

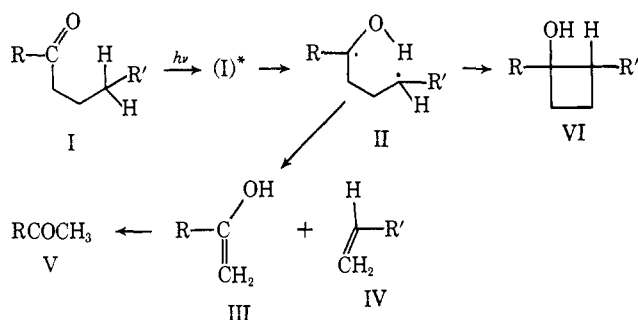
Organic Photochemistry. IX.¹ Intramolecular Photoreactions of Simple γ - and *para*-Substituted Butyrophenones

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Contribution from the Dyson Perrins Laboratory, Oxford University, Oxford, England. Received March 2, 1968

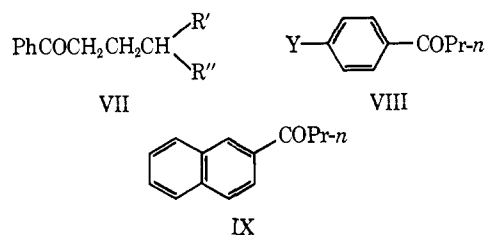
Abstract: The "Norrish type-II" photoelimination reaction of aryl alkyl ketones and the accompanying cyclization reaction which yields a cyclobutanol are shown to have a common intermediate which is the $^3(n, \pi^*)$ state of the ketone. The effect of polar solvents in enhancing the quantum yield of both reactions is described, and the variation of the quantum yield with temperature is related to the bond strength of the C-H bond involved in the intramolecular hydrogen abstraction. The lowest triplet state of *p*-methoxybutyrophenone switches from n, π^* to π, π^* with a change from nonpolar to polar solvents.

The intramolecular photoelimination reaction of ketones with a hydrogen atom on the γ -carbon atom (I) to give a shorter chain ketone (V) and an olefin (IV) is a well-documented reaction of current interest which has been known for some time.² It has been shown³ to proceed by way of the initial formation of the enol of the product ketone (III) for pentan-2-one (I, R = Me; R' = H). Another product of the irradiation of these ketones is a cyclobutanol (VI),⁴ and both reactions can be visualized as proceeding by way of a 1,4-biradical intermediate (II). The reactions of



aliphatic ketones involve both singlet and triplet excited states of the parent ketones,⁵⁻⁷ but for the photoelimination reactions of butyrophenone, ring-substituted butyrophenones, and valerophenone (I, R = aryl) it has been concluded^{5,8} that the reactive excited state (I) is a triplet state. Further, it has been found⁸ that butyrophenones with lowest π, π^* triplet states do not undergo the type-II process, whereas those with lowest n, π^* triplet states do, the quantum yield being dependent on the electron-donating character of the ring substituent. The effect of solvent polarity on the quantum yield of photoelimination for valerophenone and butyrophenone has been described and attributed⁹

to the effectiveness of hydrogen-bonding solvents in preventing reversal of the hydrogen-abstrating process, and to the change with solvent polarity in the relative energies of the reactive n, π^* and unreactive π, π^* triplet states.¹⁰ This paper is concerned with a detailed examination of the photochemistry of the ketones VII (R', R'' = H or Me), VIII (Y = Cl, OH, OMe, O-K⁺), and IX.



Results

The assignment of lowest triplet states (n, π^* or π, π^*) to aryl ketones can be attempted on the basis of ultraviolet absorption spectroscopy or phosphorescence emission spectroscopy. The former has the disadvantage that singlet-triplet absorption is very weak, and assignments are generally based on the position of singlet-singlet absorption bands, taking into account that singlet-triplet splittings are normally much smaller for n, π^* states than for π, π^* states. Phosphorescence spectroscopy has the advantage that emission occurs from the lowest triplet state, but the data obtained in a rigid glass at 77°K cannot be applied without reserve to liquid solution at room temperature.

Table I gives the absorption and emission spectral data for the compounds studied. The values of λ_{\max} for absorption at wavelengths greater than 300 nm are given for solution in cyclohexane and in acetonitrile or a more polar solvent; the values of the molar extinction coefficients are given in parentheses. The figures for phosphorescence are the positions in nanometers of the presumed 0-0 vibrational bands, *i.e.*, those bands which are of lowest energy in excitation (absorption) and of highest energy in emission; these values were the same to within 3 nm in polar or nonpolar glasses, except in the case noted. Our values for the positions of the 0-0 bands in the excitation spectra of butyrophenone and *p*-chlorobutyrophenone and in the emission spectra of these two ketones and of *p*-hy-

(10) R. D. Rauh and P. A. Leermakers, *ibid.*, **90**, 2246 (1968).

(1) Part VIII: J. A. Barltrop and N. J. Bunce, *J. Chem. Soc., C*, 1467 (1968).

(2) See, *e.g.*, C. H. Bamford and R. G. W. Norrish, *ibid.*, 1504 (1935); A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

(3) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **86**, 3602 (1964).

(4) See, *e.g.*, N. C. Yang and D.-D. H. Yang, *ibid.*, **80**, 2913 (1958); R. B. LaCount and C. E. Griffin, *Tetrahedron Letters*, 1549 (1965).

(5) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(6) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(7) J. A. Barltrop and J. D. Coyle, *Tetrahedron Letters*, 3235 (1968).

(8) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **88**, 2652 (1966).

(9) P. J. Wagner, *Tetrahedron Letters*, 1753 (1967); *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

Table I. Absorption and Emission Spectral Data

Ketone	Absorption (uv), λ_{\max} , nm		Phosphorescence (0-0 band), nm	
	C_6H_{12}	MeCN	Excitation	Emission
VII, R', R'' = H	322 (41)	317 (50)	367	396
VII, R' = H, R'' = Me	321 (40)	316 (50)	367	393
VII, R', R'' = Me	322 (43)	316 (50)	367	394
VIII, Y = Cl	324 (59)	317 (63)	367	393
VIII, Y = OMe	312 (104)	No max	365 ^c	388 ^c
			355 ^d	395 ^d
VIII, Y = OH	...	No max	355	410
VIII, Y = O-K ⁺	...	325 (20,200) ^a
IX	326 (1650)	328 (1770) ^b	390	485
	341 (1620)	338 (1680) ^b		

^a Water. ^b Ethanol. ^c Nonpolar glass. ^d Polar glass.

droxybutyrophenone agree within a few nanometers with those already published by Kearns and Case,¹¹ though that for the excitation spectrum of *p*-hydroxybutyrophenone is significantly different (they report a value of 345 nm). Values for the emission spectra published in another paper⁸ agree for *p*-chloro- and *p*-methoxybutyrophenone, but are somewhat lower for butyrophenone and *p*-hydroxybutyrophenone (values of 383 and 403 nm, respectively, are reported).

The phosphorescence data suggest that the unsubstituted phenyl ketones (VII) and *p*-chlorobutyrophenone (VIII, Y = Cl) have lowest $^3(n, \pi^*)$ states, and also that *p*-methoxybutyrophenone (VIII, Y = OMe) in a nonpolar glass has a lowest $^3(n, \pi^*)$ state. The emission spectra for these compounds show very distinct vibrational fine structure (δE around 1500 cm^{-1}), and the energy gaps between the 0-0 bands in emission and absorption are less than 2000 cm^{-1} (these criteria are used by Kearns and Case¹¹). 2-Butyronaphthone (IX), *p*-hydroxybutyrophenone (VIII, Y = OH), and *p*-methoxybutyrophenone in a polar glass appear to have lowest $^3(\pi, \pi^*)$ states, since the spectra show no distinct vibrational fine structure, and the energy gaps between the 0-0 bands in emission and absorption are approximately 5000, 4000, and 3000 cm^{-1} , respectively. The absorption data suggest that the conclusions reached about the nature of the lowest triplet state in a glass at 77°K may still be valid in liquid solution at room temperature, since only those ketones which are thought to have a lowest $^3(n, \pi^*)$ state in a glass as solvent show a low-intensity ($\epsilon < 100$) absorption maximum (shifted to shorter wavelengths in a more polar solvent) at wavelengths longer than those at which the intense $\pi-\pi^*$ absorption occurs. One interesting feature that arises from the spectra is the apparent changeover for *p*-methoxybutyrophenone (VIII, Y = OMe) from a lowest $^3(n, \pi^*)$ state in a nonpolar solvent to a lowest $^3(\pi, \pi^*)$ state in a polar solvent. If this occurs in solution at room temperature, there should be an inhibition of n, π^* reactions in polar solvents.

Irradiation of the unsubstituted phenyl ketones and of *p*-chlorobutyrophenone in acetonitrile solution with light from a 450-W medium-pressure mercury arc filtered through Pyrex glass (or through Pyrex glass and 4.8 mm of a chromate-carbonate filter solution to

(11) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

isolate the 313-nm line) gave an acetophenone (V, R = Ar) and a 1-arylcyclobutanol (VI, R = Ar).

The yields of cyclobutanol, based on acetophenone + cyclobutanol = 100%, are given in Table II, together

Table II. Percentage Yields of Cyclobutanols

Solvent	Yield of cyclobutanol, %			
	PhCO- Pr- <i>n</i>	PhCO- Bu- <i>n</i>	PhCO- Am- <i>i</i>	<i>p</i> -ClC ₆ H ₄ - COP- <i>n</i>
MeCN	9	20	16	8
Benzene	10	19	14	7

with the corresponding yields in benzene solution. The differences in the yields for the four ketones reflect only small changes in the differences in activation energies for the cyclization and elimination reactions.

The following ketones were all stable to irradiation in the stated solvents: *p*-methoxy- and *p*-hydroxybutyrophenone (in acetonitrile and in ethanol), the corresponding phenate (VIII, Y = O-K⁺, in water), and 2-butyronaphthone (in ethanol and in cyclohexane). However, when irradiated in cyclohexane or benzene solution, *p*-methoxybutyrophenone gave *p*-methoxyacetophenone and two minor products. This seems to confirm the changeover from lowest $^3(n, \pi^*)$ state in nonpolar solvents to lowest $^3(\pi, \pi^*)$ state in polar solvents which was suggested by the phosphorescence data, and it further supports the idea that the reactive state in both the intramolecular reactions is the $^3(n, \pi^*)$ state.

It was found that the predominant mode of breakdown under electron bombardment in the mass spectrometer was analogous to the photoinduced cycloelimination reaction for all the ketones (the phenate was not examined), not only those which undergo the reaction under the influence of light. This analogy has been pointed out previously for several photochemical Norrish type-II reactions.¹²

In the reaction of butyrophenone in acetonitrile, a small amount (0.5%) of dibenzoylthane (PhCOCH₂-CH₂COPh) was formed and isolated, but this was not detected after irradiation of acetophenone alone under the same conditions. It may be that it is formed by the action of excited acetophenone on the enol of acetophenone, which is the primary product of the Norrish type-II reaction of butyrophenone. A similar mechanism has been suggested¹³ to account for the efficient photoconversion of acetophenone to dibenzoylthane in the presence of phenol as a specific enolizing agent.

The Norrish type-II reaction of butyrophenone and valerophenone has been shown to be quenched by piperylene^{5,8} and naphthalene,¹⁴ known to be efficient triplet quenchers. We find that both the elimination and cyclization reactions of all the ketones which underwent reaction could be quenched completely by piperylene. Naphthalene, anthracene, and biacetyl were also effective in quenching the reaction of butyrophenone. To find out if the two reactions have a

(12) J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, **4**, 323 (1964).

(13) H.-D. Becker, *J. Org. Chem.*, **32**, 2140 (1967).

(14) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 7S.

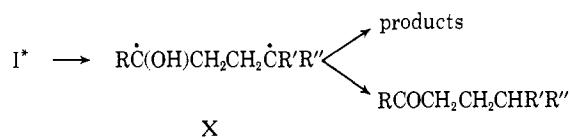
common intermediate, butyrophenone was irradiated with various quenchers (piperylene, naphthalene, benzophenone) present in amounts insufficient to quench the reactions completely. The products were analyzed and found to contain the same ratio of acetophenone to 1-phenylcyclobutanol as for the unquenched reaction. This strongly supports the concept that the $^3(n,\pi^*)$ state is a common intermediate for both reactions.

The enhancement of the quantum yield for the Norrish type-II reaction of butyrophenone and valerophenone in polar as opposed to nonpolar solvents has been reported previously.^{9,10} In the present work the unsubstituted phenyl ketones and *p*-chlorobutyrophenone were irradiated in four different solvents (cyclohexane, benzene, dry acetonitrile, and methanol) in a "roundabout" apparatus designed to ensure that each solution receives the same amount of light from the centrally placed lamp (the apparatus was first checked for uniformity by running a set of identical samples of butyrophenone and analyzing the products). The products were analyzed by vpc using *m*-dichlorobenzene as internal standard, and the relative quantum yields for disappearance of starting material were calculated using an expression similar to that used by Wagner and Hammond.⁵ The values obtained are set out in Table III, and they are given relative to that for valerophenone in methanol ($\phi = 1.00$).

Table III. Relative Quantum Yields for Disappearance of Reactant in Different Solvents

Solvent	Relative quantum yield			
	PhCO-Pr- <i>n</i>	PhCO-Bu- <i>n</i>	PhCO-Am- <i>i</i>	<i>p</i> -ClC ₆ H ₄ -COPr- <i>n</i>
Cyclohexane	0.45	0.43	0.36	0.37
Benzene	0.47	0.44	0.35	0.37
Acetonitrile	0.68	0.79	0.74	0.75
Methanol	0.98	1.00	0.88	0.95

This solvent effect is explained by Wagner⁹ in terms of a mechanism involving a biradical intermediate (X).



The biradical X gives rise to the elimination and the cyclization products, and it is postulated that radiationless decay occurs from X by reversal of the hydrogen-abstraction step to give the ground state of the starting ketone. In polar solvents the hydroxyl group of the biradical is hydrogen-bonded to the solvent, and reversal of the hydrogen abstraction is hindered; the quantum yield of the forward reaction therefore increases, and it has been measured⁹ as 1.00 for valerophenone in alcoholic solvents. This increase of the value to unity suggests that radiationless decay occurs solely from the biradical and not from the triplet state itself.

The variation of the quantum yield of reaction with temperature has been reported for butyrophenone in benzene to have an apparent activation energy of about 2 kcal/mole, and it was suggested⁸ that this may be the energy required to attain the six-membered transition

state required for abstraction of the γ -hydrogen atom. We have examined this phenomenon for the three ketones (VII) which were irradiated with filtered light in dry acetonitrile solution at temperatures between 20 and 60°. The results obtained for the relative quantum yields of disappearance of reactant and for the apparent activation energies for the reaction are given in Table IV.

Table IV. Variations of the Relative Quantum Yield of Photoreaction with Temperature

PhCOPr- <i>n</i>		PhCOBu- <i>n</i>		PhCOAm- <i>i</i>	
<i>T</i> , °C	ϕ	<i>T</i> , °C	ϕ	<i>T</i> , °C	ϕ
24	1.00	22.5	1.00	25	1.00
33.5	1.46	32.5	0.99	33	0.948
45	2.22	43	1.01	42	0.852
53	2.49	53	1.01	50	0.763
E_a	5.8 ± 1.2	0.0 ± 0.5		-2.1 ± 0.6	

T is the temperature of the solution, ϕ is the relative quantum yield of reaction (taken arbitrarily as 1.00 at the lowest temperature in each case), and E_a (kcal/mole) is the apparent activation energy. This apparent "activation energy" describes the variation of quantum yield with temperature ($\phi = A \exp(-E_a/RT)$) and is calculated from the gradient of the graph of $\ln \phi$ against T^{-1} . It should be emphasized that ϕ is not expected to be a simple exponential function of temperature, and the value for E_a is an approximate one for the range of temperatures considered.

Discussion

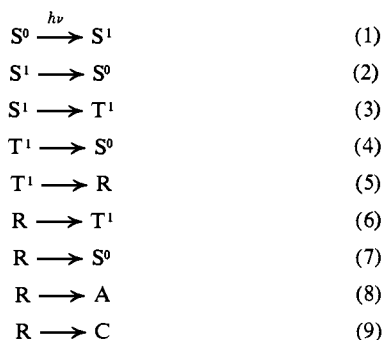
The excited state involved in the intramolecular reactions is without doubt a triplet state, since the reactions can be totally quenched by triplet quenchers such as piperylene. Singlet quenching by piperylene has been reported,¹⁵ though not for carbonyl compounds. That there is a common triplet state for the cyclization and elimination reactions is shown by the constant product ratio for reactions partially quenched to different extents. That only $^3(n,\pi^*)$ states are reactive and not $^3(\pi,\pi^*)$ states is shown by the correlation between ketones which undergo reaction and those which from spectroscopic data appear to have lowest $^3(n,\pi^*)$ states. *p*-Methoxybutyrophenone is interesting in that a change from polar to nonpolar solvent at 77°K appears to change the lowest state from $^3(\pi,\pi^*)$ to $^3(n,\pi^*)$, and at room temperature the ketone undergoes a Norrish type-II reaction in a nonpolar solvent but not in a polar solvent. This change is in the opposite sense to that caused by the general effect of solvent polarity on quantum yield and is greater in magnitude.

The general solvent effect (increase in quantum yield as the polarity of the solvent increases) can be explained in terms of a biradical intermediate as described above. The present work on the solvent effect shows that for four different aromatic ketones (VII, R', R'' = H or Me, and VIII, Y = Cl) the quantum yield of disappearance of reactant increases as the solvent polarity increases in the series benzene

(15) G. S. Hammond in "The Chemistry of Ionization and Excitation," G. R. Johnson and G. Scholes, Ed., Taylor and Francis Ltd., London, 1967.

or cyclohexane \rightarrow acetonitrile \rightarrow methanol. The ratio of cyclization to elimination product does not vary greatly with solvent, showing that both reactions are similarly affected to a first approximation.

The possible steps in the mechanism of the reaction are



S represents a singlet state of the ketone, T a triplet state, R a biradical intermediate, A an acetophenone, and C a cyclobutanol. Step 1 is excitation, and step 2 is internal conversion from the first excited singlet state to the ground state, which occurs to a negligible extent since the competing step (3) is intersystem crossing and is known¹⁶ to be very efficient for aryl ketones. A biradical species R must exist for some time, however short, since the ring-closure reaction requires that the spin of the electrons forming the new bond be opposed, and this is not possible directly from the triplet state. The radiationless decay process may occur from the triplet itself (step 4) or from the biradical (step 7), and, for the reasons set out in the discussion of the solvent effects, (7) is probably more important than (4), and the latter is therefore neglected in comparison with (7) in deriving the rate equation. Further support for this simplification comes from the values calculated for rate constants by other workers. For benzophenone k_4 has been measured¹⁷ as $2 \times 10^5 \text{ sec}^{-1}$, and k_5 has been measured⁵ for butyrophenone and valerophenone as 2×10^6 and $5 \times 10^7 \text{ sec}^{-1}$, respectively. If the value of k_4 for other aryl ketones is similar to that for benzophenone, then the triplet states of these ketones will react to give the biradical much faster than they decay to the ground state.

The steady-state treatment applied to the species S^1 , T^1 , and R gives the following equations when the above assumptions are made.

$$I' = k_3[S] \quad (10)$$

$$k_3[S] + k_6[R] = k_5[T] \quad (11)$$

$$k_5[T] = (k_6 + k_7 + k_8 + k_9)[R] \quad (12)$$

I' is the intensity of light absorbed by the starting material. These expressions lead to

$$I' = (k_7 + k_8 + k_9)[R] \quad (13)$$

By definition

$$\phi = (k_8 + k_9)[R]/I' = (k_8 + k_9)/(k_7 + k_8 + k_9) \quad (14)$$

Writing rate constants in the Arrhenius form $k = A \exp(-\Delta E/RT)$, and noting that $\Delta E_8 \approx \Delta E_9$ since temperature has little effect on the product ratio, then

(16) R. F. Borkman and D. R. Kearns, *Chem. Commun.*, 446 (1966).
 (17) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, 83, 2789 (1961).

$$k_8 + k_9 = (A_8 + A_9) \exp(-\Delta E_8/RT)$$

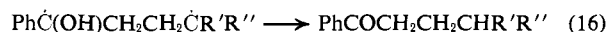
Hence from eq 14

$$\ln \left(\frac{1}{\phi} - 1 \right) = \text{constant} - (\Delta E_7 - \Delta E_8)/RT \quad (15)$$

For butyrophenone, $(\Delta E_7 - \Delta E_8)$ must be negative in order to account for the observed increase in quantum yield with increasing temperature. Similarly, for valerophenone, the difference must be close to zero over the temperature range studied, and, for 1-phenyl-4-methylpentan-1-one, the difference must be negative.

This activation energy difference may be thought of in terms of a partitioning of the diradical X. Factors which raise the activation energy (ΔE_7) for return to the ground state or which diminish the activation energy (ΔE_8) for the formation of the products will make $(\Delta E_7 - \Delta E_8)$ more positive.

There seem to be two such factors. Firstly, in the radiationless decay step (7), which involves a reversal of the hydrogen-abstrating step as in (16), the energy term which varies for the three ketones studied is the bond energy of the C-H bond which is about 98 kcal/mole for butyrophenone and 94 and 91 kcal/mole for valerophenone and 1-phenyl-4-methylpentan-1-one, respectively. These figures are based on those for the



nearest corresponding alkane (propane, butane, and isobutane, respectively) as given in the table compiled by Calvert and Pitts.¹⁸ On this basis, ΔE_7 would be expected to increase in the order $\text{PhCOPr-}n < \text{PhCOBu-}n < \text{PhCOAm-}i$.

Secondly, the product-forming step (8) involves the production of acetophenone and an olefin. Since olefin stability increases with methyl substitution (heats of hydrogenation¹⁹ show a difference of approximately 2.5 and 2.0 kcal/mole between ethylene and propylene and between propylene and isobutylene), we shall expect a similar, though lesser, decrease in ΔE_8 for the sequence $\text{PhCOPr-}n > \text{PhCOBu-}n > \text{PhCOAm-}i$.

We thus conclude that the variation with temperature of the quantum yield for the photolysis of phenyl alkyl ketones is a manifestation of the differences in activation energies involved in the return of the biradical intermediate X to the ground state and in the product-forming reactions. The dangers involved in using quantum yields as a measure of reactivity are underlined by these results which show the effect that solvent and temperature can have in a particular case. A full kinetic scheme should be set up and considered before quantum yields are interpreted in terms of excited-state reactivity.

Experimental Section

Butyrophenone (Koch-Light Laboratories Ltd.) was purified by vacuum distillation, and *p*-hydroxybutyrophenone (Koch-Light) by recrystallization from water. 2-Butyronaphthone was prepared by a standard Friedel-Crafts acylation of naphthalene with butyryl chloride in nitrobenzene and was purified by recrystallization from

(18) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 824.

(19) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 57, 882 (1935).

glacial acetic acid. *p*-Methoxybutyrophenone was made from the *p*-hydroxy compound and methyl iodide in the presence of sodium hydroxide and was purified by vacuum distillation. Valerophenone, 1-phenyl-4-methylpentan-1-one, and *p*-chlorobutyrophenone were prepared from the corresponding benzaldehyde and alkylmagnesium bromide by oxidation of the first-formed substituted benzyl alcohol. Typically, benzaldehyde (0.17 mole) in ether (20 ml) was added slowly to *n*-butylmagnesium bromide (0.20 mole) in ether (100 ml), and the mixture was refluxed for 30 min, then hydrolyzed with ice and concentrated hydrochloric acid. The 1-phenylpentan-1-ol was extracted with ether, and the crude product was oxidized by warming to 65° for 6 hr with acidified potassium dichromate solution. The product was extracted with ether, and the crude ketone was purified by vacuum distillation. The over-all yields were in the range 50–75%.

Ultraviolet spectra were recorded on a Unicam SP800 spectrometer, phosphorescence spectra on an Aminco-Bowman spectrofluorometer with phosphoroscope, and mass spectra on an AEI MS9 instrument. The glasses used for phosphorescence were 1:5 methylcyclohexane:isopentane or 2:1 methylcyclohexane:*n*-hexane (nonpolar), and 2:1 ethanol:ether, 1:1 ethanol:methanol, or 5:5:2 ether:isopentane:ethanol (polar).

Irradiations. Large-scale irradiations were carried out in a reactor with a centrally placed 450-W medium-pressure mercury lamp. The acetophenone and cyclobutanol products were isolated by preparative vpc on a column of 30% Perkin-Elmer Silicon Fluid FS1265 on "Anakrom", 40–50 Å. The structures of acetophenone itself, *p*-chloroacetophenone, *p*-methoxyacetophenone, 1-phenylcyclobutanol, and 2-methyl-1-phenylcyclobutanol were confirmed by analysis and by infrared, nmr, and mass spectra.

2,2-Dimethyl-1-phenylcyclobutanol was isolated as a colorless oil. *Anal.* Calcd for C₁₂H₁₆O: C, 81.8; H, 9.1. Found: C, 81.7; H, 9.0. Infrared showed no carbonyl absorption, and nmr

showed a signal at τ 7.54 (CCl₄) which was reduced with D₂O. The cyclobutanol from *p*-chlorobutyrophenone could not be isolated by this method nor could it be satisfactorily isolated by column chromatography on silica gel.

From the product of the irradiation of butyrophenone in acetonitrile dibenzoyl ethane was isolated as colorless crystals by chromatography on a column of silica gel with chloroform as eluent. This compound was recognized by its melting point (139–140°) and by its simple infrared, nmr, and mass spectra.

Comparative experiments were carried out in a roundabout apparatus having 12 equally spaced quartz reaction tubes suspended vertically near the outer rim of a metal disk; this disk rotates about the vertical axis through its center. The lamp, contained in a water-cooled Pyrex probe, was positioned to lie along the axis. A filter solution containing potassium chromate (0.002 *M*) and potassium carbonate (0.05 *M*) in water, and of path length 4.8 mm, was used to isolate the 313-nm region. The ketone solutions were about 0.15 *M*, and the product solutions were analyzed by vpc on a column of Perkin-Elmer Silicone Fluid FS1265, with a detector of the hydrogen flame combustion type, the response of which was known from calibration against the pure compounds. The reactions were not allowed to proceed beyond 10% conversion, and in some cases *m*-dichlorobenzene was used as an internal standard.

To investigate the reaction at different temperatures, the large-scale apparatus was used in a water bath maintained at a constant temperature, and for each measurement the conditions other than temperature were as nearly as possible identical. In order to obtain reliable results, conversions of more than 10% were necessary in most of these runs.

Acknowledgment. We thank the Science Research Council for a grant to purchase the spectrophosphorimeter.

Thermodynamics of Proton Ionization from Some Substituted 1,2,3-Triazoles in Dilute Aqueous Solution

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Contribution from the Department of Chemistry, The University of New Mexico, Albuquerque, New Mexico 87106. Received June 27, 1968

Abstract: ΔH° , ΔS° , and pK values valid at 25° and zero ionic strength are reported for 1,2,3-triazole, 4,5-dibromo-1,2,3-triazole, 1,2,3-triazole-4-carboxylic acid, 1,2,3-triazole-4,5-dicarboxylic acid, benzotriazole, 1-phenyl-1,2,3-triazole-4-carboxylic acid, 1-phenyl-1,2,3-triazole-4,5-dicarboxylic acid, and 1-phenyl-5-methyl-1,2,3-triazole-4-carboxylic acid. Unusual substitution effects on the thermodynamics of proton ionization from the triazole ring are found.

A study of proton ionization from the 1,2,3-triazole ring is of interest for several reasons: (a) it is isoelectronic with the biologically important imidazole ring, (b) the bond structure of the ring is as yet poorly known, (c) the change in acidity of 1,2,3-triazoles do not seem to follow the same pattern with substitution as more familiar acid groups do, and (d) very little thermodynamic data were previously available on this system.

No ΔH values have previously been reported for proton ionization from 1,2,3-triazoles, and the only pK values reported for the compounds included in this study are those for triazole¹ and benzotriazole.¹ The purpose of this study was to determine the effects of

substituents on the ΔH° , ΔS° , and pK values for proton ionization from the 1,2,3-triazole ring.

Experimental Section

Materials and Equipment. Compounds used for this study were prepared by known methods,² and the structures were verified either from the synthesis procedure or by proton nuclear magnetic resonance spectra. Equivalent weight determinations by titration

(2) (a) 1,2,3-Triazole: O. Dimroth and G. Fester, *Ber.*, **43**, 2222 (1910); (b) 1,2,3-triazole-4-carboxylic acid: E. Oliveri-Mandala and A. Coppola, *Gazz. Chim. Ital.*, [II] **40**, 436 (1910); (c) 1,2,3-triazole-4,5-dicarboxylic acid: J. Bladin, *Ber.*, **26**, 545 (1893) (subsequently treated with strongly acidic cation-exchange resin to remove the K⁺); (d) benzotriazole: Eastman, Practical grade, crystallized from EtOH and then from H₂O; (e) 4,5-dibromo-1,2,3-triazole: R. Huttel and A. Gebhardt, *Ann.*, **558**, 34 (1947); (f) 1-phenyl-1,2,3-triazole-4,5-dicarboxylic acid, 1-phenyl-5-methyl-1,2,3-triazole-4-carboxylic acid, and 1-phenyl-1,2,3-triazole-4-carboxylic acid: O. Dimroth, *Ber.*, **35**, 1029 (1902).

(1) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth & Co. (Publishers), Ltd., London, 1965.