

Equation 4 was also ignored. Again, the analysis is carried out in detail in order to segregate deviations from the various linear and multiple regressions from the remainder terms (Table IV). In this case it appears that, the linear regressions are again highly significant, the model

$$\log k = Y_{ij} = (\sigma_{pi} - \bar{\sigma}_{pi})\rho_1 + (\sigma^*_j - \sigma^*_{j'})\rho + Y_{\infty} \quad (5)$$

is as satisfactory as the much more complicated model of Equation 4.

Discussion. Maybe the most striking features of Tables I-IV are the tremendous values of the variance ratios (F) for the differences in group means, and the manner in which the vast majority of the corresponding variances are accounted for by the simple linear regressions. As noted above, this fact is not surprising since the relations involved are well established and have long been apparent in extensive sets of data without recourse to more than the most rudimentary statistics. It is not a purpose of the present statistical technique to demonstrate their significance; rather, if they turned out not highly significant, the technique would be open to question.

Although more subtle, more important is the fact that in many cases deviations from regression (both individual, and when appropriate, average) are *not* significant. The search for a good criterion of "fit" to an empirical relation has gone on for a long time. It would appear that the fact that deviations

from regression are not significant was the best possible criterion. Unfortunately, this criterion is rarely applicable to published data, since, in the analysis of a single regression, no DF remain to make such a test, unless data for duplicate determinations are available to provide an independent estimate of error. In the types of analysis presented in the present paper, also, it has been necessary to use higher order interactions as estimates of error; although these interactions probably provide a reliable estimate, an independent estimate of error would be preferable, since it would also permit the testing of these interactions. Unfortunately, it appears to have become customary *not* to publish duplicate values, except under special circumstances, or in a few instances to illustrate the type of reproducibility obtained.

Finally, the method developed provides the most sensitive possible test of the significance of differences between regression coefficients (slopes) and of improvements due to inclusion of additional independent variables. The total amount of labor involved in the types of analyses outlined is negligible compared with the work involved in the accumulation of the experimental data. The most complicated of the analyses reported here can be completed with the use of a desk calculator in 1-2 hr.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

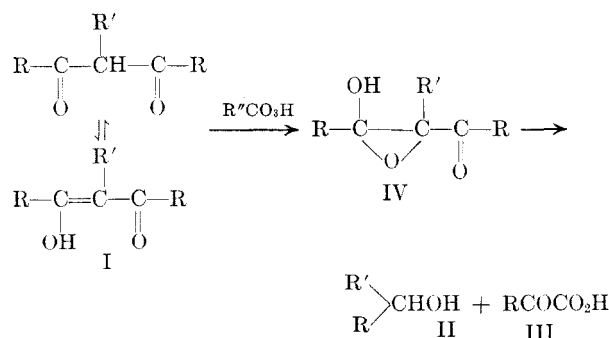
Reaction of β -Diketones with Peracids

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The reactions of 4-methyl-3,5-heptanedione and 3-benzyl-2,4-pentanedione with monopero-phthalic acid have been studied. The heptanedione derivative yielded 4-hydroxy-4-methyl-3,5-heptanedione which underwent thermal isomerization to form the propionic acid ester of 2-hydroxy-3-pentanone. 3-Benzyl-2,4-pentanedione underwent a similar series of transformations.

In 1936 Boeseken and Jacobs reported² a study of the reaction of peracetic acid with a series of β -diketones and β -keto esters. The reaction, which occurred only with enolizable β -dicarbonyl compounds I, was said to yield an alcohol II and an α -keto acid III as shown in the accompanying equation when one equivalent of the peracid was employed. With an excess of the peracid a mixture of acids was obtained. In certain cases isolation of the supposed intermediates IV was also reported. Subsequently, a portion of the work claimed to yield the intermediates IV ($R' = H$) was repeated by Karrer and co-workers, perbenzoic acid being used as the peracid to facilitate isolation of products.³⁻⁵



(3) P. Karrer, J. Kebrle, and R. M. Thakkar, *Helv. Chim. Acta*, **33**, 1711 (1950).

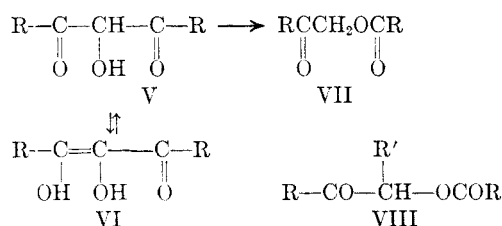
(4) P. Karrer, J. Kebrle, and U. Albers-Schonberg, *Helv. Chim. Acta*, **34**, 1014 (1951).

(5) P. Karrer, U. Albers-Schonberg, and J. Kebrle, *Helv. Chim. Acta*, **35**, 1498 (1952).

(1) Rohm & Haas Research Assistant, 1957.

(2) J. Boeseken and J. Jacobs, *Rec. trav. chim.*, **55**, 804 (1936).

The products originally assigned structure IV,² were shown to be mixtures of the tautomeric forms V and VI of α -hydroxy- β -diketones.⁶ Karrer and co-workers³ also confirmed the previously reported⁷ thermal rearrangement of the hydroxy diketone V (R = C₆H₅) to the ester VII and reported that the same isomerization occurred when a solution of the hydroxy diketone V (R = C₆H₅) was treated with sodium bicarbonate.



In other studies⁸⁻¹⁰ the reactions of certain triacylmethane derivatives with peracids were reported to yield the α -acyloxy derivatives of β -dicarbonyl compounds, the products expected from a normal Baeyer-Villiger reaction. Thus, if the reaction of enolizable β -dicarbonyl compounds I were analogous, the expected products would be esters of the type VIII.

Consideration of these previous reports raises questions as to what are the expected products when enolizable β -dicarbonyl compounds I (especially where R' \neq H) react with peracids and, also, whether there is any justification for the formation of the cleavage products II and III in such reactions. In an effort to answer these questions the reactions of two β -dicarbonyl compounds IX and X with peracids have been studied.

In a preliminary study 4-methyl-3,5-heptanedione (IX) was allowed to react with peracetic acid in methylene chloride, the reaction being followed both by measurement of the optical density of the reaction mixture at 291 m μ (absorption attributable to the enol form XI of the diketone IX) and by vapor-phase chromatographic analysis. Although the enol content of the reaction mixture fell to a low level within 2 hr. complete consumption of the β -diketone IX required several days. These observations are in agreement with the contention of Boeseken and Jacobs that the enol form of the β -dicarbonyl compound reacts with the peracid. The only product which could be detected was propionic acid; presumably a part of the acetic acid present in the reaction mixture was also derived from the diketone IX. To facilitate the isolation of products, subsequent reactions employed an

ether solution of monoperphthalic acid rather than peracetic acid. Even the latter reaction conditions did not eliminate the presence of extraneous by-products since the decomposition of monoperphthalic acid in pure ether resulted in the formation of a number of low molecular weight materials including ethanol, acetic acid, and ethyl acetate. Ether solutions of the diketone IX were allowed to react with one equivalent and with four equivalents of monoperphthalic acid at room temperature until the peracid content of each reaction mixture had fallen to 5% or less of its initial value. The reaction mixture obtained by the use of an excess of the peracid contained propionic acid and acetic acid as well as the ethyl esters of these two acids but no higher boiling materials and no 2-butanol (the expected cleavage product II according to the scheme of Boeseken and Jacobs). The reaction of the diketone IX with one equivalent of monoperphthalic acid afforded acetic and propionic acids accompanied by the unchanged diketone IX and a second high-boiling component subsequently shown to be 4-hydroxy-4-methyl-3,5-heptanedione (XII). Thus, it was apparent that the initial reaction product, the hydroxy diketone XII, reacted relatively rapidly with additional peracid. As in previous cases no 2-butanol, the cleavage product of the type II predicted by the general reaction scheme of Boeseken and Jacobs, could be detected in the reaction mixture.¹¹

The initial reaction product, the hydroxy diketone XII, was quantitatively isomerized to the ester XIII when heated to 200°. Both compounds XII and XIII underwent facile hydrolytic cleavage in the presence of aqueous alkali to yield propionic acid (XIV), characterized as its *p*-bromophenacyl ester, and 2-hydroxy-3-pentanone (XV or the tautomeric keto alcohol XVI), characterized as its osazone. The infrared, ultraviolet, and nuclear magnetic resonance spectra of the initial reaction product were all consistent with structure XII. However, it must be noted that these data do not rigorously exclude the possibility that the product either has the epoxy alcohol structure IV or is an equilibrium mixture of structures XII and IV.

Reaction of 3-benzyl-2,4-pentanedione (X) with one equivalent of monoperphthalic acid in ether produced a mixture which could not be completely resolved either by fractional distillation or by vapor-phase chromatography. The mixture was shown to contain acetic and phenylacetic acids as well as 4-phenyl-2-butanone (presumably formed by hydrolytic cleavage of the starting diketone X)

(6) It is unlikely that small amounts of the epoxy alcohol IV (R = H), also a tautomer of structures V and VI, would have been detected if present.

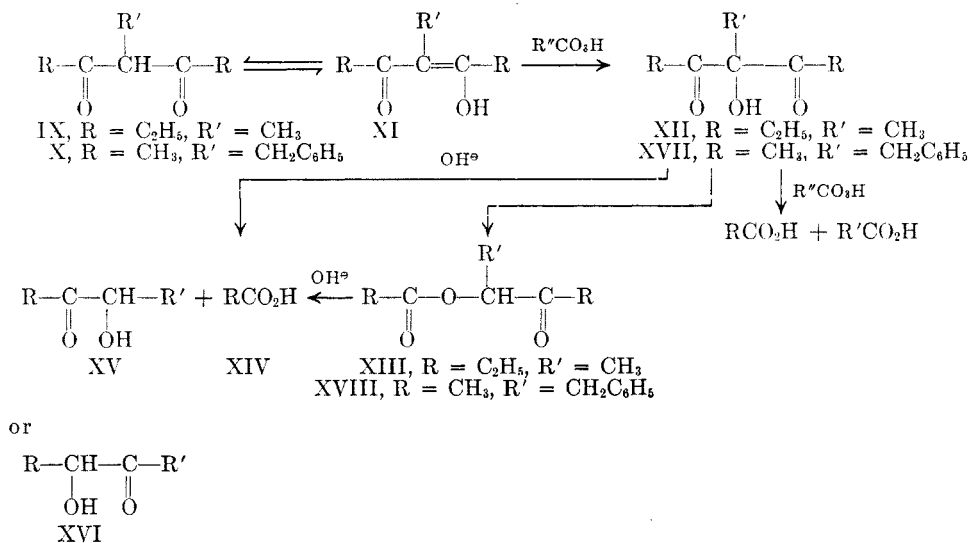
(7) A. H. Blatt and W. L. Hawkins, *J. Am. Chem. Soc.*, **58**, 81 (1936).

(8) C. H. Hassall, *Org. Reactions*, **9**, 73 (1957).

(9) L. H. Briggs, C. H. Hassall, and W. F. Short, *J. Chem. Soc.*, 706 (1945).

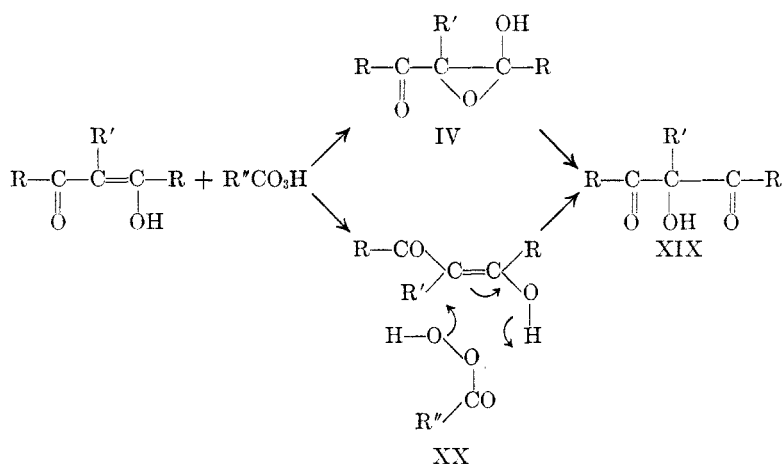
(10) C. H. Hassall, *J. Chem. Soc.*, 50 (1948).

(11) Since the hydroxy diketone XII was heated with substantial quantities of acetic, propionic, and phthalic acids during the distillation required for isolation of the reaction products, it does not seem reasonable to attribute the results reported by Boeseken and Jacobs to the acid-catalyzed rearrangement of hydroxy diketone XII or its tautomer IV in the acetic acid solution used by these workers.



and a mixture of higher boiling materials. No benzylmethylcarbinol, one of the compounds which was reported² to be formed when the diketone X reacted with peracetic acid, could be detected in the reaction mixture. The infrared spectrum and chemical properties (*i.e.*, positive ferric chloride test, base-cleavage products) of the high boiling mixture isolated from the reaction were consistent with the presence of the starting diketone X and the hydroxy diketone XVII. Some of the ester XVIII may also have been present. After a portion of the mixture had been heated above 200°, the infrared spectrum of the resultant mixture was consistent

products, which are readily cleaved by further reaction with peracids, may be isomerized to esters of the type VIII by heat or bases;³ alternatively, the initially formed hydroxy diketones may be cleaved by treatment with bases.¹² The formation of the hydroxy diketones XIX may be supposed to occur either by the intermediate formation of an epoxy alcohol IV¹³ or by direct hydroxylation of the enol by a process such as that represented by XX. The rearrangement of the hydroxy diketones XIX to esters XXI may be most easily rationalized by processes involving the epoxy alcohol IV as an intermediate. For example, the thermal and base-cata-



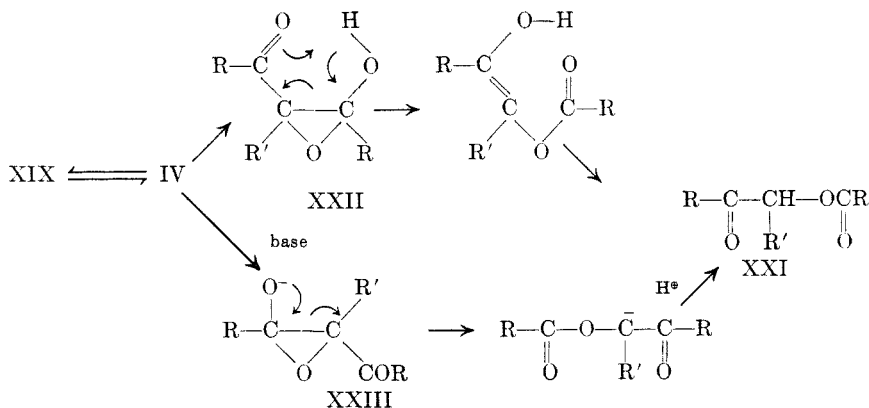
with the presence of the starting diketone X and the ester XVIII. Hydrolytic cleavage of the crude product afforded acetic and phenylacetic acids plus 4-phenyl-2-butanone, characterized as its 2,4-dinitrophenylhydrazone, and 4-phenyl-3-hydroxy-2-butanone (XV or the tautomeric keto alcohol XVI), characterized as its osazone.

Thus, our results, like those of Karrer and co-workers,³⁻⁵ indicate that enolizable β -dicarbonyl compounds react with peracids to yield α -hydroxy- β -dicarbonyl compounds. These initial reaction

lyzed isomerizations might be represented as shown in formulas XXII and XXIII, respectively.

(12) The hydroxy diketones of type V, which can form stable enolate anions, would be expected to be relatively resistant to base cleavage compared with hydroxy diketones such as XII.

(13) This reaction is analogous to the reaction of enol esters and enol ethers with peracids. For examples and leading references see (a) C. L. Stevens and J. Tazuma *J. Am. Chem. Soc.*, **76**, 715 (1954); (b) P. D. Gardner, *J. Am. Chem. Soc.*, **78**, 3421 (1956).

EXPERIMENTAL¹⁴

4-Methyl-3,5-heptanedione (XII). A mixture of 170 g. (1.84 moles) of 3-pentanone and 600 g. (4.6 moles) of propionic anhydride was saturated rapidly with boron trifluoride gas, the temperature of the reaction mixture being kept below 10° by means of a Dry Ice-acetone cooling bath. After the resulting mixture had been allowed to stand overnight at room temperature, it was poured into a solution of 750 g. of sodium acetate trihydrate in 1500 ml. of water. The mixture was boiled under reflux for several hours and then cooled and extracted with ether. The ether extract was washed with saturated, aqueous sodium bicarbonate, dried over magnesium sulfate, and distilled through a 70-cm. Vigreux column. The diketone, b.p. 90.5–92.5° (16 mm.), n_D^{25} 1.4377 [lit. b.p. 95–97° (20 mm.),¹⁵ 94–97° (20 mm.)¹⁶], amounted to 94 g. (36%). The ultraviolet spectrum¹⁷ of the product has a maximum at 291 $m\mu$ (ϵ 1580) attributable to the presence of the enol form of the diketone. The infrared spectrum¹⁸ has bands at 1725 and 1700 cm^{-1} (C=O of a non-enolized β -diketone) as well as a broad band at 1600 cm^{-1} attributable to an enolized β -diketone. The product reacted with cupric acetate to give a copper complex which crystallized from benzene as gray-green needles which partially melted with decomposition at temperatures ranging from 165–166° to 177–180° (lit. 176–178°,¹⁵ 171–173°¹⁶). The position of the decomposition range was very dependent on the rate of heating of the melting point bath, the higher values being obtained when the sample was heated rapidly or placed in a bath at temperatures above 150°.

Anal. Calcd. for $C_{16}H_{24}O_4Cu$: C, 55.55; H, 7.58. Found: C, 55.63; H, 7.69.

Reaction of the diketone with 2,4-dinitrophenylhydrazine afforded *3,5-diethyl-1-(2,4-dinitrophenyl)-4-methylpyrazole* as orange needles, m.p. 93.5–94°, yield 82.5%. The infrared

spectrum¹⁹ of the product exhibited no band in the 3 μ region attributable to an N—H group and no band in the 6 μ region attributable to a carbonyl function.

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.51; H, 5.49; N, 18.41.

Reaction of 4-methyl-3,5-heptanedione with peracetic acid. To a solution of 2.0 g. (0.014 mole) of the diketone in 20 ml. of methylene chloride was added 2.05 g. of a solution of 1.13 g. of sodium acetate trihydrate and 0.021 mole of peracetic acid in acetic acid. The resulting mixture was stirred at room temperature, aliquots being removed periodically for analysis. After 2 hr. the optical density of the reaction mixture at 291 $m\mu$ had fallen to 1% of its initial value. After 48 hr. vapor-phase chromatographic analysis indicated that a substantial amount of the ketone remained. An additional portion of peracetic acid, equivalent to the amount used initially, was added and the mixture was stirred for a total of fourteen days. At this time no β -diketone could be detected in the reaction mixture. The acidic and neutral components of the reaction mixture were separated by extraction with aqueous sodium hydroxide followed by appropriate manipulations. Only the reaction and extraction solvents were detected in the neutral fraction. The vapor-phase chromatogram of the acid fraction exhibited peaks attributable to acetic and propionic acids.

Reaction of 4-methyl-3,5-heptanedione with monoperphthalic acid. Procedure A. In an initial experiment 5.85 g. (0.0411 mole) of the diketone was treated with a solution of 0.0411 mole of monoperphthalic acid²⁰ in 100 ml. of ether and aliquots of the solution were removed periodically for iodometric titration. After 30 hr., at which time the peracid content of the mixture had fallen to 4% of its initial value, the bulk of the phthalic acid was filtered from the reaction mixture and the filtrate was distilled under reduced pressure. Analysis of the various fractions of the distillate by vapor-phase chromatography indicated the presence of acetic and propionic acids as well as the starting diketone and the major component of the mixture, subsequently shown to be 4-hydroxy-4-methyl-3,5-heptanedione. All four components were collected from the chromatogram and the three known compounds were identified by comparison of their infrared spectra with the spectra of authentic samples.

In a subsequent experiment a solution of 42.2 g. (0.297 mole) of the diketone and 0.393 mole of monoperphthalic acid in 1 l. of ether was allowed to stand at room temperature until the peracid content was negligible and then worked up as described previously. The high-boiling materials were fractionally distilled through an 18-in. spinning band column and each of the fractions collected was analyzed

(14) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined either with a Baird, Model B, or a Perkin-Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11MS. The microanalyses were performed by Dr. S. M. Nagy and his associates. The vapor-phase chromatograms were obtained with 8 mm. \times 215 cm. columns packed with suspensions of silicone oil, polyethylene glycol, or di-2-ethylhexyl sebacate on 50–80 mesh ground firebrick. The fractions, eluted with helium, were detected with a thermal conductivity cell.

(15) R. Levine, J. A. Conroy, J. T. Adams, and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 1510 (1945).

(16) B. M. Perfetti and R. Levine, *J. Am. Chem. Soc.*, **75**, 626 (1953).

(17) Determined as a solution in 95% ethanol.

(18) Determined in carbon tetrachloride solution.

(19) Determined as a suspension in a potassium bromide pellet.

(20) The peracid was prepared by the procedure of E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).

by vapor-phase chromatography. From these data the yields of the principle components were estimated to be: propionic acid, 11%²¹; 4-hydroxy-4-methyl-3,5-heptanedione, 32%; 4-methyl-3,5-heptanedione, 5% recovery; 3-keto-2-pentyl propionate (or its tautomer), 2%.²² Redistillation of the appropriate fractions from the first distillation permitted the separation of 7.15 g. (15.2%) of the pure 4-hydroxy-4-methyl-3,5-heptanedione, b.p. 93–95° (18 mm.), n_D^{20} 1.4295.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.61; H, 9.09.

The infrared spectrum¹⁸ of the product exhibits bands at 3450 cm^{-1} (O—H) and 1704 cm^{-1} with a slight shoulder at 1715 cm^{-1} (C=O of a non-enolized β -diketone). The ultraviolet spectrum²¹ has maxima at 213 $m\mu$ (ϵ 750) and 304 $m\mu$ (ϵ 165). The nuclear magnetic resonance spectrum^{23,24} has the following peaks (expressed as cycles per second relative to the proton resonance of water): a singlet at -5 sec.⁻¹ (O—H); a singlet at -150 sec.⁻¹ (CH_3 adjacent to a carbon atom not bonded to a hydrogen atom); a triplet with its center peak at -173 sec.⁻¹ (CH_3 adjacent to a CH_2); a series of 4 or 5 partially resolved peaks within the range -97 to -120 sec.⁻¹ (CH_2 adjacent to CH_3). It was not possible to decide whether or not the latter group of peaks represented two methylene groups in identical environments.

A solution of 3.0 g. (0.019 mole) of the hydroxy diketone in ether was shaken with about two equivalents of 10% aqueous sodium hydroxide. The aqueous phase was extracted with several additional portions of ether and concentrated to dryness under reduced pressure. A portion of the residual solid was neutralized and converted to the *p*-bromophenacyl ester in the usual way. The product, m.p. 64–65.5°, was shown to be identical with an authentic sample of *p*-bromophenacyl propionate both by a mixed melting point determination and by comparison of the infrared spectra of the two samples.

The combined ethereal extracts from the base-cleavage, which were shown to contain one component other than ether by vapor-phase chromatography, were dried over magnesium sulfate, concentrated and distilled. The product, 2-hydroxy-3-pentanone (or its tautomer), b.p. 56–57° (16 mm.), n_D^{20} 1.4174,²⁵ amounted to 0.95 g. (49%). The infrared spectrum¹⁸ of the product has bands at 3510 cm^{-1} (O—H), 1715 cm^{-1} (C=O), and 1125 cm^{-1} (C—O of a secondary alcohol). The material exhibits no significant absorption in the ultraviolet region. A solution of 0.45 g. sample of the hydroxy ketone, 2 ml. of phenylhydrazine,

and several drops of acetic acid in 10 ml. of water was refluxed for several hours and then cooled. When the crude material which separated was recrystallized from ethanol, the pure osazone of 2,3-pentanedione separated as yellow prisms, m.p. 162–163° [lit.²⁶ 161–162.5°], yield 0.604 g. (50%), which was shown to be identical with an authentic sample²⁷ both by a mixed melting point determination and comparison of the infrared spectra of the two samples.

A 1.0-g. sample of the hydroxy diketone XII, sealed in a Pyrex tube, was heated to 205–210° for 1 hr. The vapor phase chromatogram of the crude product exhibited only one major peak whose retention time differed only slightly from the retention time of the starting hydroxy diketone. Since a mixture of the starting material and the product was only partially resolved by vapor phase chromatography, a reliable estimate of how much, if any, of the starting hydroxy diketone remained was not possible. Distillation of the product afforded 3-keto-2-pentyl propionate, b.p. 90.5–91.5° (16 mm.), n_D^{20} 1.4173.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.58; H, 8.93.

The infrared spectrum¹⁸ of the product has bands at 1735 cm^{-1} (C=O of an ester) with a shoulder at 1705 cm^{-1} (C=O of a ketone), 1185 cm^{-1} (C—O—C of an ester) with a very weak band at 3480 cm^{-1} attributable either to the O—H group of some unchanged hydroxy diketone present or to an overtone of the carbonyl band at 1735 cm^{-1} . The material exhibits no significant absorption in the ultraviolet region.

An ether solution of the product was shaken with aqueous sodium hydroxide and the acid and neutral products were separated as described in the base-cleavage of the hydroxy diketone. The vapor phase chromatogram of the neutral product indicated the presence of a 2-hydroxy-3-pentanone (or its tautomer) shown to be identical with the product previously described by comparison of the infrared spectra of the two samples. The acidic fraction contained propionic acid accompanied by a small amount of acetic acid.

Procedure B. A solution of 1.46 g. (0.0103 mole) of 4-methyl-3,5-heptanedione and 0.0411 mole of monoperphthalic acid in 100 ml. of ether was allowed to stand at room temperature, the reaction being followed as described in Procedure A. After 240 hr., at which time the peracid content of the mixture had fallen to 5% of its initial value, the reaction mixture was worked up and analyzed as described in procedure A. The components other than ether and phthalic acid found in the mixture were acetic acid, ethyl acetate, propionic acid, and ethyl propionate.

3-Benzyl-2,4-pentanedione (XVII). To a solution of 50 g. (0.5 mole) of 2,4-pentanedione and 25 g. (0.4 mole) of potassium hydroxide in 100 ml. of water was added, dropwise and with stirring, 70 g. (0.55 mole) of benzyl chloride. After the addition was complete, the mixture was refluxed overnight with stirring and then cooled and extracted with ether. After the extract had been dried over magnesium sulfate and concentrated, distillation of the residue afforded 29.43–42.94 g. (31–45%) of the β -diketone, b.p. 110–112° (2 mm.), n_D^{20} 1.5313 [lit.²⁸ b.p. 143–146° (10 mm.)]. The infrared spectrum¹⁸ has a band at 1700 cm^{-1} with a shoulder at 1725 cm^{-1} (C=O of a non-enolized β -diketone), as well as a broad band at 1605 cm^{-1} (enolized β -diketone). The ultraviolet spectrum¹⁷ has a maximum at 290 $m\mu$ (ϵ 3500).

A 2.0-g. sample of the product was converted to its copper complex by reaction with cupric acetate. The copper complex separated from benzene as gray-green crystals, m.p.

(26) H. v. Pechmann, *Ber.*, 21, 1411 (1888).

(27) Oxidation of 3-pentanone with an aqueous solution of selenium dioxide afforded a mixture of the starting material and 2,3-pentanedione which was treated with phenylhydrazine. The desired osazone, m.p. 161.5–163.5°, was isolated from the mixture by fractional crystallization.

(28) J. M. Sprague, L. J. Beckham, and H. Adkins, *J. Am. Chem. Soc.*, 56, 2665 (1934).

(21) This yield is based upon the assumption that each mole of the diketone IX can yield two moles of propionic acid. The yield reported here is judged to be well below the actual amount of propionic acid produced since substantial quantities of the acid were lost as the solvent was distilled from the mixture. For this reason, no attempt was made to estimate the amount of acetic acid, ethanol, ethyl acetate, and ethyl propionate present in the initial fractions from the distillation.

(22) This ester, which appeared only in the latter fractions of the distillation, was apparently formed by thermal isomerization of the hydroxy diketone during the distillation. The properties of the pure material are described subsequently.

(23) Determined as a pure liquid.

(24) Determined with a Varian Associates high-resolution nuclear magnetic resonance spectrometer, Model V4300B.

(25) The properties reported for 2-hydroxy-3-pentanone are b.p. 63° (20 mm.) [M. D. Gauthier, *Compt. rend.*, 152, 1100 (1911)] and b.p. 45–48° (11 mm.), n_D^{20} 1.4218 [E. Schmidt and A. Ascherl, *Ber.*, 58, 356 (1925)]. The properties reported for 3-hydroxy-2-pentanone are b.p. 77° (35 mm.) [H. v. Pechmann and F. Dahl, *Ber.*, 23, 2421 (1890)] and b.p. 59–59.5° (27 mm.) [E. Venus-Daniloff, *Bull. soc. chim. (France)*, 43, 582 (1928)].

187.5–188° (dec.) (lit.²⁹ 176°) yield 1.5 g. (55%). Because of the discrepancy in melting point values the composition of our sample was determined.

Anal. Calcd. for $C_{24}H_{26}O_4Cu$: C, 65.21; H, 5.93. Found: C, 65.30; H, 5.97.

A suspension of the pure copper complex in ether was shaken with 20% aqueous sulfuric acid. After the ether solution of the regenerated diketone had been dried and concentrated, distillation of the residue afforded the pure β -diketone, b.p. 97–98° (0.5 mm.), n_D^{20} 1.5300. The infrared spectrum of the product was essentially identical with the spectrum of the initial alkylation product indicating the absence of a significant amount of *O*-alkylated product.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.64; H, 7.64.

Reaction of 3-benzyl-2,4-pentanedione with monoperphthalic acid. After a solution of 42.9 g. (0.226 mole) of the diketone and 0.34 mole of monoperphthalic acid in 745 ml. of ether had been allowed to stand for seven days, the bulk of the phthalic acid was removed by filtration and the filtrate was concentrated. The entire residue was distilled under reduced pressure, the final fraction being taken at 119–122° (5 mm.). The vapor-phase chromatogram of the combined distillate indicated the presence of low-boiling components, several fractions of intermediate molecular weight, subsequently shown to be 4-phenyl-2-butanone, phenylacetic acid, and phthalic anhydride, and a mixture of high-boiling compounds which was not resolved in the chromatogram. Comparison of this chromatogram with the vapor phase chromatograms of authentic samples of benzylmethylcarbinol and benzyl methyl ketone demonstrated that no peak corresponding to either the ketone or the alcohol was present in the chromatogram of the reaction mixture. Fractional distillation of the crude product through an 18-in. spinning band column effected only partial separation of the mixture. The infrared spectrum¹⁸ of the mixture of higher boiling components, 25.91 g., b.p. 82.5–86° (0.2 mm.), has a band at 3500 cm^{-1} (O—H) with a doublet at 1710 and 1735 cm^{-1} (nonenolized β -diketone).

A sample of the mixture, which gave a violet color with ethanolic ferric chloride indicating the presence of the starting diketone, was subjected to vapor-phase chromatography at 240° and the mixture of high-boiling components was collected. The infrared spectrum¹⁸ of the mixture has a broad band at 1600 cm^{-1} (enolized β -diketone), a band at 1730 cm^{-1} (C=O of an ester) with a shoulder at 1700 cm^{-1} (C=O of a ketone) and a band at 1230 cm^{-1} (C—O—C of an ester).

An ether solution of the mixture of products from the reaction mixture was shaken with aqueous sodium hydroxide and the resulting neutral and acidic components were

(29) G. T. Morgan and C. J. A. Taylor, *J. Chem. Soc.*, 127, 797 (1925).

separated as previously described. The two neutral components, one of which corresponded to one of the components of the original reaction mixture, were separated by vapor phase chromatography. The infrared spectrum¹⁸ of the first component eluted from the chromatogram has a band at 1725 cm^{-1} (C=O) and is essentially identical with the spectrum of an authentic sample³⁰ of 4-phenyl-2-butanone. The product was converted to its 2,4-dinitrophenylhydrazone which separated from ethanol as orange prisms, m.p. 125.8–127.2°. The material was shown by a mixed melting point determination and by comparison of infrared spectra to be identical with the 2,4-dinitrophenylhydrazone, m.p. 126–127.5° (lit.³¹ 128–129°), prepared from an authentic sample³⁰ of 4-phenyl-2-butanone.

The infrared spectrum¹⁸ of the second component eluted from the chromatogram has bands at 3550 cm^{-1} (O—H) and 1720 cm^{-1} (C=O). The product was characterized as its osazone, prepared as previously described, which crystallized from aqueous ethanol as pale yellow plates, m.p. 170–171.5°. The product was shown both by a mixed melting point determination and by comparison of infrared spectra to be identical with the osazone, m.p. 171–172.5° (lit.³² 171–173°), prepared from an authentic sample³³ of 1-phenyl-2,3-butanedione.

Analysis of the mixture of acid components from the basic extraction by vapor-phase chromatography indicated the presence of acetic acid and a high boiling acid. The high boiling component which crystallized from petroleum ether as white plates, m.p. 75–76.5°, was shown to be identical with an authentic sample of phenylacetic acid both by a mixed melting point determination and by comparison of the infrared spectra of the two samples.

Benzylmethylcarbinol. Benzyl methyl ketone (10 g., 0.735 mole) was reduced with 2.1 g. (0.055 mole) of lithium aluminum hydride in 125 ml. of ether and the reaction mixture was worked up by the precipitation of the aluminum salts with a small amount of aqueous sodium hydroxide in the usual manner. The alcohol, collected at 103.5–104.5° (13 mm.), n_D^{20} 1.5171 [lit.³⁴ b.p. 125° (25 mm.), n_D^{20} 1.5190] amounted to 6.86 g. (69%).

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(30) Prepared by the procedure of Y. Chen and W. F. Barthel, *J. Am. Chem. Soc.*, 75, 4287 (1953).

(31) G. D. Johnson, *J. Am. Chem. Soc.*, 75, 2720 (1953).

(32) T. I. Temnikova and V. A. Kropachev, *J. Gen. Chem. (U. S. S. R.)*, 19, a541 (1949).

(33) Prepared by the method of H. Moreau, *Ann. chim. (Paris)*, [10] 14, 339 (1930).

(34) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 105, 1115 (1914); S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Am. Chem. Soc.*, 74, 1140 (1952).