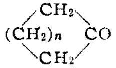
high reactivity. It is conceivable[4] though that some process other than the addition step may be rate-determining for the small ring compound I.

Further rate data on the entire series of ketones were obtained at three temperatures covering the interval 19.7–30.2°, making possible the calculation of Arrhenius energies of activation ($E^{\mathrm{Arr.}}$) and the other thermodynamic quantities of activation. Values of $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated at 25°, taken as the center of the temperature interval employed. These results are summarized in Table I.

TABLE I

DATA DERIVED FROM TEMPERATURE COEFFICIENT RUNS

Ketone  n	$E^{\mathrm{Arr.}}$, kcal./mole	$\Delta F^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
1	9.1 ± 0.4	24.0	−54
2	15.4 ± 1.0	22.1	−24
3	11.6 ± 0.2	20.7	−33
4	13.3 ± 1.0	24.0	−38
5	14.7 ± 2.7	24.3	−34

A notable result from Table I is to be found in the large negative values for $\Delta S^{\ddagger}$, reminiscent of the *ca.* −40 e.u. found for the peracid reactions with substituted acetophenones,[3] and with acetylcyclanes.[5] Also, it would appear significant that cyclobutanone displays a relatively low value for $E^{\mathrm{Arr.}}$ and a relatively large numerical value for $\Delta S^{\ddagger}$, compared to the values for the other members of the series.

An incidental point noted in the rate work on I was the susceptibility of these rates to acid catalysis, as previously observed[2] for other ketones in the series. As a result, aged chloroform solutions of low peracid titer (and hence increased benzoic acid content) gave slightly higher k_2 values than freshly prepared solutions. In a more direct demonstration of this acid catalysis, the addition of 0.133 M benzoic acid to an approximately 0.24 M peracid solution resulted in an increase in rate constant for I by a factor of 1.8.

With the data of Fig. 1 furnishing a relationship between ring size and carbonyl group reactivity, a point of further interest was to compare this relationship with that between ring size and the state of polarization of the carbonyl group, as reflected in the position of the carbonyl peak in the infrared spectrum of each ketone. Previously, a rough parallelism between these relationships was observed[6] for substituted acetophenones. In the present series, no such simple parallelism was found. For comparison purposes, positions of the carbonyl bands in the ketone spectra were redetermined[7] using a single instrument for all members of the series, with the following observed values for carbonyl wave numbers (cm.$^{-1}$) as ring size increases (n = 1, 2 . . . 5); 1784, 1742, 1704, 1703, 1702. These values indicate a sharp drop in wave number for the carbonyl group vibration as ring size increases from the minimum in compound I, and form a far different relationship from that displayed by the reactivity data of Fig. 1.

Experimental

Preparation of Ketones.—Cyclobutanone was prepared using the recently developed method of Roberts and Sauer[7]; b.p. 97–98°, n^{25}D 1.4183. Cycloöctanone was prepared essentially according to Kohler[8]; b.p. 95–96° (37 mm.), n^{20}D 1.4717. The remaining ketones of the series were purified just before use.

Stoichiometric Runs.—Preparative scale runs on a 0.1 mole basis were made on ketones I and II as in the previous study,[2] using roughly a 20% excess of peracid in each reaction. Compound I had consumed a mole of peracid at the end of 192 hours at room temperature, while II required 42 days to reach this level of consumption. The crude lactone products were converted directly into the ω-hydroxyhydrazides, after the usual separation from residual perbenzoic and benzoic acids.

In the work-up of the butyrolactone from I, its high solubility in water made a revision of the usual procedure necessary. After removal of solvent, the lactone was extracted from the crude mixture with three 15-ml. portions of ice-cold water, and the combined aqueous extract refluxed with excess 100% hydrazine hydrate for two hours. The solvent was then removed under reduced pressure and the resulting hydrazide recrystallized from ethyl acetate in 70% yield, m.p. 89–89.5° (lit.[9] value, 89–90°).

In isolating the ω-hydroxyhydrazide from II, residual unreacted ketone was first separated and recovered by use of Girard Reagent T. The crude lactone was then converted to the hydrazide in the usual way; yield (based on unrecovered ketone) 61%; m.p. 130.5–132°. *Anal.* Calcd. for $C_8H_{18}O_2N_2$: C, 55.14; H, 10.41. Found: C, 55.00; H, 10.69.

Rate Runs.—These were carried out essentially according to the previous[2] method. A 30-minute interval was allowed for reaction mixtures to attain thermal equilibrium after being placed in the constant temperature bath. Temperatures were held constant to ±0.05°.

Infrared Data.—Machine tracings were obtained on each of the liquid ketones using a Perkin–Elmer single beam recording infrared spectrometer (model 12 AB), through the courtesy of Mr. Carl Whiteman. A cell of 0.025 mm. thickness was used.

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(6) S. L. Friess and A. H. Soloway, *ibid.*, **73**, 5000 (1951).

(7) For previous determinations of infrared spectra of these ketones, see: (1) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949); (2) J. Lecomte, *J. phys. radium*, **6**, 257 (1945); *C. A.*, **40**, 2739 (1946); (3) C. Cherrier, *Compt. rend.*, **225**, 1063 (1947).

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(9) A. L. Dounce, R. H. Wardlow and R. Connor, *ibid.*, **57**, 2556 (1935).

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Beckmann Rearrangements. A New Method

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Since the original observation by Beckmann[1] that benzophenone oxime was converted to benzanilide in the presence of acidic dehydrating agents, extensive investigations of this rearrangement have appeared. Applications of the rearrangement have been important in both theoretical and preparative chemistry, and a variety of conditions have been developed for effecting the reaction; these matters have been the subject of periodic reviews.[2,3]

In our investigations of the Beckmann rearrangement, we have found that the transformation can be carried out by a method which involves reaction

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(1) E. Beckmann, *Ber.*, **19**, 988 (1886).

(2) B. Jones, *Chem. Revs.*, **35**, 335 (1944).

(3) A. H. Blatt, *ibid.*, **12**, 215 (1933).

TABLE I

Oxime	Product	Temp., °C.	Yield, %	M.p., °C.	Reported m.p., °C.	Procedure
Benzophenone	Benzanilide	130	99–100	161–162	162–163	A
p,p'-Dimethoxybenzophenone	Anisoylanisidine	130	91	199–203	202	A
Acetophenone	Acetanilide	95	97	103–106	114	A
p-Methoxyacetophenone	*p*-Methoxyacetanilide	120	99–100	122–124	127	A
Cyclohexanone	ε-Caprolactam	115	89	60–62	65–68	B
Cyclopentanone	δ-Valerolactam	130	74	31–35	39–40	B

circumstances different from those which might be expected for a general acid-catalyzed reaction of oximes. In this method, the oxime is heated in polyphosphoric acid[4] at moderate temperatures ranging from 95–130°. Solution of the oxime is sometimes accompanied by mild heating effects, but no evidence of reaction is otherwise noted. Amides are formed in essentially quantitative yield; such losses as occur on isolation are apparently due to variations in physical properties of the products.

This procedure, described briefly in the experimental section, may be illustrated by the case of benzophenone oxime, the compound originally investigated by Beckmann. There are no isomeric forms of the ketoxime; the product is crystalline, easily isolated, and has a well-defined melting point. With polyphosphoric acid, the rearrangement of the oxime was accomplished in ten minutes at 130°; the clear solution was diluted with water to yield crystalline benzanilide in 99–100% yield; the melting point and infrared spectrum showed no impurities in amounts which would affect these two properties.

Other examples are given in Table I. The reaction is satisfactory for oximes of diaryl ketones, alkylaryl ketones and aliphatic ketones of the cyclic type. When the products are soluble in the aqueous phosphoric acid resulting after treatment of the mixture with water, special isolation methods are necessary and the yields are lowered.

It is not possible to describe the precise course of the reaction. A phosphate ester of the oxime may be involved as an intermediate. Dehydration of the products does not occur, although the reagent is also a strong dehydrating agent. The rearrangement is probably initiated by acid catalysis, but here polyphosphoric acid is the solvent and proton donor as well. Other examples of the Beckmann rearrangement are currently under investigation, and while these studies are not completed, we have observed that in cases of so-called abnormal Beckmann reactions our products do not correspond to those previously reported.

While exceptions may possibly be found to the generality of the method described here, our results at present indicate that polyphosphoric acid may be the reagent of choice for the rearrangement.

Experimental

General Procedure A.—A mixture of 2.00 g. of the oxime and 60 g. of polyphosphoric acid was heated with manual stirring to the indicated temperature (Table I). The resulting solution was maintained at the specified temperature for ten minutes and then poured into 300 ml. of water. The water solution was extracted with 1:1 ether–ethyl acetate. The organic layer was washed with water, saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The product was isolated by filtration and evaporation of the solvents to give the crude yields reported in Table I. All crude products were colorless crystalline materials; melting points are given for the crude material as an indication of purity; identity was confirmed before and after recrystallization.

General Procedure B.—The initial reaction was conducted according to Procedure A. The products may be extracted from water only with difficulty, and it was therefore necessary to follow the isolation procedure essentially as given in reference 5.

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The Absorption of Radiation by Inhomogeneously Dispersed Systems

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Because of a lack of suitable solvents, a great deal of qualitative infrared analysis is performed on solid preparations. To control sample thickness and minimize light scatter, the absorbing material is usually pressed out as a film, deposited from solution on a silver chloride or sodium chloride plate or mulled with a mineral oil or with perfluorokerosine. A technique involving dispersion in solid potassium bromide has also been described.[1]

These techniques have also been adapted for quantitative analysis,[2–4] in spite of the difficulties inherent in the preparation of films or mulls of reproducible optical quality. Quantitative results can be obtained by the use of empirical calibration curves derived from measurements on standard samples, but it is the object of this communication to emphasize that when the absorbing material is agglomerated into macro particles, separated by regions of high transmittance, or when variations occur in the thickness of the sample in the beam, the laws governing the absorption of radiation by isotropic material are no longer applicable. These limitations are inherent in the absorption laws themselves; they apply where the particles are large in comparison with the wave length of the light, and are additional to the scattering effects of reflection and refraction at the boundaries of the absorbing areas, which have been discussed by Pfund,[5] Henry[6] and others.

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[2] R. B. Barnes, R. C. Gore, E. F. Williams, S. G. Linsley and E. M. Patterson, *Anal. Chem.*, **19**, 620 (1947).

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