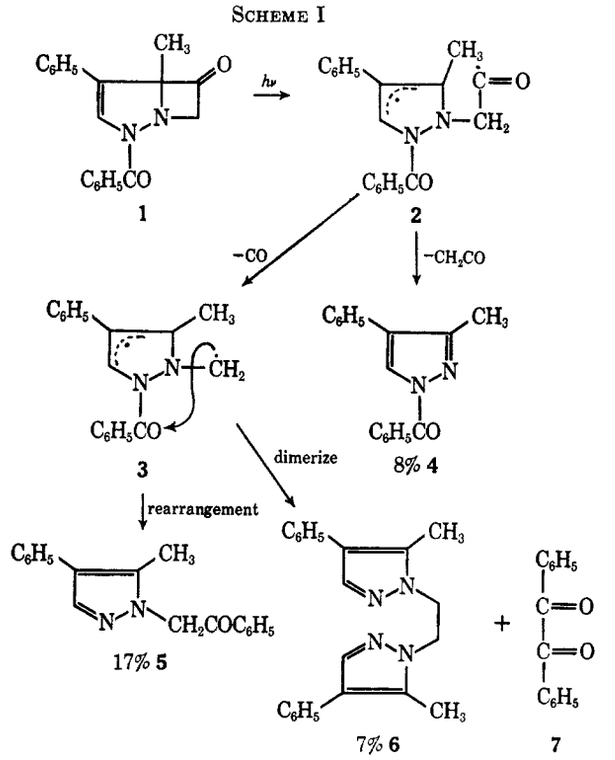
2-Acyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-ones (*e.g.*, **1**) undergo several novel rearrangements under mild solvolytic and thermal conditions.[2] We now report briefly on the photochemical behavior of **1** and some related compounds.

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-

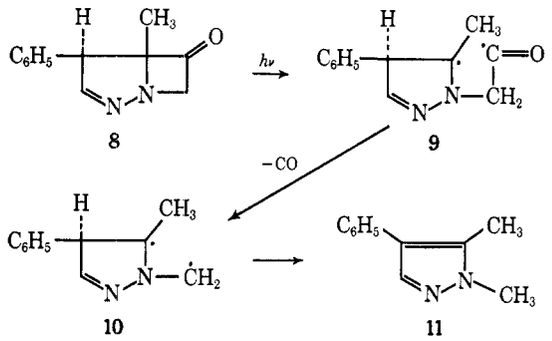
(1) Supported by Grant GP-5219 from the National Science Foundation.
(2) (a) J. A. Moore, R. L. Wineholt, F. J. Marascia, R. W. Medeiros, and F. J. Creegan, *J. Org. Chem.*, **32**, 1353 (1967); (b) J. M. Eby and J. A. Moore, *ibid.*, **32**, 1346 (1967).
(3) J. A. Moore and C. L. Habraken, *ibid.*, **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**.

pyrazole. The nmr spectrum showed δ 1.81 (s, 3), 4.55 (s, 2), and 7.65 (s, 1). The methyl peak is significantly upfield from the position (2.2 ppm)[6a] expected for a 1-alkyl-5-methylpyrazole. An important point bearing on the structure is the mass spectrum, with peaks at *m/e* 342 for the molecular ion and *m/e* 171 for the monomeric fragment ion $C_{10}H_9NCH_2 \cdot^+$; the base peak was *m/e* 184, possibly representing $C_{10}H_9N \cdot {}^+CH{=}CH_2$. There was no indication among the reaction products of the thermal isomerization product of **1**.[2b]

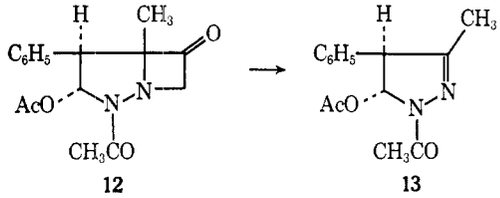
Irradiation of **1** in methanol gave **4** (18%), **5** (13%), **6** (5%), and an additional product in 15% yield which was shown to be 1,5-dimethyl-4-phenylpyrazole (**11**).[6]

The Δ^2-diazabicycloheptenone **8** in benzene or methanol solution gave the dimethylpyrazole **11** as the major photolysis product (Scheme II). In benzene solution the yield of **11** by nmr analysis was 54%, and in methanol, 80–90%. Much longer irradiation times were required for **8** than for **1**.

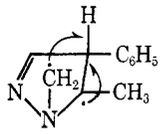
SCHEME II



Finally, the 2-acetyl-3-acetoxy ketone **12** was irradiated to examine the behavior of a saturated compound. In methylene chloride solution, one major product was obtained; after partial purification the nmr spectrum [δ 1.98 (s, 3), 2.09 (s, 3), 2.39 (s, 3), 3.93 (br s, 1), 6.63 (br s, 1), 6.8–7.5 (m, 5)] suggested the acetoxypyrazoline structure **13**.[7] Attempted purification on silicic acid gave 1-acetyl-4-methyl-5-phenylpyrazole,[3] arising from a not unexpected elimination of acetic acid from **13**. In methanol, however, photolysis of **12** gave the dimethylpyrazole **11** as well as a larger amount of **13**.



These photolysis products can be accounted for very well by the familiar type-I ketone cleavage[8] (Scheme I). With the 2-acyl-Δ^3 ketone **1**, the resonance-stabilized radical (**2**) can undergo loss of ketene to give directly the aromatic pyrazole **4** or decarbonylation to **3** followed by rearrangement, dimerization, or hydrogen abstraction from methanol. In the case of the Δ^2 ketone **8**, on the other hand, an aromatic product is not achieved by loss of ketene from the intermediate radical **9**, and products arise exclusively from the decarbonylation path. The fact that radical **10**, in contrast to **3**, leads to the dimethylpyrazole **11** in either benzene or methanol, suggested the possibility of internal hydrogen abstraction (**14**) in the former solvent. The preference for the ketene fragmentation pathway in the substituted ketone **12** appears inconsistent with the other results; the *endo*-acetoxy group apparently plays a role in this case.



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Experimental Section[9]

Determination of Product Yields.—Yields of individual products in the mixture from photolyses were determined from the nmr spectrum of the total product mixture using either the methoxyl singlet of methyl *p*-bromobenzoate (A) or the two-proton methine singlet of "disalicylaldehyde"[10] (B) as internal standards.

The height of the integral step for a CH_3 or CH_2 peak, or both, due to each component relative to that due to the step for the singlet in the standard was determined from the average of three integral sweeps and the molar amount of product was determined from the ratio of integral steps per proton for standard and product peaks.

Photolysis of 1 in Benzene.—A solution of 1 g of the bicyclic ketone in 325 ml of benzene was chilled in ice and stirred with a nitrogen stream. After irradiation for 50 min with a 450-W medium pressure mercury lamp in a Pyrex filter sleeve, the ir spectrum showed complete absence of the 1800-cm^{-1} peak of **1**. The solution was evaporated and the product distribution was determined from the nmr spectrum of an aliquot of the total residue; using 16.7 mg of standard A, the integration steps for standard, CH_3 peak of **4**, CH_2 peak of **5**, and CH_2CH_2 peak of **6** were 22.5, 9.83, 10.9, and 10.0 mm, respectively.

The combined material from six 1-g irradiations (6 g of **1**), in chloroform solution, was passed over a short column of 30 g of silicic acid to remove colored polymeric impurities. The eluate was evaporated and 650 mg of crystals was obtained from a concentrated solution of the residue in ether plus pentane. Three recrystallizations from ether gave 120 mg of white prisms of 5-methyl-1-phenacyl-4-phenylpyrazole (**5**): mp 155°, λ_{max}^{MeOH} 248 mμ (27,000); ν_{max}^{KBr} 1705, 1600, 1240 cm^{-1}; δ^{CDCl_3} 2.31 (s, 3), 5.59 (s, 2), 7.3–8.2 (m, 11).

Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.23; H, 5.84; N, 10.14. Found: C, 77.87; H, 5.87; N, 10.08.

Material remaining after crystallization of **5** was chromatographed from benzene on 150 g of silicic acid; fractions were collected on the basis of tlc and nmr behavior. The first group of fractions, 620 mg, contained a mixture of 1-benzoyl-3-methyl-4-phenylpyrazole (**4**) and benzil. These compounds were separated by vpc (6 ft × 0.25 in. SE-30 on Chromosorb W, 200°) and identified by vpc retention time and ir with authentic samples.

The next fractions gave an additional 310 mg of crystalline **5**. Final fractions from the column gave 620 mg of crude crystals containing mostly the dimer **6**. Rechromatography on 35 g of silica and recrystallization from benzene–ether gave 150 mg of white prisms of 1,2-bis[(3-methyl-4-phenyl)-1-pyrazolyl]ethane (**6**): mp 183–184°; λ_{max}^{MeOH} 242 mμ (ϵ 28,000); δ^{CDCl_3} 1.81 (s, 3 or 6), 4.55 (s, 2 or 4), 7.3 (s, 5 or 10), 7.65 (s, 1 or 2); *m/e* 342.

(6) (a) C. L. Habraken and J. A. Moore, *J. Org. Chem.*, **30**, 1892 (1965), (b) P. Cohen-Fernandes and C. L. Habraken, *Rec. Trav. Chim.*, **86**, 1249 (1967).

(7) The peaks at δ 3.93 and 6.63 were considerably broadened singlets due to H-4 and H-5, respectively. In the spectrum of **12** and related 3-substituted bicyclic ketones, the corresponding proton signals were slightly broadened singlets, with J = 0 Hz.[2a]

(8) See, for example, R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., New York, N. Y., 1966, p 71.

(9) General experimental techniques are given in part XXII of this series, *J. Org. Chem.*, **31**, 52 (1966).

(10) 3,4,7,8-Dibenzo-2,6,9-trioxabicyclo[3.3.1]nona-3,7-diene, Aldrich Chemical Co.

Anal. Calcd for $C_{22}H_{22}N_4$ (342.3): C, 77.16; H, 6.48; N, 16.36. Found: C, 77.34; H 6.33; N, 16.47; mol wt (osmometric in benzene), 346.

5-Methyl-1-phenacyl-4-phenylpyrazole (**5**) was synthesized by addition of 0.6 ml of 2 *N* phenyllithium in ether–benzene to a suspension of 107 mg of 5-methyl-4-phenylpyrazole-1-acetic acid in the same solvents. After refluxing for 5 hr the reaction mixture was poured into 50 ml of iced aqueous NH_4Cl. The organic layer was washed, dried, and evaporated to a dark oil which crystallized to give 55 mg (39%) of **5**, mp 145°. Recrystallization gave white crystals, mp 148–149°, ir identical with that of the material isolated from photolysis of **1**.

1-Benzoyl-4-methyl-5-phenylpyrazole (**4**) was prepared by addition of 89 mg of benzoyl chloride and 65 mg of pyridine to a solution of 100 mg of 5-methyl-4-phenylpyrazole[3] in CH_2Cl_2. After 1 hr water was added and the organic phase was washed with carbonate and acid, dried, and evaporated to an oil. Addition of pentane gave 80 mg of yellowish crystals, mp 65–67°. Repeated recrystallization at 0° from ether–pentane gave colorless crystals of **4**: mp 68–69°; λ_{max}^{MeOH} 233 mμ (ε 17,000), 283 (11,000); ν^{KBr} 1680 cm^{-1} (CO); δ^{CDCl_3} 2.4 (s, 3), 7.1–7.5 (m, 8), 8.0–8.4 (m, 3).

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.80; H, 5.33; N, 10.58.

Photolysis of 1 in Methanol.—Irradiation of solution of 500 mg of **1** in 300 ml of methanol as described above for 35 min caused complete disappearance of the starting ketone. The nmr spectrum of the total mixture revealed the presence of compounds **4**, **5**, and **6** together with another component **11** (δ 2.3, 3.8); using 15.1 mg of standard B, the integral steps for CH of standard, CH_3 of **4**, CH_2 of **5**, CH_2CH_2 of **6**, and NCH_3 of **11** were 10.3, 13.9, 6.6, 5.1, and 11.3 mm, respectively. Chromatography (35 g of silicic acid) was carried out to isolate the last compound. After preliminary fractions containing **4** and **5**, 1,5-dimethyl-4-phenylpyrazole (**11**) was eluted with benzene–ether 9:1, giving 36 mg of oil. The compound was purified by vpc (30% SE-30; 20 ft, 225°); the sample was identical (nmr, ir, vpc) with that described below.

Photolysis of 5-Methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-2-hepten-6-one[11] (**8**).—A solution of 1.0 g of slightly impure bicyclic ketone **8** (mp 43–48°) in 350 ml of methanol was irradiated as described for **1**. After 17 hr, the solution was evaporated; the nmr spectrum showed only peaks due to **11** (80% based on total integral) and unreacted **8**.

In a second run, a solution of 62 mg of **8** (0.31 mmol) in 300 ml of methanol was irradiated for 2.7 hr. The nmr spectrum of the product mixture plus 31 mg of standard A showed peaks due to **11**, unreacted starting material, and standard in a molar ratio of 0.15:0.14:0.14, representing a yield of **11**, based on starting material consumed, of 90%. A small impurity peak was present at δ 1.35.

The residue from the 1-g run was chromatographed on 36 g of silicic acid (benzene–5% ether); fractions containing 590 mg of oil containing **11** were collected, followed by 200 mg of material containing some unreacted **8**. The early fractions crystallized on standing for 10 days at 5°; sublimation [60° (0.2 mm)] followed by repeated recrystallization from ether–pentane gave 285 mg of white plates of **11**, mp 65–66°; λ_{max}^{MeOH} 241 (ε 16,000); δ^{CDCl_3} 2.33 (s, 3), 3.8 (s, 3), 6.9–7.4 (s, 5), 7.52 (s, 1); *m/e* 172 (base peak).

Anal. Calcd for $C_{11}H_{12}N_2$ (172.2): 76.71; H, 7.02; N, 16.27. Found: C, 76.78; H, 7.21; N, 16.36.

A sample of this material was treated with methyl iodide in a sealed tube at 100° for 50 hr, giving 1,2,3-trimethyl-4-phenylpyrazolium iodide, mp 156–157° (lit.[6] mp 148–149°), mixture melting point with earlier sample[6] recrystallized from ethanol–ether, 156–157°.

Photolysis of 3-Acetoxy-2-acetyl-5-methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-6-heptanone (**12**).—A solution of 250 mg of **12**[11] in 300 ml of methylene chloride was irradiated as described above; 3 hr was required for disappearance of the 1800-cm^{-1} ir band. After evaporation the residue was extracted with ether; 70 mg of dark polymer remained insoluble. The pink ether soluble oil was chromatographed on alumina. The benzene eluent gave 120 mg of oil, ir ($CHCl_3$) 1750 and 1670 cm^{-1}, consisting mainly of one compound. The nmr spectrum contained peaks attributed to **13** (see discussion) and also minor peaks due to 1-acetyl-3-methyl-4-phenylpyrazole. Further chromatography of the oil on silicic acid gave fractions which crystallized to give 1-acetyl-3-methyl-4-phenylpyrazole, mp 59–60° (lit.[3] mp 66–67°).

After photolysis of **12** in methanol solution for 2 hr and evaporation, nmr analysis (using fractions of total integral) indicated the presence of **13** (40%) and the dimethylpyrazole **11** (20%); with internal standard B, the yields were 36 and 20%, respectively. Injection of this mixture at 150° onto a vpc column (8 ft × 0.25 in., SE-30) produced peaks due to the dimethylpyrazole (**11**) and 1-acetyl-3-methyl-4-phenylpyrazole in a ratio of 1:1.5, indicating nearly complete pyrolysis of **13** to the acetylpyrazole.

Registry No.—**4**, 21297-76-7; **5**, 21297-77-8; **6**, 21297-78-9; **11**, 1706-46-3.

(11) J. A. Moore, F. J. Marascia, R. W. Medeiros, and R. L. Wineholt, *J. Org. Chem.*, **31**, 34 (1966).

A Practical Synthesis of Tetraphenylcyclopentadiene from Tetracyclone

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1,2,3,4-Tetraphenylcyclopentadiene (**1**) and related tetraarylcyclopentadienes are valuable as intermediates for the synthesis of a variety of other compounds, particularly fulvenes, diazo compounds, and ferrocenes. The usual synthesis of **1** involves a rather lengthy procedure[2,3] and is intrinsically inapplicable to the synthesis of unsymmetrical derivatives of **1**. Since tetracyclone (**2**, tetraphenylcyclopentadienone) and a large number of both symmetrical and unsymmetrical analogs of **2** can be prepared readily,[4] the conversion of **2** to **1** represents a process of real synthetic utility. A detailed study of the reduction of ketone **2** has been reported, the major objective of which was to find a practical conversion of **2** to **1**; all conditions investigated gave unexpectedly complex mixtures, the best yield of **1** (18%) being obtained by an inverse lithium aluminum hydride reduction followed by a chromatographic separation.[5]

We have now found that the reduction of **2** to **1** can be carried out very cleanly and essentially quantitatively by the use of excess lithium aluminum hydride in the presence of aluminum chloride, as described in the Experimental Section. This procedure should be applicable to the synthesis of a wide variety of unsymmetrical substitution products of **1**. As an illustration, we have carried out the reduction of 3-(*p*-methoxyphenyl)-2,4,5-triphenylcyclopentadienone (**3**)[6] to 2-(*p*-methoxyphenyl)-1,3,4-triphenylcyclopentadiene (**4**) in good yield. Diene **4** has been available previously by way of a complex multi-step synthesis.[7]

During the course of this work, we also investigated briefly the reduction of tetracyclone (**2**) with sodium

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(2) J. Wislicenus and H. Carpenter, *Ann.*, **302**, 223 (1898).

(3) K. Ziegler and B. Schnell, *ibid.*, **445**, 266 (1925).

(4) M. A. Ogliarusso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 293 (1965).

(5) N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, **75**, 2283 (1953).

(6) S. B. Coan, D. E. Trucker, and E. I. Becker, *ibid.*, **75**, 900 (1953).

(7) L. Mehr, E. I. Becker, and P. E. Spoerri, *ibid.*, **77**, 984 (1955).