N-Benzoyloxazolidone showed also (in $CHCl_3$) bands at 3160, 2925, 1602, 1481, 1450, 1379, 1328, 1186, 1100, 1041, 987, 912 and 882 cm.$^{-1}$.

N-Benzoyl-4,5-tetramethyleno-2-oxazolidone showed also (in CCl_4) bands at 2925, 1596, 1454, 1355, 1330, 1309, 1253, 1205, 1177, 1126, 1099, 1059, 999, 969, 942, 907 and 896 cm.$^{-1}$.

2-Pyrrolidone and **N-methyl-2-pyrrolidone** were commercial products purified by vacuum distillation.

REHOVOTH, ISRAEL

[CONTRIBUTION OF THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

Polar Factors in Radical Dissociations. Kinetics of Decomposition of *meta*-Substituted Phenylazotriphenylmethanes[1a]

BY STANLEY SOLOMON, CHI HUA WANG AND SAUL G. COHEN[1b]

RECEIVED JANUARY 9, 1957

meta-Substituted phenylazotriphenylmethanes, *m*-X—$C_6H_4N{=}NC(C_6H_5)_3$, X = CH_3, Br, NO_2, (H), have been prepared and decomposed in toluene at two temperatures. The decompositions showed first-order kinetics with activation energies in the range 26–30 kcal. mole^{-1}. The substituent CH_3 led to increased rates, the substituents Br and NO_2 to decreased rates of decomposition, the effects being quite similar to those of *p*-substituents studied previously. The results for *m*-substituents were correlated by the Hammett equation, ρ −0.85, and indicated that phenyl radicals may be rendered less stable by electron withdrawal. Factors affecting homolytic dissociation processes are discussed. Decomposition of phenylazotriphenylmethane in acetic acid led to benzene (>40% yield), to biphenyl (10% yield) and to no succinic acid. The origin of the products is discussed.

As part of our study of the effects of structure on the homolytic dissociation of organic compounds, which lead to the formation of free radicals, we have been examining the effects of substituents in the phenyl group of phenylazotriphenylmethanes on the kinetics of their decomposition. The ease with which homolytic dissociation occurs, or the strength of the bond or bonds concerned may be considered in terms of steric effects, polar factors, and the difference in the resonance stabilization of the ground states and transition states.

The decomposition of substituted ethanes[2] R_3–C–C–R_3 shows marked increase in rates and decrease in activation energies as the alkyl groups R are made more complex or are changed to aryl groups, the variations resulting from steric factors, which affect the central carbon–carbon bond, and resonance stabilization of the radicals. Azo-bis-alkanes and azo-bis-arylalkanes $R_3C{—}N{=}N{—}CR_3$ are related materials, in which the azo linkage facilitates decomposition while reducing steric effects. Substitution of α-alkyl and aryl groups for hydrogen in the parent compound azomethane, R = H, leads to successive and approximately additive increase in rate and decrease in activation energy, which have been interpreted in terms of resonance stabilization of the radicals,[3] and hence of the transition states. Steric effects have also been observed in the decomposition of certain azo compounds, largely due to β-substituents.[4]

Substituents in the nuclei of hexaarylethanes, whether electron attracting or electron donating, increase the extent of their dissociation, the large effects of *o*-substituents commonly being attributed to steric and resonance factors, and the effects of *p*-substituents, to resonance.[5] The effect of *m*-substituents, often attributed to steric factors, may result largely from the charge (+ or −) which they impose upon the aromatic rings to which they are attached, leading, in symmetrically substituted ethanes, to electrostatic repulsions between the two halves and weakening of the central bond. That the effect of *m*-substituents is comparable to and frequently greater than that of *p*-substituents indicates that this polar factor may be of importance in the latter case also.

In the decomposition of substituted benzoyl peroxides,[6] electron-donating substituents were found to increase the rates, electron-attracting substituents, (except nitro) to decrease them, and the data fitted the Hammett equation fairly well, ρ −0.38. This was interpreted[6a] in terms of the effects of the substituents on the size of the negative ends of the dipoles, postulated to exist at the central oxygen–oxygen bond and thus on repulsive forces operating between the two halves of the molecules. Similar effects of substituents were observed in the decomposition of *t*-butyl perbenzoates.[7] Also, in the dissociation of five symmetrically substituted 1,1,4,4-tetraphenyl-2,3-dibenzoyltetrazanes,[8] in which the phenyl substituents were CH_3, H and Br, the equilibrium constants were correlated with the Hammett equation, ρ −1.52. This was interpreted as resulting from stabilization by electron-donating substituents of the positive charge on the α-nitrogen in one of the resonance forms of the hydrazyl radicals. Further study of the dissociation of these tetrazanes indicated that the Hammett equation success-

---

(1) (a) Taken in part from a dissertation submitted by Stanley Solomon in partial fulfillment of the requirements for the M.A. degree in Chemistry, Brandeis University. (b) To whom inquiries should be addressed.

(2) K. Ziegler and W. Deparade, *Ann.*, **567**, 123 (1950).

(3) S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 2457, 3628 (1955).

(4) C. G. Overberger, W. F. Hale, M. B. Berenbaum and S. B. Firestone, *ibid.*, **76** 6185 (1954).

(5) For discussion with references, see G. W. Wheland, "Advanced Organic Chemistry," 2nd edition, John Wiley & Sons, Inc., New York, N. Y., 1949, pp. 694–697, and J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 377–383.

(6) (a) C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950); (b) A. T. Blomquist and A. S. Buselli, *ibid.*, **73**, 3883 (1951).

(7) A. T. Blomquist and J. A. Berstein, *ibid.*, **73**, 5546 (1951).

(8) W. K. Wilmarth and N. Schwartz, *ibid.*, **77**, 4543 (1955).

fully correlated the rates of both the dissociation and the recombination.[9]

In the decompositions of *p*-substituted phenylazotriphenylmethanes[10] we observed that both electron-donating substituents (*e.g.*, *p*-CH_3O, σ -0.27) and electron-attracting substituents (*e.g.*, *p*-NO_2, σ $+0.78$) led to decreases in the rates of decomposition, and the results would of course not be correlated by the Hammett equation with conventional σ-values. It was pointed out that both types of substituents could increase the resonance stabilization of the ground state by increasing conjugation of the phenyl and azo groups and strengthen the phenyl–nitrogen bond. It was suggested that this effect might be modified by the effects of the substituents on the stability of the phenyl radical and thus on the stabilization of the transition states, with electron-donating substituents stabilizing the radicals and partly counteracting the stabilization of the ground states. Alternatively the observed order could be interpreted in terms merely of the inductive effect, $-I$ substituents decreasing the stability of phenyl radicals. In order to minimize the effect of the substituent on the conjugation of the azo linkage with the phenyl group and to isolate the effect of the substituent on the phenyl radical, it seemed desirable to study some *m*-substituted phenylazotriphenylmethanes. The compounds *m*-X—C_6H_4-N=NC$(C_6H_5)_3$, X = CH_3, Br, NO_2 and (H) were each synthesized by (1) preparation of the substituted phenylhydrazine hydrochloride, (2) condensation of the hydrazine salts with triphenylmethyl chloride to form the hydrazo compounds, *m*-X-C_6H_4-NH-NH-C$(C_6H_5)_3$, and oxidation of the latter to the azo compounds. The unsubstituted hydrazo compound autoxidized during purification leading directly to the azo compound. The *m*-nitro compound was resistant to oxidation, treatment with amyl nitrite finally proving effective. This reagent was used to oxidize the *m*-bromo and *m*-methyl compounds, the reaction in the latter case being quite vigorous. We were unfortunately unable to prepare *m*-methoxyphenylhydrazine and *m*-acetaminophenylhydrazine.

The rates of decomposition of the azo compounds in *ca.* 0.01 *M* solution in toluene were determined under oxygen-free nitrogen at two temperatures by measurement of the volume of evolved nitrogen (V_t) as a function of time, essentially as described previously.[10] Several runs were made at each temperature. Small induction periods (*ca.* 5 minutes) were observed, and zero time readings were obtained by linear extrapolation of a zero-order plot for the first 10% of the reaction back to zero time. These values were used in calculation of V_∞. Linear plots of ln $V_\infty/(V_\infty - V_t)$ *vs.* time were obtained, indicating that the decompositions were first order. Typical plots are given in Fig. 1. One compound, X = *m*-Br, was decomposed at 0.02 mole/l. and at 0.007 mole/l. concentration with no change in rate constant. Rate constants were determined from the slopes, activation energies from the Arrhenius equation and entropies of activation according to the transition state theory. The data are summarized in Table I.

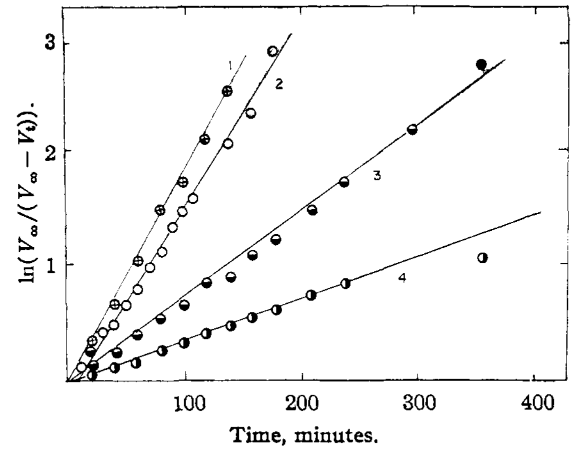

Fig. 1.—Decomposition of *m*-XC_6H_4—N=NC$(C_6H_5)_3$ in toluene, 53.80°: curve 1, X = CH_3; curve 2, X = H; curve 3, X = Br; curve 4, X = NO_2.

TABLE I

DECOMPOSITION OF SUBSTITUTED PHENYLAZOTRIPHENYLMETHANES, *m*-X—C_6H_4N=NC$(C_6H_5)_3$

m-X	*T*, °C. ±0.05	No. of runs	$k_1 \times 10^4$ sec.$^{-1}$	$E_{kcal.}$, mole^{-1}	$\Delta S^\pm$, cal. mole^{-1} deg.$^{-1}$
CH_3	53.80	7	2.77 ± 0.10	27.2 ± 1.5	6 ± 4
CH_3	43.80	3	0.74 ± 0.02		
H	53.80	8	2.40	27.6	7
H	43.80	3	0.63		
Br	53.80	4	1.14	29.9	13
Br	64.00	2	4.58		
NO_2	53.80	4	0.58	26.5	1
NO_2	64.00	3	1.99		

The CH_3 substituent increased the rate of decomposition slightly while the groups Br and NO_2 led to decreased rates. The results are correlated satisfactorily by the Hammett equation (Fig. 2), ρ -0.85; σ CH_3, Br, NO_2: -0.07, $+0.39$, $+0.71$, respectively. The entropies of activation are not constant, but since they change with the energies of

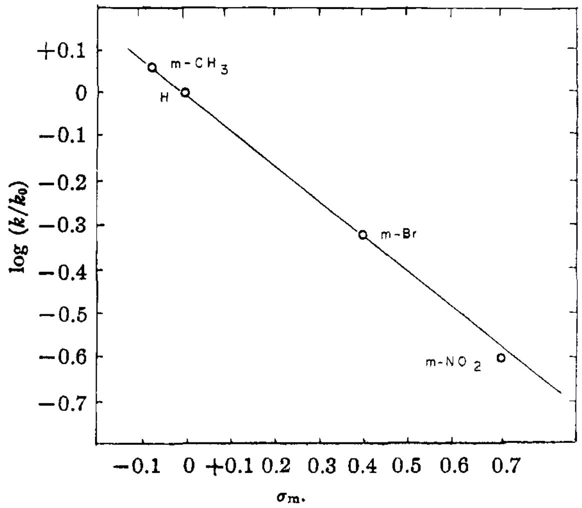

Fig. 2.—ρ–σ plot for decomposition rate constants, *m*-X—C_6H_4N=NC$(C_6H_5)_3$, in toluene at 53.80°.

---

[9] W. K. Wilmarth and N. Schwartz, THIS JOURNAL, **77**, 4551 (1955).

[10] S. G. Cohen and C. H. Wang, *ibid.*, **75**, 5504 (1953).

activation perhaps they may be incorporated into them.[11] It would be desirable to examine this relationship with other *m*-substituents having negative σ-values, but these may not be accessible except for other alkyl groups. It seems unlikely that the *m*-substituents influence the rate by affecting the resonance stabilization of the ground state or the transition state. It appears that the phenyl radical is stabilized by electron accession which tends toward completion of an octet, and destabilized by electron depletion. Such an explanation has been offered for the stabilization of alkyl radicals by alkyl substituents,[12] although in those cases hyperconjugation offers an alternate explanation.

The values of the rate constants and activation energies and thus the effects of the substituents are quite similar for the *m*-substituted and for the *p*-substituted compounds in the cases in which we can make comparisons. (It may be noted that *m*- and *p*-substituents show similar effects in the dissociation of hexaarylethanes.) Indeed, if log k/k_0 for the *p*-substituted phenylazotriphenylmethanes[10] (CH_3, CH_3O, HO, Br, NO_2) is plotted against *meta* σ-values, the points, with the exception of *p*-methoxyl, lie fairly close to the line drawn through the *m*-values. Whether this is fortuitous, the *p*-effects being the resultant of the several factors discussed above, or whether the effect of *p*-substituents arises in similar fashion to the *m*-effects, possibly from electrostatic effects on the phenyl radicals, is not clear.[13]

Products of Decomposition.—Previous studies of the products of decomposition of phenylazotriphenylmethane have indicated that benzene[14a] was formed in low yield, but that diphenyl was not found except when the decomposition was carried out in benzene,[14b] the solvent contributing one phenyl group to this product, which was formed in low yield. In our work, decomposition of phenylazotriphenylmethane in acetic acid led to benzene, 40% yield (58% cor.); to diphenyl, 10% yield; to a large amount of tar, and apparently to low yields of tetraphenylmethane and other products. The benzene results from extraction of hydrogen by phenyl from a component of the solution. Succinic acid was not found, indicating that phenyl radical does not extract hydrogen under these conditions from acetic acid, neither from the α-carbon which would lead directly, nor from the carboxyl which would lead indirectly to succinic acid. It seems likely that phenyl radical dehydrogenates the triphenylmethyl radical, leading to quinonoid products and thus to tars. The diphenyl may well result from dimerization of phenyl radicals, although it cannot be excluded that it results from substitution by phenyl radical into the benzene which is formed in low concentration during the course of the reaction.

Experimental[15]

m-**Nitrophenylhydrazine Hydrochloride.**[16]—A solution of 10 g. (0.145 mole) of sodium nitrite in 70 ml. of water was added dropwise to a solution of 20 g. (0.145 mole) of *m*-nitroaniline (Fisher) in 200 ml. of concentrated hydrochloric acid at 0–5°. The solution was stirred at room temperature for one hour and recooled, and to it was added slowly a solution of 65 g. (0.29 mole) of $SnCl_2 \cdot 2H_2O$ in 65 g. of concentrated hydrochloric acid. A tan precipitate was collected and crystallized from absolute ethanol, m.p. 208–210°, 16.8 g., 61% yield. *Anal.* Calcd. for $C_6H_8N_3O_2Cl$: C, 38.02; H, 4.24. Found: C, 38.50; H, 4.54.

m-**Bromophenylhydrazine Hydrochloride.**[17]—A solution of 20 g. (0.116 mole) of *m*-bromoaniline (Eastman Kodak Co.) in 200 ml. of hydrochloric acid was treated at 0–5° first with a solution of 8.0 g. (0.116 mole) of sodium nitrite in 16 ml. of water for 0.5 hour, and then with a solution of 52 g. (0.23 mole) of $SnCl_2 \cdot 2H_2O$ in 52.5 g. of hydrochloric acid. A white precipitate was collected, dissolved in 250 ml. of boiling water, neutralized with 3 *N* sodium hydroxide, cooled and extracted with ether. The extract was dried over calcium chloride and treated with dry hydrogen chloride leading to a precipitate which was crystallized from 2-propanol, m.p. 225°, 8.4 g., 32% yield. *Anal.* Calcd. for $C_6H_8N_2BrCl$: C, 32.24; H, 3.60. Found: C, 32.04; H, 3.96.

m-**Tolylhydrazine Hydrochloride.**[18]—A solution of 20 g. (0.19 mole) of *m*-toluidine (Eastman Kodak Co.) in 200 ml. of hydrochloric acid was treated at 0.5° with a solution of 13 g. (0.19 mole) of sodium nitrite in 50 ml. of water, stirred at room temperature for 0.5 hour, recooled and treated with 84 g. (0.37 mole) of $SnCl_2 \cdot 2H_2O$ in 84 ml. of hydrochloric acid. The product was collected, dissolved in hot water, saturated with hydrogen sulfide, filtered, made slightly alkaline with 3 *N* sodium hydroxide, cooled and extracted with ether. The extract was dried, treated with dry hydrogen chloride until precipitation was complete. Excess hydrogen chloride led to decomposition. The product was crystallized from 2-propanol, m.p. 168–170°, 8.6 g., 32% yield. *Anal.* Calcd. for $C_7H_{11}N_2Cl$: C, 52.99; H, 6.99. Found: C, 52.34; H, 6.99.

Toward a-*m*-Methoxyphenylhydrazine and *m*-Acetaminophenylhydrazine.—A. *m*-Aminophenol, 1.0 mole, was converted to *m*-hydroxyacetanilide, 0.87 mole, m.p. 149°, reported[19] 148°. This product, 0.73 mole, treated with methyl sulfate, led to *m*-methoxyacetanilide, 0.30 mole, m.p. 79–80°, reported[19] 80–81°. This was hydrolyzed with dilute hydrochloric acid, leading to *m*-anisidine, b.p. 249°, reported 251°.[20] Attempts to diazotize the amine and reduce the diazonium compound led to a product which decomposed at room temperature.

b. An unsuccessful attempt was made to prepare *m*-acetaminophenylhydrazine by treatment of a solution of 5 g. (0.27 mole) of *m*-aminoacetanilide hydrochloride in 200 ml. of hydrochloric acid with 1.85 g. (0.027 mole) of sodium nitrite in 15 ml. of water, followed by treatment with 12 g. (0.053 mole) of $SnCl_2$ in 12 g. of hydrochloric acid. No precipitate formed and treatment with alkali, extraction with ether and treatment with dry hydrogen chloride led to a dark oil.

m-**X-Phenylazotriphenylmethanes.**—Equimolar quantities of the substituted phenylhydrazine hydrochloride and triphenylmethyl chloride were allowed to react in dried pyridine at 20° with stirring for three hours. Quantities of materials used are summarized in Table II.

Pyridine hydrochloride was filtered off and washed with cold pyridine and the filtrates were diluted with water. The precipitates were collected and worked up along with ether extracts of the diluted filtrates.

---

[11] H. H. Jaffe, *Chem. Revs.*, **53**, 193 (1953).

[12] H. Eyring, THIS JOURNAL, **75**, 5183 (1953).

[13] A referee kindly brought to our attention an article which became available after this manuscript was complete (G. L. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 4397 (1956)) in which our earlier work (ref. 10) and related studies are interpreted in terms of desolvation in the transition state. It is regrettable that an unequivocal interpretation cannot be given.

[14] (a) H. Wieland, E. Popper and H. Seefried, *Ber.*, **55**, 1816 (1922); (b) D. H. Hey, *J. Chem. Soc.*, 1966 (1934); W. A. Waters, "The Chemistry of Free Radicals," 2nd Edition, Oxford, 1948, pp. 147–148.

[15] Melting points are uncorrected; elementary microanalyses are by Dr. S. M. Nagy, Massachusetts Institute of Technology.

[16] A. Bischler and S. Brodsky, *Ber.*, **22**, 2809 (1889).

[17] M. Gomberg and A. Campbell, THIS JOURNAL, **20**, 786 (1898).

[18] K. Buchka and F. Schachtebeck, *Ber.*, **22**, 841 (1889).

[19] F. Neverdin and A. de Luc, *ibid.*, **47**, 7537 (1914).

[20] F. Pfaff, *ibid.*, **16**, 614 (1883).

a. X = H.—The hydrazo compound was partially oxidized during evaporation of the ether, leading to a yellow solid. This was dissolved in 600 ml. of absolute ethanol and concentrated in vacuum below room temperature leading to 14.7 g. (0.0425 mole), 77% yield, of crude azo compound, m.p. 107–108° dec., reported 111°.[21] Decomposition of a sample at 100° in decalin led to 67% of the theoretical yield of nitrogen. The nitrogen was swept with carbon dioxide and collected over 50% potassium hydroxide. Four additional crystallizations from absolute ethanol led to a product melting at 110–112° which, when decomposed, led to 96% yield of nitrogen.

TABLE II

REACTION OF TRIPHENYLMETHYL CHLORIDE WITH PHENYLHYDRAZINE

m-X-$C_6H_4NHNH_2HCl$ X	g.	$(C_6H_5)_3CCl$, g.	C_5H_5N, ml.
H	8.0	16.0	120
NO_2	9.7	14.1	130
Br	5.0	6.2	80
CH_3	4.1	8.0	80

b. X = *m*-NO_2.—The crude hydrazo product melted at 140–150° and was somewhat difficult to oxidize. It was not affected by treatment in ether solution at room temperature with 35% hydrogen peroxide in the presence and absence of sodium bicarbonate. It was oxidized slowly by hydrogen peroxide in acetone. It was apparently oxidized by nitrogen dioxide in acetic acid, but the results were not consistent. Amyl nitrite led to satisfactory results and was used in subsequent syntheses. The hydrazo compound, 2.32 g., was suspended in anhydrous ether and treated with two molar equivalents of amyl nitrite and a few drops of acetyl chloride, a clear yellow solution resulting. The solution was filtered and evaporated in vacuum and the azo compound was crystallized from methanol, m.p. 111–112°, reported[17] 111–112°.

c. X = *m*-Br.—The crude hydrazo product was suspended in ether and oxidized as described above. The ether was evaporated and the product was washed with methanol, m.p. 108–109°, reported[17] 110°, 3.9 g. (0.0091 mole), 41% yield. The yields of nitrogen from this and the preceding compound, when determined in the kinetic runs were 100 ± 3%.

d. X = *m*-CH_3.—The crude hydrazo compound was oxidized as described above, the reaction in this case being vigorous and requiring cooling in ice. The ether was evaporated and the azo compound was crystallized from methanol, m.p. 108–109°, 6.0 g., (0.0165 mole), 64% yield. *Anal.* Calcd. for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12. Found: C, 84.88; H, 6.16. The yield of nitrogen from this compound in the kinetic runs was 100 ± 2%.

Products of Decomposition.—Phenylazotriphenylmethane, 8.6 g. (0.025 mole), was heated in 100 ml. of acetic acid at 63° for 24 hours under nitrogen. Air was then passed through the solution with no apparent effect. The solution was distilled through a 10″ glass spiral column, leading to benzene, b.p. 78–80°, 0.80 g., (0.010 mole), 40% yield; this was converted to *m*-dinitrobenzene, 1.5 g. (0.009 mole), m.p. and mixed m.p. 88–89°. In a blank run distillation of a solution of 1 g. of benzene in 100 ml. of acetic acid through the same apparatus led to recovery of benzene in 70% yield. The remainder of the acetic acid was distilled off and the residue was extracted with 40 ml. of hot water. Concentration of the aqueous extract to dryness led to no succinic acid.

The residue was further extracted with 80 ml. of hot ethanol, leading to an insoluble tar; a suspended solid, 0.025 g., m.p. 270°, apparently tetraphenylmethane, 0.3% yield, reported[21] m.p. 267°; and the alcoholic extract. The latter was cooled, leading to a tar; a solid, 0.5 g., m.p. 120–140°, from which, after recrystallization from alcohol there was obtained a product, 0.030 g., m.p. 146°, possibly hexaphenylethane 0.5% yield, reported[22] m.p. 145–147°; and the alcohol solution. The latter was steam distilled, leading to biphenyl, 0.2 g. (0.0013 mole), 10% yield, m.p. and mixed m.p. 68–69°. Extraction of the tars with hot benzene led to an impure solid, 0.42 g., m.p. 80–92, which was not worked up further.

Acknowledgment.—We are pleased to acknowledge generous support of this work by the National Science Foundation.

WALTHAM, MASSACHUSETTS

[21] M. Gomberg, *Ber.*, **30**, 2044 (1897).

[22] M. Gomberg and L. H. Cone, *ibid.*, **37**, 2037 (1904).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SIR JOHN CASS COLLEGE]

The Kinetics of Ring Closure of Alkyl-substituted 3,3-Dimethyl-5-keto-hexanoic Acids by Sulfuric Acid

BY W. E. SILBERMANN AND T. HENSHALL[1]

RECEIVED JANUARY 4, 1957

Acid-catalyzed ring-closures of 3,3-dimethyl-5-keto-hexanoic acid and of 6-alkyl-substituted homologs have been found to give dimedone and 3,3-dimethyl-6-alkyl-cyclohexanediones-1,5, respectively. The kinetics of the cyclizations of the hexanoic acid and of four alkyl-substituted derivatives have been investigated in aqueous sulfuric acid. The reaction has also been followed in acetic acid–sulfuric acid solution. The kinetic results are consistent with a reaction sequence in which the rate-controlling stage is electrophilic attack by C_1^+ on the double bond of the enolized form of the keto-acid.

The results of preliminary experiments on the cyclization of 3,3-dimethyl-5-keto-hexanoic acid (III, R = H) to dimedone by aqueous sulfuric acid already have been reported.[2] In further work on this reaction, the range of acid concentrations has been extended, and it has been observed that the activation energy for the process is markedly dependent on the acidity of the solvent, decreasing as the concentration of sulfuric acid increases (Table II). This effect is interpreted in terms of an acid–base equilibrium involving the keto-acid and the oxonium ions present in the solution and suggests that the reaction proceeds by way of a protonated intermediate. The most reasonable reaction path appears to involve the protonated carboxyl group of the keto-acid and the enolic double bond at $C_5{=}C_6$ (see Discussion). Accordingly it was thought that the most profitable approach toward the elucidation of this reaction lay in an investigation of the effects of substituent groups with definite electronic properties on the π-electrons of the enol form. The choice of suitable substituents, is, however, strictly limited both by the ease of unambiguous synthesis and by the stability

---

[1] Material taken from part of a thesis presented by W.E.S. in support of candidature for the Ph.D. degree of London University.

[2] T. Henshall, W. E. Silbermann and J. G. Webster, THIS JOURNAL, **77**, 6656 (1955).