The mixture of diols thus produced, 1.18 g. in all, was placed in a small distilling flask with 0.135 g. of sulfur and heated first to 180° when dehydration occurred and then to 225–230° for one hour for dehydrogenation. After adding a little zinc dust the material was vacuum distilled to yield 0.62 g. (60.5%) of a light yellow oil which soon crystallized. Repeated crystallization from Skellysolve B afforded a total of 0.35 g. (34%) of good 1-methylbenzo(c)phenanthrene, m.p. 136.8–141.0°. A pure sample, m.p. 139.6–141.0°, was compared with a sample of the same hydrocarbon previously synthesized by a different method[6] and found to be identical by mixed m.p. and by X-ray powder diffraction analysis.[8]

COLUMBUS 10, OHIO RECEIVED DECEMBER 20, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

Proportions of Isomeric Ketone Enol Acetates from O-Acetylations of Methyl-methylene Ketones with Isopropenyl Acetate[1]

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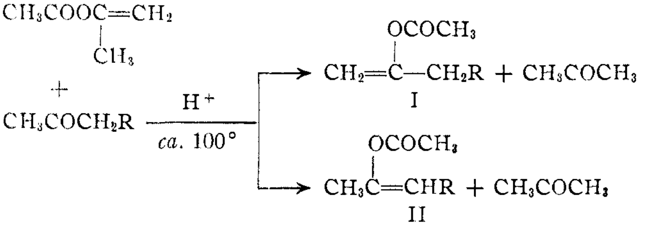
The structures of ketone enol acetates produced by the O-acetylation of methyl-methylene ketones by the isopropenyl acetate method were determined. Methyl *n*-hexyl ketone gave entirely the methylene derivative, whereas methyl neopentyl ketone formed entirely the methyl derivative. Other methyl-methylene ketones produced mixtures of the two isomers. These structures were based on those of corresponding β-diketones produced on C-acetylation with acetic anhydride by boron trifluoride. The alkali extraction method for separating isomeric β-diketones was refined and developed. Syntheses of a new ketone and of several new ketone enol acetates and β-diketones are described.

The O-acetylation of ketones to form ketone enol acetates may be effected with acetic anhydride,[4] ketene[5] or isopropenyl acetate[5,6] in the presence of a catalytic amount of strong acid. The reaction involves presumably the acid-catalyzed enolization of the ketone, and the acetylation of the resulting enol. The O-acetylation of methyl-methylene ketones may form the methyl derivative (I) or the methylene derivative (II), depending on whether a methyl or methylene hydrogen is enolized. The isopropenyl acetate method is particularly convenient and generally produces good yields of the ketone enol acetates; it involves an acetate–ketone exchange and the volatilization of the by-product acetone (equation 1).



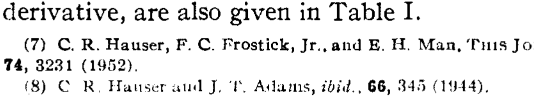
$$\mathrm{CH_3COOC(CH_3){=}CH_2 + CH_3COCH_2R} \xrightarrow[ca.\ 100^\circ]{H^+} \begin{cases} \mathrm{CH_2{=}C(OCOCH_3){-}CH_2R + CH_3COCH_3} & \mathrm{I} \\ \mathrm{CH_3C(OCOCH_3){=}CHR + CH_3COCH_3} & \mathrm{II} \end{cases} \quad (1)$$

This method has previously been employed to prepare the ketone enol acetates of several methyl-methylene ketones[6]; but apparently the structure of the product was established only for the acetate from methyl *n*-amyl ketone which gave exclusively the methylene isomer (II, R = C_4H_9).[5]

In the present investigation, the relative proportions of methyl and methylene derivatives produced from various methyl–methylene ketones by the isopropenyl acetate method were determined. These proportions were established by effecting the C-acetylations of the ketone enol acetates with acetic anhydride by boron trifluoride to form corresponding β-diketones (equations 2 and 3). It has previously been shown[5] that ketone enol acetates having structures I and II, as determined by ozonolysis, give β-diketones having structures III and IV, respectively. This conversion of the O-acetyl derivatives to the C-acetyl derivatives with the retention of the methyl or methylene structure is to be expected on the basis of the mechanism.[7]

The isomeric β-diketones III and IV were readily separated by the preferential extraction of the relatively more acidic methyl derivative (III) from an ether solution of the two by means of dilute alkali, according to the general method described previously.[8] This alkali extraction method, which has now been refined and developed, gave relative yields of isomeric β-diketones that were reproducible to within ±3% with mixtures of isomers containing 10% or less of the methyl derivative, and to within ±6% with mixtures containing 50% or more of the methyl derivative.

$$\mathrm{(CH_3CO)_2O + I} \xrightarrow{BF_3} \xrightarrow{NaOAc} \underset{\mathrm{III}}{\mathrm{CH_3COCH_2COCH_2R}} + \mathrm{CH_3COOH} \quad (2)$$



$$\mathrm{(CH_3CO)_2O + II} \xrightarrow{BF_3} \xrightarrow{NaOAc} \underset{\mathrm{IV}}{\mathrm{CH_3CO\underset{R}{CH}COCH_3}} + \mathrm{CH_3COOH} \quad (3)$$

The results are summarized in Table I. The relative proportions of the two isomeric ketone enol acetates I and II, given in the last column of this table, are based on the relative yields of the two isomeric β-diketones III and IV. Results with dibenzyl ketone, which can form only a methylene derivative, are also given in Table I.

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(1) This work was supported in part by a grant from the Duke University Research Council.

(2) E. I. du Pont de Nemours and Co. Fellow, 1950–1951.

(3) Carbide and Carbon Chemicals Co. Fellow, 1949–1950.

(4) P. Z. Bedoukian, THIS JOURNAL, **67**, 1430 (1945).

(5) F. G. Young, F. C. Frostick, Jr., J. J. Sanderson and C. R. Hauser, *ibid.*, **72**, 3635 (1950).

(6) W. M. Quattlebaum, Jr., and C. A. Noffsinger, U. S. Patent 2,466,737 (1949); *C. A.*, **43**, 7037 (1949); see also H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(7) C. R. Hauser, F. C. Frostick, Jr., and E. H. Man, THIS JOURNAL, **74**, 3231 (1952).

(8) C. R. Hauser and J. T. Adams, *ibid.*, **66**, 345 (1944).

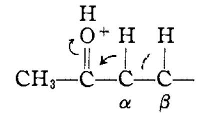
TABLE I

PROPORTIONS OF ISOMERIC KETONE ENOL ACETATES FROM METHYL-METHYLENE KETONES (EQUATION 1) DETERMINED BY CONVERSION TO ISOMERIC β-DIKETONES (EQUATIONS 2 AND 3)

Ketone, methyl	Ketone enol acetate I and or II B.p., °C.	Mm.	Yield, %	β-Diketone Methyl deriv. III B.p., °C.	Mm.	Yield, %	Methylene deriv. IV B.p., °C.	Mm.	Yield, %	Proportions of isomeric ketone enol acetates, % I	II
n-Hexyl	79–83	11	42[a]				111–113	15	60[b]	0	100
3,3-Dimethylbutyl	85–90	35	67[c]	107	20	9[d]	104–108	20	41[e]	18	82
Isobutyl	68–71	50	57[f]	78–80	20	31[b]	82–86	20	12[b]	72	28
Neopentyl	73–78	40	65[g]	99	40	37[h]				100	0
Dibenzyl ketone	159–163	3	58[i]				64–66 (m.p.)		55[j]	...	...

[a] *Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.92; H, 10.90. [b] Reference 8. [c] *Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 71.02; H, 10.41. [d] *Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.84; H, 10.76. Blue copper enolate, m.p. 143–144°. [e] *Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.64; H, 10.68. Dark green copper enolate, m.p. 156–158.5° (dec.). [f] Reference 5. [g] *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.10; H, 10.08. [h] *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 68.79; H, 10.34. Gray copper enolate, m.p. 117–118°. [i] *Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.09; H, 6.39. [j] 1,3-Diphenylpentanedione-2,4. *Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.01; H, 6.13. Gray-green copper enolate, m.p. 173–174.5°.

Like methyl *n*-amyl ketone,[5] methyl *n*-hexyl ketone gave, on O-acetylation, exclusively the methylene derivative (II, R = n-C_5H_{11}) but methyl isobutyl ketone produced largely the methyl derivative (I, R = isopropyl) while methyl neopentyl ketone formed exclusively the methyl derivative (I, R = *t*-butyl). These results are in agreement with the concept of hyperconjugation (V) the effect of which would decrease as the number of hydrogens on the β-carbon is decreased. However, in contrast to the methyl *n*-alkyl ketones which have two β-hydrogens, methyl 3,3-dimethylbutyl ketone (neopentylacetone), which likewise has two β-hydrogens, gave partly the methyl derivative. This suggests the operation also of a steric factor.



V

Although the results in Table I are considered reproducible when the isopropenyl acetate method is employed under the usual conditions (at approximately 100°), the proportions of the methyl and methylene derivatives from methyl isobutyl ketone were almost reversed when the reaction was carried out at room temperature,[9] being 18 and 82%, respectively. The formation of relatively more of the methyl derivative at the higher temperature appears to be connected with the enolization of the ketone rather than with a subsequent conversion of the methylene enol acetate (II) to the methyl enol acetate (I), since there appears to be little if any tendency for the methylene derivative to be converted to the methyl derivative under the conditions of the isopropenyl acetate method. Thus, when the enol acetate of methyl isobutyl ketone[10] (prepared by the ketene method), consisting of 13% of the methyl derivative and 87% of the methylene derivative, was heated with isopropenyl acetate at 100° for three hours, the recovered ketone enol acetate consisted of only slightly more of the methyl derivative (17%) and slightly less of the methylene derivative (83%). Similarly, the enol acetate of methyl *n*-hexyl ketone, consisting exclusively of the methylene derivative, failed to be converted to any of the isomeric methyl derivative on heating with methyl *n*-hexyl ketone at 100° for seven hours.

It should be pointed out, that, although the acetic anhydride exchange method has similarly given exclusively the methylene derivative with methyl *n*-amyl ketone,[4] the ketene method, which presumably does not involve an exchange reaction, has given with this ketone a mixture of the two isomers consisting of 10% of the methyl and 90% of the methylene derivatives.[5] Rather surprisingly, the ketene method has given exclusively the methylene isomer with methyl isobutyl ketone,[5] but mixtures of the two isomers have also been obtained under certain conditions (see above).

In connection with this work, several new ketone enol acetates and β-diketones were synthesized (Table I). Also, 3,3-dimethylbutyl ketone appears to be new; it was prepared by the reactions represented in equation 4.[11]

$$\begin{aligned}(CH_3)_3CMgCl + CH_2{=}CHCOCH_3 &\xrightarrow{\text{1,4-addition}} \\ (CH_3)_3CCH_2CH{=}C(CH_3)OMgCl &\xrightarrow{H_2O} \\ (CH_3)_3CCH_2CH_2COCH_3 &\quad (4)\end{aligned}$$

Experimental[12]

Commercial methyl isobutyl,[10] methyl *n*-hexyl[10] and dibenzyl ketones were purified by redistillation.

Methyl neopentyl ketone was prepared by the dichromate oxidation of diisobutylene. This method has been previously mentioned, but no experimental details were provided.[13a] To 193.8 g. (1.73 moles) of diisobutylene stirred rapidly in a 1-l. 3-necked flask was added during two days a hot (100–120°) solution of 588 g. (2 moles) of potassium dichromate in 600 ml. of water and 400 ml. of sulfuric acid, keeping the temperature at 60° or below. The resulting mixture was distilled with steam and the distillate ex-

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[9] The mixture of methyl isobutyl ketone, isopropenyl acetate and sulfuric acid was kept at room temperature at 90 mm. until the theoretical amount of acetone had collected in a Dry Ice trap (10 hours). There was obtained a 36% yield of the enol acetate, b.p. 63.5–69° (50 mm.).

[10] We are indebted to the Carbide and Carbon Chemicals Co., South Charleston, W. Va., for a generous sample of this material.

[11] Methyl 3,3-diethylpentyl ketone (b.p. 110–111° at 20 mm.) was similarly prepared from $(C_2H_5)_3CMgCl$ and methyl vinyl ketone. *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.03. Found: C, 77.45; H, 12.79. The 2,4-dinitrophenylhydrazone melted at 95–96°.

[12] Melting points and boiling points are uncorrected. Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill.

[13] (a) A. Butlerow, *Ann.*, **189**, 78 (1877); (b) F. C. Whitmore and co-workers, THIS JOURNAL, **60**, 2461 (1938).

tracted with ether. The ether solution was washed with 5% potassium carbonate solution, dried over Drierite, and the solvent distilled. The residue was fractionated in a packed column to yield 85.8 g. (44%) of product, b.p. 124–127° (reported b.p. 122–124°[13b]).

The use of permanganate instead of dichromate in this preparation gave inferior yields of the ketone.

Methyl 3,3-Dimethylbutyl Ketone.—A solution of *t*-butylmagnesium chloride, prepared from 61 g. (2.5 moles) of magnesium turnings and 235 g. (2.54 moles) of *t*-butyl chloride[14] in 1100 ml. of ether, was separated from unused magnesium and stirred with 15 g. more of *t*-butyl chloride to ensure reaction of the last traces of magnesium.

To the rapidly stirred Grignard solution, cooled in an ice-bath, was added 70 g. (1 mole) of methyl vinyl ketone (b.p. 80–81°)[15] in 400 ml. of dry ether during 4 to 5 hours, the stirring being continued another hour.[16] After standing overnight, the reaction mixture was decomposed with 2 kg. of ice containing 500 g. of ammonium chloride. The ether layer, combined with several ether extracts of the aqueous layer, was filtered through sodium sulfate and dried over Drierite. The solvent was distilled and the residue fractionated to give 40.7 g. (32%) of the ketone, b.p. 69–72° (35 mm.), and, on redistillation, at 71–72° (35 mm.).

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.17; H, 12.38.

The 2,4-dinitrophenylhydrazone melted at 105.5–108°.

Preparation of Ketone Enol Acetates.—Mixtures of isopropenyl acetate[10] and ketones (2:1 molar ratio) were heated (around 100°) in the presence of catalytic amounts of sulfuric acid until an amount of acetone equivalent to the higher ketone had distilled, according to the general method described previously.[6] The mixtures were neutralized with anhydrous sodium acetate, the excess isopropenyl acetate distilled, and the ketone enol acetates isolated by fractionation. The yields and other data are given in Table I.

Acylation of Ketone Enol Acetates with Acetic Anhydride by Boron Trifluoride.—These acylations were carried out by a modification of the procedure previously described.[5] A mixture of 1.5 parts anhydride and 1 part ketone enol ester was saturated in 5 to 10 minutes with boron trifluoride, the temperature of the mixture being maintained at 0–20° by immersion of the flask in a Dry Ice–acetone-bath. After saturation, the boron trifluoride was added slowly for an additional 20 minutes, and the mixture then stirred 4 hours in an ice-bath. The reaction mixture was refluxed one hour in sodium acetate solution (two moles of sodium acetate to one of anhydride), cooled, and extracted with ligroin (b.p. 30–60°) or ether. The extracts were washed free of acid with saturated sodium bicarbonate solution, dried over Drierite and the solvents distilled. The β-diketones were distilled from the residue *in vacuo*. The isomeric β-diketones were separated by the alkali extraction method described below. The yields and other data are given in Table I.

Alkali Extraction Method for Separating Mixtures of Isomeric β-Diketones.—The mixture of isomers (15–20 g.) was dissolved in approximately 150 ml. of ether in a separatory funnel, and crushed ice added with shaking to cool the solution to 0–5°. The ether solution was then extracted with successive 100-ml. portions (relatively smaller portions for mixtures containing less than 10% of the methyl isomer to be extracted) of 1 or 2% sodium hydroxide solution containing crushed ice. To a solution of a few drops of each alkali extract in 1–2 ml. of methanol or ethanol was added 5% hydrochloric acid (2 drops) followed by 5% ferric chloride solution (1–2 drops). The separation of the two isomers was indicated when the alkali extract no longer gave the red enol test characteristic of methyl derivatives but instead gave the purple or negative test characteristic of the methylene derivative. The two colors were readily distinguishable in natural daylight, but ordinary artificial light made the distinction somewhat difficult. The extract giving the purple (or negative) enol test was acidified and recombined with the ether solution of the methylene isomer. The combined alkali extracts (all giving the red enol test)—which were kept ice cold at all times—were acidified and extracted with ether. Both ether solutions containing the separated methyl and methylene isomers were washed with a small amount of sodium bicarbonate solution and dried over Drierite. The solvent was distilled and the residues were fractionated. In practically every case the liquid did not begin to distil until within about 5° of the boiling point of the β-diketone. A forerun was usually obtained, but since it presumably consisted of only slightly impure β-diketone, its weight was added to that of the pure β-diketone in the calculation of the proportion of isomers.

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[14] S. V. Puntambekar and E. A. Zoellner, in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

[15] This ketone was prepared as needed from an azeotrope containing 15% water by saturating with potassium carbonate at 0° and distilling under nitrogen in the presence of a trace of hydroquinone. We are indebted to the Jackson Laboratory of E. I. du Pont de Nemours and Co., Wilmington, Del., for a generous sample of the azeotrope.

[16] For the use of Grignard reagents in similar 1,4-additions see E. R. Alexander and G. R. Coraor, THIS JOURNAL, **73**, 2721 (1951).