Anal. Calcd for $C_{17}H_{28}O_2$ (264.41): C, 77.22; H, 10.67. Found: C, 77.03; H, 10.92.

Des-A-pregn-9-ene-5α-20β-diol (**16**) was isolated in 5% yield from thin layer chromatograms of the mother liquor as colorless needles: mp 144–146° (ether–petroleum ether); infrared spectrum (in $CHCl_3$), 3620 cm^{-1} (OH); nmr spectrum (in $CDCl_3$), 10-CH_3 band at δ 1.76, 13-CH_3 singlet at 0.86, 17β-CH(β-OH)CH_3 methyl doublet (J = 6 cps) at 1.15, and 5β-H and 20α-H at 3.88 (narrow band) and 3.75 (broad), respectively.

Anal. Calcd for $C_{17}H_{28}O_2$ (264.41): C, 77.22; H, 10.67. Found: C, 77.06; H, 10.79.

B.—Oxidation of 2 g of des-A-pregn-9-ene-5β,20β-diol (**15**) (mp 155–164°) in 200 ml of chloroform with 25 g of highly active manganese dioxide gave 1.85 g of oily product, with an ultraviolet absorption at 250 mμ (ε 4970) and 292.5 mμ (ε 4410). In addition to 20β-hydroxy-des-A-pregn-9-en-5-one (**17**), chromatographic separation of this product gave a 15% yield of 20β-hydroxy-des-A-pregna-9,11-dien-5-one (**21**) as colorless needles: mp 158–159° (aqueous methanol); $[\alpha]^{25}D$ −73.4° (c 0.5, in C_2H_5OH); infrared spectrum (in $CHCl_3$), 3610 (–OH), 1650 and 1600 cm^{-1} (dienone); uv spectrum (in 95% C_2H_5OH), λ_{max} 292.5 mμ (ε 24,300); nmr spectrum (in $CDCl_3$), 10-CH_3 doublet (J = 2 cps, indicating long-range coupling) at δ 1.85, 13-CH_3 singlet at 0.91, 17β-CH(β-OH)CH_3 methyl doublet (J = 6 cps) at 1.20, and AB quartet for C_{11} and C_{12} olefinic protons (J = 10 cps) centered at 6.66, with $\Delta\delta_{AB}$ = 0.60 ppm.

Anal. Calcd for $C_{17}H_{24}O_2$ (260.38): C, 78.42; H, 9.29. Found: C, 78.68; H, 8.92.

C.—To a solution of 1 g of **17** in 50 ml of methanol at 5° was added 1 g of sodium borohydride, and the reaction mixture was stirred for 1.5 hr at this temperature. Glacial acetic acid was added to the cold solution until the pH was 7; the solution was diluted with chloroform, washed with water, dried over sodium sulfate, and evaporated to dryness. Crystallization of the residue gave 758 mg of crude **15**, mp 155–162°. The mother liquor residue (222 mg), which appears (thin layer chromatogram) to be a (1:1) mixture of diols **15** and **16**, was oxidized with manganese dioxide (Code No. 37, General Metallic Oxides) to an oil (202 mg), which appears (thin layer chromatogram) to contain **16** and **17** but no **15**. From this oil by thin layer chromatography, 56 mg of crude crystalline **16** was obtained. Recrystallization from ether–petroleum ether gave colorless needles, mp and mmp 144–146°.

20β-Acetoxy-des-A-pregn-9-en-5-one (**19**) had mp 118–119°, $[\alpha]^{25}D$ +11.9° (c 0.88 in $CHCl_3$). The infrared spectrum (in $CHCl_3$) had bands at 1725 (acetoxy carbonyl), 1660 (conjugated ketone), and 1605 cm^{-1} (double bond); the uv spectrum (in 95% C_2H_5OH) showed λ_{max} 248 mμ (ε 16,150); nmr spectrum (in $CDCl_3$) showed 10-CH_3 at δ 1.80, 13-CH_3 at 0.80, 17β-CH(β-OAc)CH_3 methyl doublet at 1.17 (J = 6 cps), and acetoxy methyl at 2.03.

Anal. Calcd for $C_{19}H_{28}O_3$ (304.41): C, 74.96; H, 9.27. Found: C, 75.04; H, 9.30.

Registry No.—**1**, 80-75-1; **3**, 10110-77-7; **5**, 15259-95-7; **6**, 10110-78-8; **7**, 15259-97-9; **8**, 15259-98-0; **9**, 10110-79-9; **10**, 10072-88-5; **12**, 10116-24-2; **13**, 10110-54-0; **14**, 15314-09-7; **15**, 15285-88-8; **16**, 15260-03-4; **17**, 10110-81-3; **17** semicarbazone, 15266-89-4; **18**, 15267-19-3; **19**, 15266-90-7; **20**, 15266-91-8; **21**, 15266-92-9.

Acknowledgment.—We thank Dr. F. Vane, Mr. S. Traiman, and Dr. V. Toome for the nmr, infrared, and ultraviolet spectra, and Dr. Al Steyermark and his staff for the elemental analyses.

A Study of Tautomerism in Arylazopyrazolones and Related Heterocycles with Nuclear Magnetic Resonance Spectroscopy

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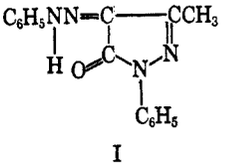
Nuclear magnetic resonance was used to determine the tautomeric forms of arylazo-3-, -4-, and -5-pyrazolones and several related azo heterocycles in chloroform. The assignments of the hydrazone structure to the 5-pyrazolones and the hydroxy structure to the 3- and 4-pyrazolones are supported by infrared data. Several conclusions emerge from the nmr spectra: (a) in the heterocyclic systems studied the hydrazone NH resonance comes 3–5 ppm lower than the azohydroxy OH resonance and (b) it appears that the hydrazone NH resonance of structurally similar azo heterocycles fall within a 2-ppm range.

Azopyrazolones have been known and used for over 100 years, but the structures of these compounds have been examined only within the last decade. The structure of arylazo-5-pyrazolones in solution has now been established,[1] but arylazo-3-pyrazolones, arylazo-4-pyrazolones, and many similar azo heterocycles have not yet been investigated.

Nmr spectroscopy has been very valuable in studies of tautomerism, but when the tautomers in question contain NH and OH protons it is frequently difficult to assign unambiguously a given acidic proton resonance to a particular functional group. The first objective of the present work, therefore, was to evaluate the applicability of nmr to the determination of the structures of azo heterocycles in solution. Since the structure of arylazo-5-pyrazolones was already known and the structures of the tautomerically simpler 3-pyrazolones were easily determined by infrared, this objective was at least partially accomplished by a study of various derivatives of these compounds. The second and related objective was to establish the structures of azo-4-pyrazolones and related azo heterocycles.

The Structure of Azopyrazolones in Chloroform.—Although there has been some disagreement about the structure of 1,3-disubstituted 4-arylazo-5-pyrazolones in solution, a recent spectroscopic investigation[1] argues convincingly for the phenylhydrazone structure (I) as the predominant form in chloroform.

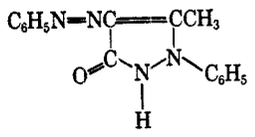


I

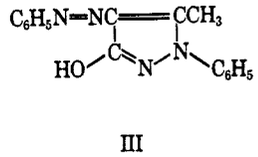
Two reasonable tautomeric forms (not involving charge separation) can be written for 1,5-disubstituted 4-arylazo-3-pyrazolones. The infrared spectra of numerous 4-arylazo derivatives in chloroform exhibit only one absorption, at 1600 ± 15 cm^{-1}, in the region be-

(1) H. Yasuda and H. Midorikawa, *J. Org. Chem.*, **31**, 1722 (1966).

tween 1550 and 2000 cm^{-1}. Since similar compounds known to exist in the carbonyl form have carbonyl absorptions above 1650 cm^{-1},[2] it is unlikely that appreciable amounts of II are present in solutions of 4-arylazo-3-pyrazolones.



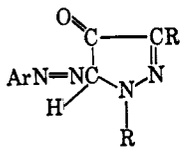
II



III

The simple 1-substituted 5-pyrazolones are known to exist in the CH form, while the 1-substituted 3-pyrazolones exist in the OH form in chloroform.[3] The arylazo function, therefore, does not influence the basic tautomeric form of the pyrazolone ring.

The 1,3-disubstituted 5-arylazo-4-pyrazolones can exist in the CH form (IV), the hydrazone form (type I),



IV

or the hydroxy form (type II). The infrared spectrum of 1-phenyl-3-carboethoxy-4-phenylazo-5-pyrazolone contains two absorptions in the carbonyl region (1650–1750 cm^{-1}), whereas the spectrum of 1-phenyl-3-carboethoxy-5-phenylazo-4-pyrazolone contains only one peak in this area. The 5-pyrazolone exists in the hydrazone form (the acidic proton resonance occurs at 14.0 ppm; see next section) and it is certainly tempting to conclude, therefore, that the 4-pyrazolone does not exist in a carbonyl form (type I or IV).

Nmr Spectra of Azopyrazolones.—The nmr spectrum of 1-phenyl-3-methyl-4-phenylazo-5-pyrazolone in chloroform contained absorptions at 2.3, 6.9–8.0, and 13.4 ppm. The peak at 13.4 ppm was broad ($w_{1/2}$ *ca.* 26 cps) and difficult to locate in solutions containing small amounts of ethanol or more dilute than *ca.* 5%. On the basis of their chemical shifts, shapes, and integrated areas, these absorptions were assigned to the 3-methyl, aromatic, and hydrazone NH protons, respectively. The last assignment assumes, of course, the validity of the structure discussed above. The spectra of the other 4-*para*-substituted phenylazo derivatives studied are similar and contain broad absorptions in the 13.4 ± 0.2 ppm region. Absorptions in this area have been observed by other workers (and assigned to the same function) in the spectra of 1,3-diphenyl-4-phenylazo-5-pyrazolone[1] and several 1-phenyl-3-substituted 4-arylazo-5-pyrazolones.[4]

The spectra of the 3-pyrazolones differed from their 5-pyrazolone analogs in only one respect—the broad low-field absorption appeared at 9.2 ± 0.3 ppm. Assuming that the 3-pyrazolone derivatives exist in the hydroxy form in chloroform, this low-field absorption must be assigned to the hydroxyl proton.

(2) For example, the carbonyl band in 4-phenylazoantipyrine appears at 1665 ± 15 cm^{-1}.

(3) A. R. Katritzky and F. W. Maine, *Tetrahedron*, **20**, 299, 315 (1964).

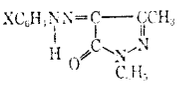
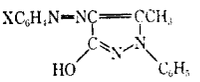
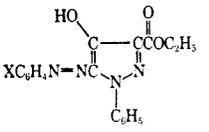
(4) R. Jones, A. J. Ryan, S. Sternhell, and S. E. Wright, *Tetrahedron*, **19**, 1497 (1963).

The spectrum of 1-phenyl-3-carboethoxy-5-phenylazo-4-pyrazolone contained the usual ethyl pattern (a triplet at 1.44 ppm and a quartet at 4.48 ppm), an aromatic proton band (7.2 – 8.0 ppm), and a broad acidic proton peak at 9.3 ppm. The low-field absorption occurred in the spectra of both 4-pyrazolone derivatives examined and, since the CH tautomer (IV) would presumably absorb above 8 ppm, this resonance must be assigned to an NH or OH group. The fact that this resonance occurs in the same region as the OH shift of the 3-pyrazolones, coupled with the observation that the shifts of the 3- (OH form) and 5- (NH form) pyrazolones are separated by *ca.* 4 ppm, strongly suggests that the azo-4-pyrazolones exist in the hydroxy form. This conclusion is reinforced by the infrared data mentioned above.

The low-field NH or OH chemical shifts and their half-height widths for the 3-, 4-, and 5-pyrazolones are given in Table I. The 5-pyrazolone shifts all fall within 0.2 ± 0.2 ppm, while the *para*-substituted 3-pyrazolones fall within 0.4 ± 0.2 ppm. The position of the NH resonance in the 5-pyrazolones suggests strong, intermolecular hydrogen bonding to the carbonyl group. The *ortho*-substituted 3-pyrazolone OH resonances show a marked downfield shift, presumably due to increased hydrogen bonding between the hydroxyl proton and the 4-(substituted phenylazo) group.

TABLE I

NH OR OH CHEMICAL SHIFTS IN AZOPYRAZOLONES

No.	X	δ ± 0.1 ppm	$w_{1/2}$ ± 4 cps	$CHCl_3$ concn, %
				
1	*p*-F	13.5	20	14
2	*p*-Cl	13.4	26	14
3	*p*-H	13.4	26	14
4	*p*-OCH_3	13.3	14	$CDCl_3$ 10
5	*p*-$N(CH_3)_2$	13.5	38	13
				
6	*p*-Cl	9.05	*a*	13
7	*p*-H	9.3	12	14
8	*p*-CH_3	9.0	30	$CDCl_3$ 10
9	*p*-OCH_3	9.1	*a*	14
10	*m*-OCH_3	8.4	22	18
11	*o*-OCH_3	10.0	>16	12
12	*o*-Cl	10.1	12	15
				
13	*p*-Cl	8.9	16	20
14	*p*-H	9.3	26	15

[a] Peak partially obscured by impurity.

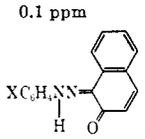
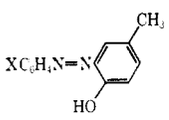
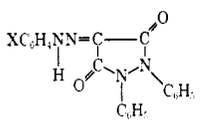
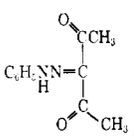
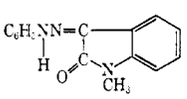
There was no evidence in the spectra of any of the pyrazolone derivatives for the existence of appreciable amounts of a second tautomeric form. It is possible, however, that more than one form exists in solution and that rapid exchange occurs between these forms.

Nmr Spectra of Related Azo Heterocycles.—Table II lists the acidic proton chemical shifts for a number of

other azo derivatives. The first four compounds listed there are 1-arylazo-2-naphthols and 2-arylazophenols, which are rather different from the pyrazolones structurally, but can also exist in either the hydrazone ketone or azohydroxy forms. The arylazophenols apparently exist only in the azohydroxy form,[5] whereas an appreciable amount of the hydrazone form is present in a chloroform solution of 2-arylazonaphthols.[6] The chemical shifts of the phenol derivatives, though certainly lower than the 3-pyrazolone shifts, are *ca.* 3 ppm higher than the naphthol derivatives. This is very roughly the same order observed with the pyrazolones (5-pyrazolone hydrazone NH *ca.* 4 ppm lower than 3-pyrazolone OH). The chemical shifts of the *o*-cresol and naphthol derivatives again suffer a paramagnetic shift.

TABLE II

NH OR OH CHEMICAL SHIFTS IN SOME AZO HETEROCYCLES

No.	X	δ ± 0.1 ppm	$w_{1/2}$ ± 4 cps	$CHCl_3$ concn, %
				
1	*p*-OCH_3	15.6	Sharp	10
2	*o*-OCH_3	16.5	10	5
				
3	*p*-OCH_3	12.6	Sharp	10
4	*o*-OCH_3	13.3	Sharp	14
				
5	*p*-H	13.4	5	10
6	*o*-SCH_3	13.9	5	10
7				
		14.6	10	20
8				
		12.7	6	12

The other azo compounds listed in Table II are two 1,2-diphenyl-4-arylazo-3,5-pyrazolidinediones, a 1-methyl-3-arylazo-2-oxyindole, and an arylazo-β-diketone. These three systems could exist in three principle tautomeric forms — the CH form, the hydrazone NH form (type I), or the hydroxy form (type III). The nmr spectra of these compounds show no evidence for a CH form and no evidence for more than one tautomer in chloroform, although again the possibility of exchange between several tautomers exists. With the exception of the β-diketone, these derivatives are structurally similar to the pyrazolones and therefore the fact that the shifts are all in the 13 ± 2 ppm region suggests that the first two systems exist in the hydrazone form. Indeed, from the evidence of previous workers and data collected during this investigation, this suggestion appears to be valid for all three systems.

Infrared, ultraviolet, and nmr data[7,8] all support the phenylhydrazone structure for the β-diketone derivatives. An absorption at 1680 cm^{-1} in the infrared spectrum of the indole derivative[8] is readily assigned to a carbonyl stretch and corroborates the hydrazone structure. The infrared spectra of the pyrazolidinedione derivatives contain two carbonyl stretches (1675, 1720 cm^{-1}).

Conclusions

Several important conclusions emerge from the above data: (a) in the heterocyclic systems studied the hydrazone NH resonance comes 3–5 ppm lower than the azohydroxy resonance and (b) it appears that the hydrazone NH resonance of structurally similar azo heterocycles falls within a 2-ppm range. These conclusions, coupled with the fact that these acidic proton resonances are not extremely dependent on solution concentration (see Experimental Section), indicate that nuclear magnetic resonance is indeed a valuable technique for studying tautomerism in azopyrazolones and similar heterocycles.

Experimental Section

Compounds.—The preparation and physical constants for the arylazo-3-pyrazolones[9] and arylazo-5-pyrazolones[10] have been previously described. The arylazo-4-pyrazolones were prepared by coupling the appropriate diazotized amine to 1-phenyl-3-carboethoxy-4-pyrazolone: 1-phenyl-3-carboethoxy-5-phenylazo-4-pyrazolone, red crystals, mp 110–111.5°; 1-phenyl-3-carboethoxy-5-(*p*-chlorophenylazo)-4-pyrazolone, red crystals, mp 166–167°. The azopyrazolidinediones were prepared by coupling the appropriate diazotized amine to 1,2-diphenyl-3,5-pyrazolidinedione: 1,2-diphenyl-4-phenylazo-3,5-pyrazolidinedione, orange crystals, mp 180–182°; 1,2-diphenyl-4-(*o*-thiomethoxyphenylazo)-3,5-pyrazolidinedione, orange crystals, mp 179–180°. Neutral equivalents for these derivatives were in agreement with their structures.

The isatin phenylhydrazone was prepared by condensation of phenylhydrazine with N-methyl isatin: mp 137–138° (lit.[11] mp 145–146°).

The azo-β-diketone was kindly furnished by Dr. W. C. Fernelius. Melting points are uncorrected.

Spectra.—Nmr spectra were recorded on a Varian A-60 spectrometer operating at 36–38°. Samples were dissolved in ethanol-free (alumina used to remove ethanol) chloroform or deuteriochloroform. Two- or threefold dilution of several samples caused a paramagnetic shift of no more than 0.15 ppm. Infrared spectra of *ca.* 2% chloroform solutions were recorded on a Perkin-Elmer Model 137 Infracord and calibrated with polystyrene film.

Registry No.—Table I: No. 1, 15096-17-0; No. 2, 15095-21-3; No. 3, 7625-02-7; No. 4, 15095-23-5; No. 5, 15095-24-6; No. 6, 15095-25-7; No. 7, 15095-26-8; No. 8, 15095-27-9; No. 9, 15095-97-3; No. 10, 15095-98-4; No. 11, 15095-99-5; No. 12, 15096-00-1; No. 13, 15096-01-2; No. 14, 15096-02-3. Table II:

(5) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 3734 (1951).
(6) K. S. Morgan, *ibid.*, 2151 (1961), and references therein.
(7) H. C. Yao, *J. Org. Chem.*, **29**, 2959 (1964).
(8) F. A. Snavely and F. R. Koeng, unpublished results.
(9) F. A. Snavely, D. A. Sweigart, C. H. Yoder, and A. Terzis, *Inorg. Chem.*, **6**, 1831 (1967).
(10) F. A. Snavely, W. C. Fernelius, and B. P. Block, *J. Am. Chem. Soc.*, **79**, 1028 (1957); F. A. Snavely, B. D. Krecker, and C. G. Clark, *ibid.*, **81**, 2337 (1959); F. A. Snavely, C. H. Yoder, and F. H. Suydam, *Inorg. Chem.*, **2**, 708 (1963).
(11) H. C. Coleman, *Ann.*, 248, 117 (1888).

No. 1, 15096-03-4; No. 2, 15096-04-5; No. 3, 15096-05-6; No. 4, 15096-06-7; No. 5, 2652-91-7; No. 6, 15096-14-7; No. 7, 6134-57-2; No. 8, 15096-16-9.

Acknowledgments.—The authors are indebted to Elizabethtown College for the use of their nmr spectrometer.

Solvent Effects on *cis–trans* Equilibria of Some Aziridine Ketones[1]

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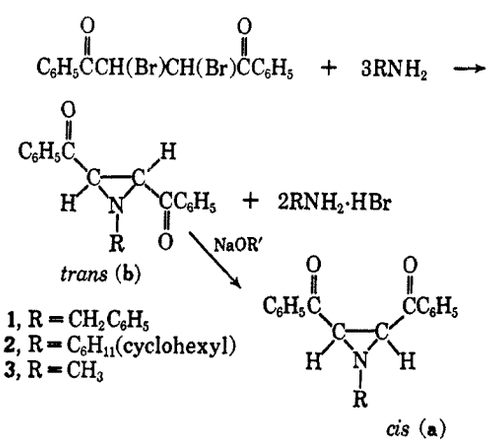
Received August 18, 1967

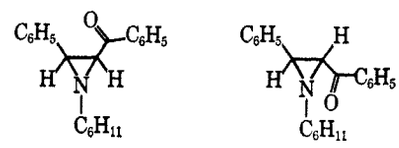
The *cis–trans* isomer ratios of 1-benzyl- and 1-cyclohexyl-2,3-dibenzoylaziridines and 1-cyclohexyl-2-phenyl-3-benzoylaziridine, when equilibrated by base catalysis in seven alcohols and the aprotic solvent dimethyl sulfoxide, have been determined. These equilibria are expressed as constants, K, which range from 5.25 in DMSO to 0.32 in *t*-butyl alcohol and which approximately parallel the dielectric constants of the solvents used. The effects on K of amounts of base and of added salt used are delineated.

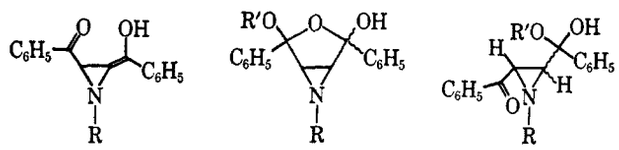
trans-1-Alkyl-2,3-dibenzoylaziridines, **1**, **2**, and **3**, the products of reactions of the primary benzyl-, cyclohexyl-, and methylamines, respectively, with *meso*- and *dl*-dibenzoylethylene dibromides,[2a,b] undergo epimerization upon treatment with strong base in ethanol solution from which the *cis* isomers crystallize exclusively.[2b] *trans*-1-Alkyl-2-aryl-3-aroylaziridines[2b] **4** and



certain *trans*-2-aryl-3-aroyloxiranes[3a] behave similarly. From these data the conclusion has been drawn recently that the *cis*-aziridines are thermodynamically the more stable forms[4] in contrast to the analogous *cis*-dibenzoylcyclopropanes, which unquestionably are the labile forms.[5] However, the actual *cis–trans* stability relationships of the benzoyl aziridines necessary for understanding these phenomena have not been determined and are the subject of this paper.

Our interest in this problem stemmed in part from an earlier study of anomalies in the *cis–trans* stability relations in basic solutions of the dibenzoylstilbenes





5a = anion 6a = anion 7a = anion

where *cis* cyclic dihemiketal and sesquiketal anions similar to **6a** had been believed to be involved.[6] The existence of *cis* cyclic α,β-disubstituted dibenzoylethylene sesquiketals, which are olefin analogs of **6**, has been demonstrated by isolation of unstable compounds of this type in a few instances.[7] Such anions as **6a** might conceivably be formed from dibenzoylaziridines **1**, **2**, and **3** but not from the monobenzoylaziridines **4**.

Results and Discussion

In order to establish the actual *cis–trans* stability relationships, *i.e.*, equilibrium constants, $K = [cis]/[trans]$, the equilibrations of aziridines **1**, **2**, and **4** were carried out using both a trace and a large amount of base. That equilibrations under the various conditions had been achieved in each case was demonstrated by obtaining the same value of K starting both from the pure *cis* isomer and from the pure *trans* isomer, respectively. These equilibrations using seven different alcohols and dimethyl sulfoxide were determined by

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(2) (a) R. E. Lutz, T. Amacker, S. M. King, and N. H. Shearer, *J. Org. Chem.*, **15**, 181 (1950). (b) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *J. Am. Chem. Soc.*, **87**, 1050 (1965). (c) A. E. Pohland, R. C. Badger, and N. H. Cromwell, *Tetrahedron Letters*, 4369 (1965). (d) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. J. Vanderhorst, F. W. Olson, and J. H. Anglin, Jr., *J. Am. Chem. Soc.*, **73**, 1044 (1951). (e) P. L. Southwick and D. R. Christman, *ibid.*, **74**, 1886 (1952).

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(4) F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967), footnote 6.

(5) (a) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963). (b) W. W. Kastenmeyer, M. S. Thesis, University of Virginia, Charlottesville, Va., 1966. (c) D. W. Boykin, Jr., A. B. Turner, and R. E. Lutz, *Tetrahedron Letters*, 817 (1967).

(6) (a) R. E. Lutz and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 2763 (1962). (b) An attractive alternative explanation for the effect of increasing base concentrations on this *cis–trans* equilibrium position is a medium effect such as is described below, and further study will be required to elucidate this point.

(7) *E.g.*, (a) *cis* cyclic hydroperoxy sesquiketals of dibenzoylstilbenes: O. W. Ridgon and R. E. Lutz, Abstracts, 18th Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 1966, p A45. (b) The unstable cyclic sesquiketal of *cis*-1,2-dibenzoyldichloroethylene: E. L. Anderson, M. S. Thesis, University of Virginia, Charlottesville, Va., 1964. (c) *Cf.* also the ready formation of a cyclic diketal from *cis*-dibenzoylstilbene oxide: R. E. Lutz, W. J. Welstead, Jr., R. G. Bass, and J. I. Dale, *J. Org. Chem.*, **27**, 1111 (1962).