with dilute hydrochloric acid. The resultant gummy solid was removed, triturated with ether–petroleum ether (5 cc., 1:1), and the extract was removed and evaporated. There remained a white solid (5 mg.) which, recrystallized from benzene, melted at 148–150°. The infrared spectrum of this compound was identical with that of XV—even though this compound was white and XV was yellow. Unfortunately, a sample of XV was no longer available for a determination of the mixed melting point.

Action of Sodium Methoxide upon XI.—The bromonitroketone XI (150 mg.) was subjected to action of methanolic sodium methoxide (10 cc., 3.0 *M*) in the same manner as described above for I. The products were benzoic acid and an unstable oil in the bicarbonate-soluble fraction; in the alkali-insoluble fraction, a white solid identical with XIII and a compound which formed a copper derivative identical with Z. Identities were established by comparison of the infrared spectra, and by mixed melting point determinations in the case of the solids.

Action of Sodiomalonic Ester upon I.—The cyclopropane I (2.0 g.) was added to a solution prepared from methyl malonate (2.7 g., 0.025 mole) and methanolic sodium methoxide (from sodium, 0.46 g., and methanol, 20 cc.). The solution was maintained at 60°; within ten minutes a bright red color appeared. After 1.5 hours the solution was cooled and added dropwise to a solution of acetic acid (5 cc.) in water (100 cc.). The solution was extracted with chloroform and the extract was washed with water and aqueous bicarbonate, and dried (magnesium sulfate). The solvent was removed under reduced pressure and the residue was fractionated, giving a middle fraction (0.8 cc.) of a yellow oil. Redistillation gave 0.4 cc. of yellow oil having n^{25}_{D} 1.5338. This was compound VIII.

Anal. Calcd. for $C_{13}H_{15}NO_4$: C, 66.92; H, 6.48. Found: C, 67.16; H, 6.74.

The 2,4-DNP melted at 139–140°, alone or when mixed with the 2,4-DNP of VIII prepared from VII.

Anal. Calcd. for $C_{19}H_{19}N_5O_6$: C, 55.20; H, 4.65; N, 16.94. Found: C, 55.64; H, 4.65; N, 16.86.

Action of Sodiomalonic Ester upon XI.—The bromonitro ketone XI (1.0 g., 0.0032 mole) was refluxed with sodiomethyl malonate (0.012 mole) in methanol (20 cc.) for 1.5 hours. The bright red solution was processed as described above. The product was a light yellow oil (450 mg.) which was neither compound VIII nor a pyrone ester.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.01; H, 6.88. Found: C, 74.66; H, 7.07; N, none.

The ultraviolet spectrum of this oil (in ethanol) showed a maximum at 215 mμ (E 1%, 1 cm. 3.56×10^3), whereas the spectrum of the known 3-carbethoxy-4-ethyl-5-methyl-6-phenyl-α-pyrone[23] showed a maximum at 327 mμ (ε 1.20×10^4). Likewise, the infrared spectrum of this oil showed none of the bands characteristic of an α-pyrone ester.

An attempt was made to synthesize 1-benzoyl-2-nitro-2-bromocyclohexane in the hope that it could be converted into the unsaturated nitro ketone G. 2-Benzoylcyclohexanone was prepared as described in the literature[24]; it was planned to prepare the monoöxime of the diketone and convert the oxime into an α-bromonitro group.[25] Unfortunately, only the isoxazole, m.p., 64°, resulted from the action of hydroxylamine upon the diketone.

An attempt was also made to prepare the bicycloheptyl homolog of I, *viz.*, 1-benzoyl-7-nitrobicyclo[4,1,0]heptane, in order to compare its behavior toward alkali with that of I. The synthetic route was analogous to that used for synthesis of I. 1-Benzoylcyclohexene,[26] however, could not be condensed with nitromethane in a Michael reaction in spite of numerous attempts under varied conditions.

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[23] L. I. Smith and R. E. Kelly, THIS JOURNAL, **74**, 3305 (1952).

[24] C. R. Hauser, B. J. Ringler, F. W. Swamer and D. F. Thompson, *ibid.*, **69**, 2649 (1947).

[25] D. C. Iffland and T.-F. Yen, *ibid.*, **76**, 4083 (1954).

[26] R. E. Christ and R. C. Fuson, *ibid.*, **59**, 895 (1937)

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Synthesis and Alkaline Hydrolysis of a β,γ-Dibromo Ketone: 3,4-Dibromo-1-phenyl-2-benzyl-2,3-dimethyl-1-butanone

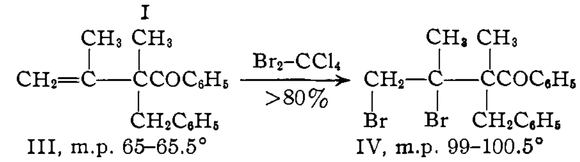
BY LEE IRVIN SMITH AND JOHN R. HOLUM[1]

RECEIVED FEBRUARY 10, 1956

The first simple open-chain β,γ-dibromo ketone, named in the title, has been synthesized, and its behavior upon hydrolysis has been studied. Alkaline hydrolysis of IV was accompanied by loss of the elements of water, and resulted in formation of a cyclic hemi-acetal VIII. Formation of VIII, which is also a vinyl ether, involved no rearrangement of the carbon skeleton of IV. The cyclic form of VIII may, in solution, exist in equilibrium with the open-chain isomer IX.

This report contains a description of the synthesis and properties of 3,4-dibromo-1-phenyl-2-benzyl-2,3-dimethyl-1-butanone (IV), a representative of a class of substances, simple open-chain β,γ-dibromo ketones, hitherto unknown. In particular, the reaction of IV with alkali has been studied.

The synthetic route to IV was



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{CH_3}{|}}{C}HCOC_6H_5 + C_6H_5CH_2Br \xrightarrow[48\%]{KO\mathit{t}\text{-}Bu}$$

I

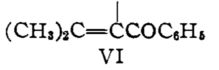
$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\underset{\underset{CH_2C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}COC_6H_5 \xrightarrow[>80\%]{Br_2{-}CCl_4} \underset{\underset{Br}{|}}{CH_2}{-}\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}\underset{\underset{CH_2C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}COC_6H_5$$

III, m.p. 65–65.5° IV, m.p. 99–100.5°

The sample of I, prepared according to Cologne and Chambion,[2] was not a pure substance but contained also (in undetermined and probably considerable amounts) the α,β-unsaturated isomer α,β-dimethylcrotonophenone (VI). Cologne and Chambion reported that the reaction between trimethylethylene and benzoyl chloride in the presence of stannic chloride led to the chloro ketone V which, by action of hot dimethylaniline, was converted into the α,β-unsaturated ketone VI. In our hands, the product of these reactions was a mixture of I and

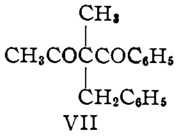
$$(CH_3)_2CClCHCH_3COC_6H_5$$

V



$$(CH_3)_2C{=}\overset{\overset{CH_3}{|}}{C}COC_6H_5$$

VI



$$CH_3CO\underset{\underset{CH_2C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}COC_6H_5$$

VII

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[1] Abstracted from a thesis by John R. Holum presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, August, 1954. National Science Foundation Pre-doctoral Fellow, 1952–1954.

[2] J. Cologne and J. Chambion, *Bull. soc. chim.*, 1001 (1947).

VI. In chloroform solution, this product rapidly absorbed bromine at −5°, but removal of the solvent left only intractable tars.

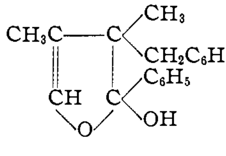
In benzene at room temperature, the mixture of I and VI reacted rapidly with potassium *t*-butoxide; action of benzyl bromide upon this product gave 1-phenyl-2-benzyl-2,3-dimethyl-3-butene-1-one (III) melting at 65–65.5°. Sodium amide or potassium amide could also be used as the base in this synthesis, although the yields were less than when the butoxide was used.

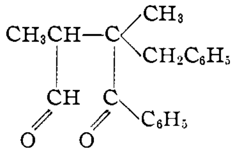
This substance III had the composition represented by $C_{19}H_{20}O$; the infrared spectrum showed bands characteristic of a terminal double bond and of a benzoyl group. The ultraviolet spectrum of III also indicated the presence of a benzoyl group. Ozonolysis of III, followed by reductive cleavage of the ozonide, led to α-methyl-α-benzylbenzoylacetone (VII) melting at 104.5–105.5°, whose identity was proved by comparison with a synthetic sample prepared by successive methylation and benzylation of benzoylacetone. Attempts to prepare a 2,4-dinitrophenylhydrazone of III were unsuccessful.

3,4-Dibromo-1-phenyl-2-benzyl-2,3-dimethyl-1-butanone (IV) was prepared by addition of a solution of bromine in carbon tetrachloride to a solution of III in the same solvent. The reaction was very slow; some hydrogen bromide was evolved. The product, isolated by removal of the solvent under reduced pressure and at low temperature, was relatively unstable and, unless it was purified immediately, it rapidly decomposed to tarry materials. Even when chromatographically purified, the material slowly darkened. Action of sodium iodide in acetone upon this product gave iodine and III (84%).

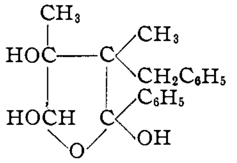
Action of a dilute solution of sodium hydroxide in aqueous dioxane upon the dibromide IV produced in about 50% yield a bromine-free solid $C_{19}H_{20}O_2$ (A). The melting point of this material was not sharply defined; on a hot-stage micro-apparatus (Kofler), the solid underwent a transition at 156° at which point tiny colorless droplets formed on the underside of the cover glass. Actual fusion of the solid occurred between 160 and 175°, depending upon the rate of heating. The temperature at which the droplets formed was more characteristic of the compound than was the temperature of fusion; at no time during the process was any gas evolved. Spectroscopic data indicated that A contained no carbonyl group, at least in the solid state. In the infrared (potassium bromide disc) there was no absorption in the region characteristic of the carbonyl group, between 1663 and 2600 cm.$^{-1}$. In ethanol, the solution of A was virtually transparent to ultraviolet light between 230–300 mμ, again indicating absence of a benzoyl group. Absorption bands in the infrared spectrum at 893, 1663, 2965, 3020 and 3050 cm.$^{-1}$ indicated the presence of a carbon–carbon double bond, and an intense band at 3355 cm.$^{-1}$ indicated presence of an hydroxyl group in the solid.[3]

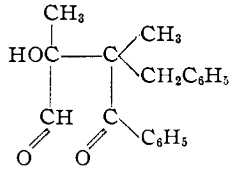
It was thus apparent, from the analytical and spectroscopic data, that mild, alkaline hydrolysis of IV was not confined to the vicinal dibromo system. Structure VIII for A was chosen as best representing the physical and chemical properties. This structure, a cyclic hemi-acetal and also a vinyl ether, accounted for the presence of an aliphatic double bond, an hydroxyl group and for the absence of a carbonyl group. Moreover, formation of VIII from IV involved no rearrangement of the carbon skeleton of IV. The tautomeric structure IX had also to be considered as a possibility under certain conditions. Although the infrared spectrum of A in the solid state showed the presence of an hydroxyl group and no carbonyl group, a Zerewitinov determination of active hydrogen showed only 0.15% of active hydrogen when A was in solution[4]; moreover, in solution, A slowly gave a silver mirror with Tollens reagent[5] and could be converted into a mono-2,4-dinitrophenylhydrazone melting at 172.5–174.5° and having the proper composition for this derivative of IX. Attempts to prepare from A a solid acetate (using isopropenyl acetate) or a 3,5-dinitrobenzoate were unsuccessful. Ozonolysis of A gave formaldehyde in 34% yield; this low yield of formaldehyde strongly indicated that the double bond in A was not a terminal one. Under the same conditions, eugenol 3,5-dinitrobenzoate and III gave formaldehyde in yields of 119 and 130%, respectively.

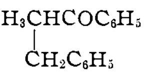

VIII


IX

A solution of A in dioxane–pyridine reacted with osmic acid, the mixture assuming the characteristic brownish-black color. After reduction of the mixture with aqueous sodium sulfite, the product was isolated as an oil. Assuming structure VIII for A, hydroxylation of the double bond would lead to the glycol X or to the hydroxyketoaldehyde XI derived from X by loss of water. The product was therefore dissolved in dioxane containing a trace of pyridine, and periodic acid was added.


X


XI


$$\underset{\displaystyle CH_2C_6H_5}{CH_3\underset{|}{C}HCOC_6H_5}$$
XII

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[3] (a) H. W. Thompson and D. H. Wiffen, *J. Chem. Soc.*, 1412 (1948); (b) M. F. Carroll, R. G. Mason, H. W. Thompson and R. C. S. Wood, *ibid.*, 3458 (1950); (c) F. A. Miller, "Applications of Infrared and Ultraviolet Spectra to Organic Chemistry," in H. Gilman, Ed., "Organic Chemistry, An Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 122.

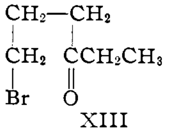
[4] The authors are indebted to Mr. R. N. Boos of Merck and Co., Inc., for carrying out this analysis.

[5] Cyclic enol esters of aldehydes; $\Delta\beta,\gamma$-butenolides are oxidized by the Tollens reagent also. Most react instantaneously (*cf.* W. A. Jacobs, A. Hoffmann and E. L. Gustus, *J. Biol. Chem.*, **70**, 1 (1926)); however, some require several hours (*cf.* W. Cocker and S. Hornsby, *J. Chem. Soc.*, 1157 (1947).

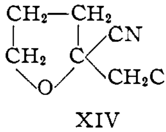
The oxidation product to be expected from either X or XI was α-methyl-α-benzylbenzoylacetone (VII). Actually, this sequence of reactions converted A, in over-all yield of 80%, into α-benzylpropiophenone (XII), identified by comparison of the 2,4-D.N.P. with an authentic specimen. Formation of XII can be explained readily as arising from XI by a reverse aldol condensation in the presence of the alkaline reagent, aqueous sodium sulfite. The other product of this reaction, pyruvic aldehyde, was not found, presumably because it decomposed in the basic solution.

Thus the chemical and physical evidence resulting from this study lead to the conclusion that A is correctly represented by structure VIII, and that, in solution, A can also exist in the open-chain form IX. It is well known that the course followed by the alkaline hydrolysis of substituted vicinal dibromides is greatly influenced by the nature and position of substituents; this has been shown by studies on α,β-dibromoaldehydes, ketones and acids and on β,γ-dibromo acids.[6] The conversion of the β,γ-dibromoketone IV into VIII constitutes the first study to be made relative to the influence of a keto group upon the alkaline hydrolysis of a vicinal dibromo system in a β,γ-dibromocarbonyl compound.

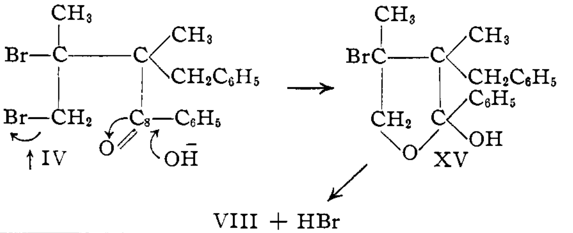
Examination of a Fisher–Hirschfelder–Taylor model of the unsaturated ketone III shows that the terminal double bond is highly hindered. Strain-free conformations of this compound involve close proximity of the bulky benzoyl and benzyl groups, as well as the methyl groups, to the double bond. The oxygen atom of the benzoyl group lies close to the double bond. This high degree of hindrance accounts for the relative unreactivity of the double bond toward bromine. The dibromo compound IV would certainly be no less hindered than III, and the γ-bromine atom would lie in space very close to the oxygen atom of the benzoyl group. The high degree of substitution in III and IV would lead to a facile ring closure, although even unsubstituted γ-bromoketones apparently undergo ring closures readily when the bromine atom undergoes a replacement. Thus Normant showed[7] that action of cuprous cyanide upon XIII led to XIV in yields of 70–80%. In the case of IV, nucleophilic attack of the hydroxyl ion at the carbon atom of the carbonyl group would render the oxygen atom more negative, and nucleophilic attack by this oxygen atom on the γ-carbon atom would release the stable bromide ion, resulting in formation of the intermediate XV.



XIII



XIV



The β-bromoether XV would readily lose the elements of hydrogen bromide to give VIII, and the ring closure to XV would be facilitated by the high degree of substitution on the carbon chain.

Experimental[8]

1-Phenyl-2,3-dimethyl-3-buten-1-one (I) **and** α,β-**Dimethylcrotonophenone. "Unsaturated Ketonic Mixture."**—The procedure followed was that reported by Colonge and Chambion.[2] The crude product (180 g., 51.7%) boiled at 80–95° (0.6–1.3 mm.), n^{25}D 1.5353. A sample boiling at 133–134° (19 mm.), n^{20}D 1.5352 (lit.[2] b.p. 134–135° (19 mm.), $n^{20.5}$D 1.5348) absorbed in the ultraviolet, in 95% U.S.P. ethanol, at 248 mμ (*K* 10,800) and 276 mμ (*K* 2680). T is material rapidly absorbed bromine at room temperature and at −5°; hydrogen bromide was evolved. At −70°, no reaction occurred.

1-Phenyl-2-benzyl-2,3-dimethyl-3-buten-1-one (III).—Some benzene (50 cc.) was distilled from a solution of the unsaturated ketonic mixture (8.71 g., 0.05 mole) in benzene (200 cc.) to remove traces of moisture. The solution was cooled to 30° while 1.33 *N* potassium *t*-butoxide in *t*-butyl alcohol (40 cc., theoretical 37.6 cc.) was added. The mixture was refluxed in an atmosphere of nitrogen, while a solution of benzyl bromide (10.7 g., 6.25×10^{-2} mole) in benzene (15 cc.) was added over a period of 15 minutes. The mixture was refluxed in an atmosphere of nitrogen for 3.5 hr. and cooled to room temperature. The salts were collected on a filter (Hy-flo), washed with ether and discarded. The filtrate was washed with water (five 25-cc. portions) until the aqueous extracts were neutral. The organic solution was dried (sodium sulfate), the solvents were removed under reduced pressure and the residual oil was distilled through a 30-cm. spiral wire column. The material (6.4 g., 48%) boiling at 90–135° (0.02 mm.) solidified. After three crystallizations from ethanol–water (1:1) the solid melted at 65–65.5°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.33; H, 7.63. Found: C, 86.69; H, 7.78.

The ultraviolet absorption spectrum of III showed a maximum at 240.5 mμ in isoöctane (*K* 10,700) and at 244 mμ in 95% U.S.P. ethanol (*K* 11,300). In the infrared, III absorbed at 890(s), 965(s), 1186(m), 1240(s), 1380(m), 1450(m–s), 1585(m), 1600(m), 1645(m–s), 1690(s) and 2960(m).[9]

Ozonolysis of III. α-**Methyl**-α-**benzylbenzoylacetone** (VII).—An ozone–oxygen mixture (8.2×10^{-4} mole of O_3 in ten minutes) was passed through a cooled (Dry Ice-acetone) solution of III (400 mg., 1.52×10^{-3} mole) in ethyl acetate (100 cc.) for 40 minutes (approximately 3.3×10^{-3} mole of ozone). The mixture was warmed to room temperature and then refluxed for 1.5 hr. with a mixture of glacial acetic acid (6 cc.), zinc dust (1.1 g.) and water (5 cc.) and then allowed to stand at room temperature overnight. Removal of ethyl acetate left an oily residue which was dissolved in ether (60 cc.) and washed with aqueous sodium bicarbonate (10%, one 20-cc. portion and two 10-cc. portions). Neutralization of the aqueous sodium bicarbonate extracts with aqueous hydrochloric acid (10%) gave a clear solution; no precipitate formed. The ether solution was dried (magnesium sulfate); removal of the ether under reduced pressure left an oil which slowly crystallized. The solid, collected on a filter and washed with cold ethanol, weighed 168 mg. Evaporation of ethanol from the filtrate yielded more solid (21 mg.), total yield, 189 mg., 48%. The solid, crystallized from ethanol and dried

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[6] (a) P. L. Viguier, *Ann. chim. phys.*, [8] **28**, 454 (1913); (b) E. P. Kohler and C. R. Addinall, THIS JOURNAL, **52**, 3728 (1930); (c) A. A. Alberts and G. B. Bachman, *ibid.*, **57**, 1284 (1935), and preceding papers; (d) E. E. Blaise and A. Courtot, *Bull. soc. chim.*, [3] **35**, 989 (1906), and preceding papers.

[7] H. Normant, *Compt. rend.*, **232**, 1942 (1951).

[8] All melting points unless otherwise specified are corrected and were determined on a Kofler hot-stage microapparatus. Analyses were carried out by the Microanalytical Laboratory of the University of Minnesota.

[9] A Perkin–Elmer double beam infrared spectrophotometer was used. The letter s denotes an intense or strong band, m a band of moderate intensity and w a weak absorption. Carbon disulfide was the solvent for the range, 667–1120 cm.$^{-1}$ and carbon tetrachloride for the range 1120–3000 cm.$^{-1}$.

(phosphorus pentoxide) *in vacuo* for several hours at 66°, melted at 104.5–105.5° (uncor., Fisher block).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.81, 80.80; H, 6.85, 6.93.

This solid, in 95% U.S.P. ethanol, showed an absorption in the ultraviolet at 248 mμ (*K* 12,400).

α-Methylbenzoylacetone.—The procedure followed was essentially that reported by Weygand and Forkel[10] for synthesis of the sodium salt of benzoylacetone and by Weygand and Forkel[11] for the conversion of this to α-methylbenzoylacetone by action of methyl iodide.

The product was distilled at 5 mm. through a 30-cm. spiral wire column. Fractions boiling at 104–106° (0.22 g., $n^{30.5}_D$ 1.5301), 106–107° (0.73 g., $n^{30.5}_D$ 1.5324) and 115–118° (3.94 g., $n^{30.5}_D$ 1.5324) were collected. In ethanol a portion of third fraction gave an instantaneous purplish-red color with ferric chloride.[12] The same test applied to benzoylacetone gave an orange-red color. Fractions two and three, combined, weighed 4.67 g. (80% based on the sodium salt of benzoylacetone).

α-Methyl-α-benzylbenzoylacetone (VII).—A mixture of sodium wire (0.52 g., 0.022 g.-atom), ether (50 cc.) and α-methylbenzoylacetone (3.95 g., 0.022 mole) was allowed to remain at room temperature overnight. The ether was removed under reduced pressure, acetone (75 cc.) was added to the salt and the mixture was refluxed for 10 minutes. Not all of the salt dissolved. The mixture was cooled to room temperature while benzyl bromide (5.75 g., 0.034 mole freshly distilled) was added. The mixture was refluxed for 80 minutes, cooled to room temperature and the acetone was removed. Ether (50 cc.) and water (50 cc.) were added to the residue and the layers were separated. The ether layer was washed with water (five 15-cc. portions) until the aqueous extract gave no precipitate with aqueous silver nitrate. The ether solution was dried (magnesium sulfate) and the ether was removed. The bright yellow, oily residue crystallized when it was rubbed with a glass rod. The solid, after washing with cold ethanol, weighed 2.70 g. (30%) and melted at 106–107° (uncor., Fisher block) after one crystallization from ethanol. A mixed melting point with the product of the ozonolysis of III showed no depression. The ultraviolet absorption spectrum of α-methyl-α-benzylbenzoylacetone in 95% U.S.P. ethanol showed a maximum at 248 mμ (*K* 12,400). The spectrum was identical with that of the product obtained by ozonolysis of III.

3,4-Dibromo-1-phenyl-2-benzyl-2,3-dimethyl-1-butanone (IV).—A solution of bromine (1.21 g., 7.56 × 10^{-3} mole) in anhydrous carbon tetrachloride (15 cc.)[13] was added in one portion to a solution of III (2.00 g., 7.56 × 10^{-3} mole) in anhydrous carbon tetrachloride (50 cc.). The solution assumed a deep wine color; it did not become translucent. Hydrogen bromide appeared almost at once. The mixture, allowed to remain at room temperature for one day, slowly became clear, bright yellow in color. Removal of the solvent under reduced pressure at room temperature left an oil (3.15 g.) which soon crystallized to a yellowish solid. A portion of the solid (0.55 g.) was chromatographed from benzene onto gypsum (55 g.) and into petroleum ether (b.p. 30–60°). The second 125-cc. fraction, on evaporation under reduced pressure, left a pure white, fluffy solid which melted at 93–94°. After three crystallizations from petroleum ether (b.p. 30–60°), the solid melted at 99–100.5°.

Anal. Calcd. for $C_{19}H_{20}Br_2O$: C, 53.80; H, 4.75. Found: C, 53.74; H, 4.85.

The solid was hygroscopic and slowly darkened. Darkening occurred rapidly unless the solid was purified by chromatography as soon as possible. A solution of this compound (IV) in isoöctane showed maximum absorption in the ultraviolet at 241.5 mμ (*K* 21,900).

A mixture of IV (504 mg., 1.19 × 10^{-3} mole) and a solution of sodium iodide in acetone was refluxed for 10 minutes and cooled. The liberated iodine was removed by action of aqueous sodium thiosulfate; acetone was removed under reduced pressure and ether (30 cc.) was added to the residue. The ether mixture was washed with small portions of water until the aqueous extract gave no precipitate with aqueous silver nitrate. The ether solution was dried (sodium sulfate) and the solvent was removed. The residual oil (328 mg.) was dissolved in petroleum ether (b.p. 30–60°) containing a trace of benzene and chromatographed onto aluminum oxide (9 g., Merck) and into petroleum ether (b.p. 30–60°)–ether (9:1). There resulted a white solid (263 mg., 84%) which melted at 64.5–65.5° after two crystallizations from 70% ethanol. A mixed melting point with an authentic sample of III showed no depression.

Alkaline Hydrolysis of IV. Solid A.—Dioxane was purified according to the procedure of Hess and Frahm.[14] A mixture of IV (604 mg., 1.43 × 10^{-3} mole), dioxane (20 cc.) and aqueous sodium hydroxide (10%, 3 cc., 8.3 × 10^{-3} mole) was refluxed for 18 hr. The mixture was concentrated under reduced pressure, ether was added and the mixture was extracted with water until the extracts were neutral. The ether solution was dried (sodium sulfate), and the ether was removed under reduced pressure. Addition of a small amount of methanol to the semi-solid residue (400 mg.) precipitated a white solid (197 mg., 48%)—solid A—which was removed by centrifugation. The solid contained no halogen as shown by a Beilstein test. An analytical sample, prepared by two crystallizations from ether–acetone followed by drying *in vacuo* overnight, melted at 166–170°. Droplets formed at 156° on the underside of the cover slide. The temperature at which this transition occurred, 156°, was found to be more characteristic than the actual melting range which was usually anywhere between 160° and 175° depending upon the rate of heating of the hot-stage.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.19; H, 7.47.

A, in 95% U.S.P. ethanol, was virtually transparent to ultraviolet light from 230–300 mμ. In the infrared (potassium bromide disk method),[9] solid A absorbed at 893(s), 1663(m), 2965(m), 3020(m) and 3050(m) cm.$^{-1}$. An intense band appeared at 3355 cm.$^{-1}$; there was virtually no absorption from 1663–2600 cm.$^{-1}$.

A was moderately soluble in ether, ethanol and ethyl acetate. It was insoluble in water, petroleum ether, carbon disulfide, carbon tetrachloride, chloroform, benzene and methanol. In pyridine and dioxane it was very soluble. It was usually obtained as hard, granular crystals which showed little tendency to form supersaturated solutions or to precipitate as an oil. In other experiments, A was produced in yields of 42, 47.5 and 52.6%. The amount of active hydrogen in A was found to be 0.15%.[4]

Action of Osmium Tetroxide and Periodic Acid upon A. Formation of α-Benzylpropiophenone.—Osmic acid (1 g., 4.1 × 10^{-3} mole) was added to a solution of A (1.04 g., 3.72 × 10^{-3} mole) in purified dioxane[14] (30 cc.) containing pyridine (1 cc.). Darkening began immediately. The mixture was allowed to remain at room temperature for two days. A solution of sodium sulfite (15 g., 0.12 mole) in water (165 cc.) was added and the mixture was refluxed for 1 hr. The black precipitate was collected on a filter (Hyflo) and washed several times with ethanol and chloroform. All the filtrates were combined and concentrated under reduced pressure until most of the organic solvents were removed. The remaining, essentially aqueous, solution was extracted several times with chloroform, benzene and ether. The organic extracts were combined and dried (sodium sulfate). Removal of the solvents under reduced pressure left an oily residue (800 mg.). This residue was dissolved in dioxane (20 cc.) containing pyridine (0.5 cc.), and a solution of periodic acid (0.58 g., 2.54 × 10^{-3} mole) in water (10 cc.) was added. The mixture was allowed to remain at room temperature for 0.5 hr. and was set aside in the refrigerator overnight. Most of the dioxane was removed under reduced pressure, chloroform was added to the residue and the mixture was extracted with water. The aqueous layer was extracted exhaustively with chloroform. The chloroform extracts were combined, dried (sodium sulfate), and the chloroform was removed under reduced pressure leaving an oily residue (796 mg.). This oil was dissolved in a minimum amount of benzene and chromatographed onto aluminum oxide (25 g., Merck). Elution by petroleum ether (b.p. 30–60°)–ether mixtures (a total of 450 cc. in which the concentration of ether was

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[10] C. Weygand and H. Forkel, *J. prakt. Chem.*, [2] **116**, 297 (1927).

[11] C. Weygand and H. Forkel, *Ber.*, **61**, 687 (1928).

[12] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 98.

[13] L. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 365.

[14] K. Hess and H. Frahm, *Ber.*, **71**, 2527 (1938).

gradually increased from 0 to 30%) gave a colorless oil (668 mg.). A portion of this oil (128 mg.) was chromatographed from petroleum ether onto aluminum oxide (18 g., Merck) and eluted in the same fashion in order to obtain as pure a sample as possible. The ultraviolet absorption spectrum of a solution of this oil in isoöctane had a maximum at 240 mμ (*K* 12,500, assuming it to be α-benzylpropiophenone).

The oil (51 mg.) was converted into a 2,4-dinitrophenylhydrazone which, crystallized once from ethanol and once from methanol–ether followed by two washings with petroleum ether (b.p. 30–60°), consisted of yellow-orange needles melting at 132.5–134°.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$ (α-benzylpropiophenone 2,4-dinitrophenylhydrazone): C, 65.33; H, 4.99; N, 13.86. Found: C, 65.54; H, 4.99; N, 13.52.

An authentic specimen of α-benzylpropiophenone 2,4-dinitrophenylhydrazone was prepared. It melted at 132.5–135°.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: N, 13.86. Found: N, 13.53.

This derivative is new. A mixed melting point between it and the 2,4-dinitrophenylhydrazone of the oil obtained *via* the degradation of A was not depressed.

Doeuvre Analysis of A and 1-Phenyl-2-benzyl-2,3-dimethyl-3-buten-1-one (III).—A modification of the method of Doeuvre[15] as improved by Karrer and Kebrle[16] was employed. Ethyl acetate was washed with six portions of water, dried (calcium chloride) and distilled once from phosphorus pentoxide through a 20-cm. Vigreux column. The product boiled over a range of one degree. A standard solution of formaldehyde containing 4.92 × 10^{-2} formaldehyde/cc.[17,18] was used in preparing solutions needed to obtain the plot of optical density (*D*) *vs.* mg. CH_2O per 100 cc.[16] Table I summarizes the data obtained from the Doeuvre analyses. Eugenol 3,5-dinitrobenzoate (m.p. 131–131.5°) was prepared and used as the "known" compound containing one terminal carbon–carbon double bond.

TABLE I

RESULTS OF THE DOEUVRE ANALYSES

Compound	Wt., mg., taken	D^a	Weight formaldehyde, mg. Theory^b	Obsd.	Cor.^{c}	CH_2O, %
Eugenol 3,5-dinitrobenzoate	5.91	0.646	0.50	0.73	0.59	119
III	4.35	.677	.49	.74	.60	130
Solid A	4.70	.150	.50	.31	.17	34
Ethyl acetate	(7 cc.)	.045	(.00)	.14	..	..

[a] Optical density determined at 595 mμ using a Beckman model B spectrophotometer. [b] Theoretical amount of formaldehyde which would be obtained if the compound contained one terminal double bond. [c] Observed (mg.) minus the ethyl acetate blank.

Action of 2,4-Dinitrophenylhydrazine upon A.—The usual procedure for the preparation of a 2,4-dinitrophenylhydrazone was used; the mixture became cloudy within 4 minutes after mixing the reagents and a precipitate formed slowly (under the same conditions III did not form a derivative). The mixture was allowed to remain at room temperature overnight. The precipitate (20 mg.) was removed by centrifugation. When this yellow solid was crystallized from hot methanol, however, it became amorphous, melting at 196–235°. More solid was obtained from the filtrate by addition of water. The latter solid was chromatographed at once from benzene onto activated silica gel (12 g.). Using petroleum ether (b.p. 30–60°)–ether mixtures (in which the concentration of ether was gradually increased from 10–20%) as the eluent, the derivative (300 mg. from 250 mg. A) was obtained in the first 1.25 liters. A portion was crystallized once from benzene–petroleum ether (b.p. 28–38°) and twice from ethanol–benzene, then washed with petroleum ether (b.p. 28–38°) and dried *in vacuo* at 56° for 2 hr. It formed bright yellow microcrystals melting at 172.5–174.5° dec.

Anal. Calcd. for $C_{25}H_{24}N_4O_6$ (mono-2,4-dinitrophenylhydrazone of A, $C_{19}H_{20}O_2$): C, 65.21; H, 5.25. Found: C, 65.86; H, 5.88.

The ultraviolet spectrum of this derivative in 95% U.S.P. ethanol showed maxima at 259 mμ (*K* 9,300) and 349 mμ (*K* 15,200). Minima occurred at 244 mμ (*K* 8,250) and 292 mμ (*K* 2,290).

Action of Silver Oxide upon A.—Tollens reagent was prepared in the usual way. In the first experiment a mixture of A (50 mg.) and pyridine (1 cc.) was warmed on the steam-bath while Tollens reagent (3 cc.) was added. The mixture became black at once; some white solid (undissolved A) remained in the mixture. When the mixture was boiled, a silver mirror appeared. In the second experiment, the mixture was allowed to remain at room temperature. A mirror appeared after 4 to 6 hr.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Organic Peracid Oxidation of Some Enol Esters Involving Rearrangement[1]

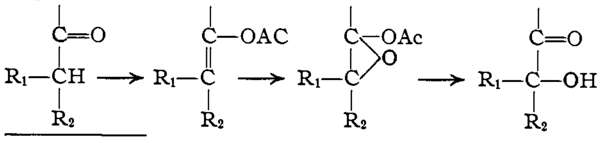
BY PETE D. GARDNER

RECEIVED JANUARY 12, 1956

The reaction of peracetic acid with 5-acetoxybenzosuber-5-ene (VI) was found to give 6-acetoxybenzosuber-5-one (IV) and the cleavage product, γ-(2-carboxyphenyl)-butyric acid (XII), whereas the use of perbenzoic acid resulted in the formation of only IV. The behavior of 3,4-dihydro-1-naphthyl acetate (V) with perbenzoic acid was the same, the corresponding ketol ester II being the only isolated oxidation product. The same transformation was brought about by perbenzoic acid in the coversion of 4-methoxy-α-acetoxystilbene (VII) to ketol ester IX. Initial experiments with an enol lactone XI are described and mechanisms are proposed to account for all of the above observations.

In the course of a program, having as its goal the development of superior methods of formation of unsaturated cyclic ketones, certain ketols and their esters became attractive as possible intermediates. Synthetic procedures were sought which would make available both of the two isomers of a given ketol, *i.e.*, RCOCH(OH)Ar and ArCOCH(OH)R.

It has been demonstrated in the steroid field that enol esters may be converted to ketols by the sequence[2]



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[1] The author is indebted to Research Corporation for the financial support of this work.

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