

product was filtered, then steeped ten times with 1-liter portions of water. Halide ions were absent in the filtrate after the third washing. After a week of steeping in acetone, the dried product was a fine white powder.

**Iodination.**—Samples of 1.5–2.5 g. of the tosylated product were treated with 75–125 g. of a 15% solution of sodium iodide in freshly distilled acetonylacetone under the conditions shown in Table II. Purification and analysis for iodine were done by the methods of Mahoney and Purves.<sup>9</sup>

**Periodate Oxidation.**—Reactions were carried out in the dark<sup>10</sup> at a pH of 5.4<sup>11</sup> in the presence of bicarbonate with the temperature at  $20 \pm 1^\circ$ . Separate 25-ml. portions of a 0.4% aqueous solution of CMC were treated with 50 ml. of oxidant solution (0.0796 N in  $\text{NaIO}_4$ ) prepared from sodium paraperiodate. The amount of oxidant consumed after a given period was determined by the method of Davidson.<sup>12</sup>

(9) Reference 3a, page 10.

(10) F. S. H. Head, *J. Textile Inst.*, **20**, A23 (1950).

(11) C. C. Price and H. Kroll, *THIS JOURNAL*, **60**, 2726 (1938).

(12) G. F. Davidson, *J. Textile Inst.*, **31**, T81 (1940); *ibid.*, **32**, T109, 132 (1941).

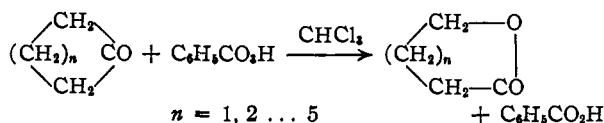
DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF DELAWARE  
NEWARK, DELAWARE

### Further Observations on the Reaction of Cyclanones with Perbenzoic Acid

BY S. L. FRIESS<sup>1</sup> AND P. E. FRANKENBURG

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In a previous communication<sup>2</sup> dealing with kinetic and stoichiometric studies of the reaction of cyclanones with perbenzoic acid, limited data were ob-



tained for those members of the ketone sequence with  $n = 2, 3$  and 4. These data have now been extended to include the reactions of the four and eight-membered ring ketones ( $n = 1, 5$ ). In addition, temperature coefficients and thermodynamic quantities of activation have been determined for the peracid reaction of the entire ketone series, as well as comparative values of rate constants for all members of the series, referred to a single peracid solution. The latter data furnish a completed picture of the reactivity of the carbonyl group toward peracid addition,<sup>2</sup> in the range  $n = 1$  to 5, as a function of ring size of the cyclic ketone.

In preliminary runs on a preparative scale, purified samples of cyclobutanone (I) and cyclooctanone (II) were allowed to react with excess perbenzoic acid in dry chloroform. The lactone products of these reactions were converted into their respective  $\omega$ -hydroxyhydrazides, for ease of handling and purification, and furnished amounts of crystalline hydrazides corresponding to product yields of 70 and 61% from I and II. The yield cited for II is based on that amount of ketone unrecovered from its sluggish reaction mixture after an extensive reaction interval at room temperature.

Since all members of the ketone series have now been shown to undergo the primary ketone  $\rightarrow$  lac-

(1) Naval Medical Research Institute, Bethesda, Md.

(2) S. L. Friess, *THIS JOURNAL*, **71**, 2571 (1949).

tone reaction, it was of considerable interest to obtain values of the rate constants for this process, referred to a single peracid solution of normal oxidative activity,<sup>2,3</sup> for comparison with other chemical indices of reactivity<sup>4</sup> of these cyclanones. Accordingly, the initial rates of reaction were determined for all members of the ketone series at  $25.65^\circ$ , and second order rate constants ( $k_2$ ) evaluated for each ketone reaction. Since a rate run on a standard ketone (cyclohexanone or cyclopentanone) was made simultaneously with runs on every other member of the series, all  $k_2$  values could be normalized<sup>3</sup> to an average  $k_2$  value for cyclohexanone of  $9.58 \times 10^{-4}$  l./mole sec., or  $1.36 \times 10^{-4}$  l./mole sec. for cyclopentanone, in a process equivalent to standardization of all runs to the activity of a single peracid solution. New data obtained in this portion of the study include  $k_2$  values for I and II at  $25.65^\circ$  of  $(7.0 \pm 1.0) \times 10^{-5}$  and  $(2.28 \pm 0.15) \times 10^{-5}$  l./mole sec., respectively. Rate constant data for the entire series at this temperature are shown plotted in Fig. 1, as a function of ketone ring size.

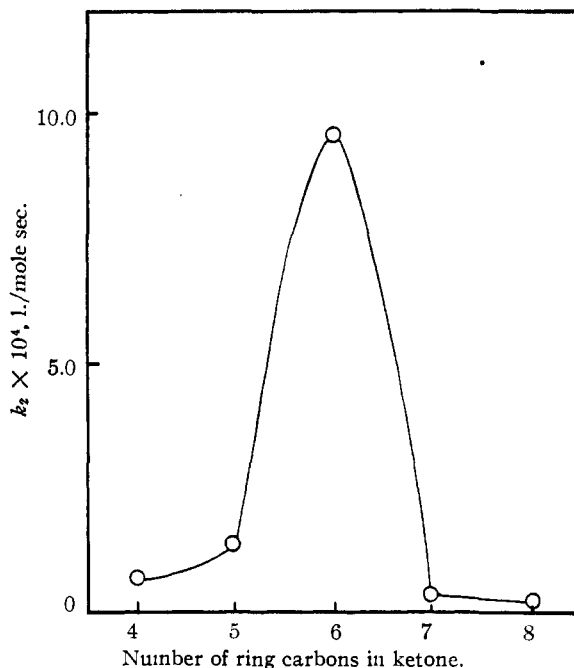


Fig. 1.—Rate constants in dry chloroform at  $25.65^\circ$ .

Significantly, the reaction rate for the six-membered ketone is at a maximum for the series, with a sustained drop in rate as ring size is either increased or decreased from this peak value. This particular result is for the most part in accord with the concept of Brown,<sup>4</sup> relating to I-strain as the determining factor in the rates of addition reactions to carbonyl groups contained in common-sized rings. However, the relatively low reactivity of the four-membered cyclanone I is surprising when viewed on this basis, since a lesser degree of strain should be inherent in the transition state for a rate-determining addition or coordination process than that present in the initial ketone molecule, with a net result of

(3) S. L. Friess and A. H. Soloway, *ibid.*, **73**, 3968 (1951).

(4) See, for example, the compilation and interpretation of reactivity data by H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

high reactivity. It is conceivable<sup>4</sup> 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 ( $E^{Arr.}$ ) 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 $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ (\text{CH}_2)_n \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{CH}_2 \\ n \end{array}$	$E^{Arr.}$ , kcal./mole	$\Delta F^\ddagger$ , kcal./mole	$\Delta S^\ddagger$ , e.u.
	1	9.1 ± 0.4	24.0
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,<sup>3</sup> and with acetylcyclohexanes.<sup>5</sup> Also, it would appear significant that cyclobutanone displays a relatively low value for  $E^{Arr.}$  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<sup>2</sup> 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<sup>6</sup> 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<sup>7</sup> using a single instrument for all members of the series, with the following observed values for carbonyl wave numbers ( $\text{cm.}^{-1}$ ) as ring size increases ( $n = 1, 2 \dots 5$ ): 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<sup>7</sup>; b.p. 97–98°,  $n_D^{25}$  1.4183. Cyclohexanone was prepared essentially according to Kohler<sup>8</sup>; b.p. 95–96° (37 mm.),  $n_D^{25}$  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,<sup>2</sup> 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  $\omega$ -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.<sup>9</sup> value, 89–90°).

In isolating the  $\omega$ -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  $\text{C}_8\text{H}_{18}\text{O}_2\text{N}_2$ : C, 55.14; H, 10.41. Found: C, 55.00; H, 10.69.

**Rate Runs.**—These were carried out essentially according to the previous<sup>2</sup> 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  $\pm 0.05^\circ$ .

**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.

(8) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *THIS JOURNAL*, **61**, 1057 (1939).

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

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF ROCHESTER  
ROCHESTER 3, NEW YORK, AND THE  
NAVAL MEDICAL RESEARCH INSTITUTE  
BETHESDA 14, MARYLAND

## Beckmann Rearrangements. A New Method

BY E. C. HORNING AND V. L. STROMBERG

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Since the original observation by Beckmann<sup>1</sup> 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.<sup>2,3</sup>

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

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

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

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

(5) S. L. Friess and Rex Pinson, Jr., *THIS JOURNAL*, **74**, 1302 (1952).

(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. Lecomette, *J. phys. radium*, **6**, 257 (1945); *C. A.*, **40**, 2739 (1946); (3) C. Cherrier, *Compt. rend.*, **225**, 1063 (1947).