[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CORPORATION]

Preparation and Properties of Ethyl Vinyl Ketone and of Methyl Isopropenyl Ketone[1]

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The vapor-phase reaction of methyl ethyl ketone and formaldehyde over a lead zeolite catalyst has been described.[4] The reaction product was considered to be methyl isopropenyl ketone, $CH_2{=}C(CH_3)COCH_3$ (MIK).

The liquid-phase reaction of methyl ethyl ketone and formaldehyde, yielding methyl isopropenyl ketone, has been studied also.[5,6,7,8] The properties reported are at considerable variance.

The polymerization experiments with material considered to be pure methyl isopropenyl ketone prepared by the vapor phase method gave erratic and anomalous results. Although clear, colorless, hard polymers sometimes could be obtained, quite often the products formed were yellow gels with varying amounts of a white, spongy solid present; these materials, unlike the clear, colorless polymers, were not soluble in organic solvents. The degree of hardness of the soluble polymers also varied. It was therefore decided that the supposedly pure methyl isopropenyl ketone was actually impure. One of the impurities suspected to be present was the isomeric ethyl vinyl ketone ($CH_2{=}CHCOC_2H_5$) (EVK), formed simultaneously with the methyl isopropenyl ketone, thus

$$CH_3COCH_2CH_3 + CH_2O \longrightarrow H_2O + CH_2{=}C(CH_3)COCH_3$$

$$CH_3COCH_2CH_3 + CH_2O \longrightarrow H_2O + CH_2{=}CHCOC_2H_5$$

Authentic samples of ethyl vinyl ketone and of methyl isopropenyl ketone were prepared, and their properties compared with those of the fraction isolated from the product of the vapor-phase reaction of methyl ethyl ketone and formaldehyde.

Authentic Ethyl Vinyl Ketone.—Ethyl vinyl ketone has been prepared in the past by the following series of reactions[9]

$$CH_2{=}CHCHO \longrightarrow ClCH_2CH_2CHO \longrightarrow ClCH_2CH_2COOH \longrightarrow ClCH_2CH_2COCl \longrightarrow \underset{\text{b. p. }57^\circ\text{ (9 mm.)}}{ClCH_2CH_2COC_2H_5} \longrightarrow \underset{\substack{\text{b. p. }31^\circ\text{ (47 mm.)}\\ 38^\circ\text{ (60 mm.)}}}{CH_2{=}CHCOC_2H_5}$$

It has also been prepared by catalytic oxidation of ethylvinylcarbinol with oxygen[10] and by sulfochromic acid mixture.[11] The physical properties of the product reported[11] were: d^{15}_4 0.8524; $n^{15}D$ 1.4233; b.p. 68–70° (200 mm.); 38° (60 mm.).

A number of unsaturated ketones have been prepared by reaction of olefins with acetyl chloride or bromide, using anhydrous aluminum chloride or bromide catalysts.[12]

The preparation of authentic ethyl vinyl ketone was accomplished by the reaction of ethylene with propionyl chloride, using anhydrous aluminum chloride catalyst, according to the reaction steps

$$CH_2{=}CH_2 + C_2H_5COCl \xrightarrow{AlCl_3} ClCH_2CH_2COC_2H_5 \xrightarrow{-HCl} CH_2{=}CHCOC_2H_5$$

In the preparation of ethyl vinyl ketone from ethylene and propionyl chloride, ethyl β-chloroethyl ketone is an intermediate and may be isolated if desired. The chloro ketone was found to be reasonably heat stable up to 50–60°.

Runs in which chloroform or nitrobenzene was used as the solvent and in which the intermediate chloroketone was isolated and dehydrohalogenated with diethylaniline, or in which carbon disulfide was the solvent and the intermediate chloroketone was thermally decomposed without isolation, gave similar over-all yields of 20–25%. In the dehydrohalogenation reaction, it was found advantageous to mix the diethylaniline and chloroketone in moderate quantities, followed by distillation. Ethyl chloride was formed in appreciable quantity during this reaction. It presumably came from reaction of diethylaniline and hydrogen chloride, whereby ethyl chloride and monoethylaniline and aniline may be produced.[13] Since it is known that primary and secondary amines will add to unsaturated ketones, quinoline probably would serve the purpose better than diethylaniline.

The identity of the product as ethyl vinyl ketone was established by 2,4-dinitrophenylhydrazine derivatives and by an aniline adduct. Infrared absorption indicated the presence of a carbonyl group in the aniline adduct. The iodoform test was negative. Catalytic hydrogenation yielded diethylcarbinol. A clear solid formed readily on warming with a peroxide catalyst, indicating the presence of an activated double bond.

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[4] Brant and Hasche, U. S. Patent 2,245,567.

[5] Morgan, *et al.*, *Chemistry and Industry*, **57**, 390 (1938); **57**, 885 (1938).

[6] Rutovskii, *et al.*, *J. Applied Chem.* (*U. S. S. R.*), **14**, 528 (1941); **14**, 535 (1941); **14**, 542 (1941).

[7] Marvel, Riddle and Corner, THIS JOURNAL, **64**, 92 (1942).

[8] Landau and Irany, *J. Org. Chem.*, **12**, 422 (1947).

[9] Blaise and Maire, *Compt. rend.*, **142**, 215 (1906); *Bull. soc. chim.*, [4] **3**, 265 (1908).

[10] Delaby, *Compt. rend.*, **182**, 140 (1926).

[11] Courtot and Pierron, *ibid.*, **188**, 1501 (1929).

[12] Krapivin, *Bull. Soc. Imp. Nat. Moscow*, 1–176 (1908); *C. A.*, **5**, 128 (1911).

[13] Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, p. 60.

Authentic Methyl Isopropenyl Ketone.—The preparation of authentic methyl isopropenyl ketone was accomplished by the following reaction steps, all of which are disclosed, either directly or indirectly, in the patent literature[14 15,16,17]

$$HC\equiv CH + CH_3COCH_3 \xrightarrow{KOH}$$

$$(CH_3)_2C(OH)C\equiv CH \xrightarrow[AcOH]{Hg(OAc)_2}$$

$$(CH_3)_2C(COCH_3)(OCOCH_3) \xrightarrow{450-500°}$$

$$CH_2{=}C(CH_3)COCH_3 + CH_3COOH$$

The route chosen for preparation of methyl isopropenyl ketone was similar to that most recently described,[18,19] in which dimethylacetylcarbinol was prepared and then dehydrated to methyl isopropenyl ketone. In the present case the desired ketone was obtained, not by dehydration of dimethylacetylcarbinol, but by pyrolysis of the corresponding acetate.

Methyl isopropenyl ketone was also prepared by catalytic hydration of isopropenylacetylene

$$CH_2{=}C(CH_3)C\equiv CH + H_2O \xrightarrow[Hg(OAc)_2]{AcOH} CH_2{=}C(CH_3)COCH_3$$

The lower homolog, methyl vinyl ketone, has been prepared in the past by catalytic hydration of vinylacetylene.[20,21]

The identity of methyl isopropenyl ketone was established through its aniline adduct, by its positive iodoform test and by its catalytic hydrogenation to methyl isopropyl ketone and methylisopropylcarbinol. The carbinol was identical with a known sample prepared from acetaldehyde and isopropyl bromide by the Grignard reaction. A solid product formed on warming the unsaturated ketone with a peroxide catalyst, indicating the presence of an activated double bond.

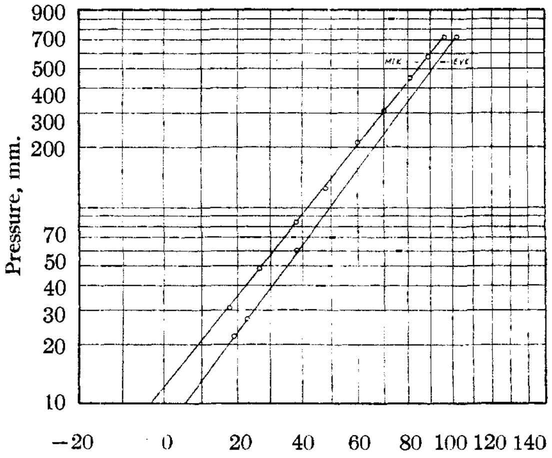

Fig. 1.—Vapor pressure data.

The properties of these two authentic ketones are presented in Table I.

TABLE I

Property or derivative	MIK	EVK
n^{20}_D	1.4235	1.4180–1.4185, 1.4192
d^{20}_4	0.8521	0.8468
M. p. semicarbazide derivative	172.6–173.5°	No deriv. formed
M. p. 2,4-dinitrophenylhydrazine derivatives	184–186°	(a) 128.8–129.0° (b) 166–166.5°
Aniline adduct	B. p. 72° (50 μ)	M. p. 56.5–57.0°
Iodoform test	Positive	Negative
Hydrogenation	Methyl isopropyl ketone and carbinol	Diethylcarbinol

The vapor pressure curves for the two authentic ketones are shown in Fig. 1. The vapor pressure curve for methyl isopropenyl ketone was obtained by the Ramsay–Young method. Under similar conditions, this information could not be obtained for ethyl vinyl ketone. Steady values could not be obtained, presumably because the highly active monomer was either dimerizing or polymerizing or both during the attempted determination. The curve shown is based on observed boiling points.

Vapor-phase Reaction between Methyl Ethyl Ketone and Formaldehyde.—The reaction between methyl ethyl ketone and formaldehyde was carried out by passing the mixture of vapors over a catalyst composed of magnesium silicate containing 10% chemically combined lead monoxide at 290–310°. The unreacted formaldehyde was removed from the product by distillation through a packed column under reduced pressure, employing counter-current scrubbing with water, the formaldehyde solution being removed at the base of the still. The crude, wet ketone mixture obtained from the top of the column was treated with salt to remove most of the water and then the unreacted methyl ethyl ketone was recovered by fractional distillation under reduced pressure. The remaining mixture of unsaturated ketones was then subjected to exhaustive fractional distillation under low pressure to separate the methyl isopropenyl ketone and the ethyl vinyl ketone. The use of pressures of the order of 10–20 mm. was adopted in order to minimize dimerization and polymerization. Progress of the separation was followed by refractive indices rather than by boiling points. A reasonable refractive index range (n^{20}_D) for methyl isopropenyl ketone was considered to be 1.4230–1.4235[22] and, for ethyl vinyl ketone, 1.4180–1.4185.

In some of these distillations, trouble was ex-

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(14) Pesta and Ebel, U. S. Patent 2,303,345.

(15) McGill, U. S. Patent 2,198,172.

(16) Allen and Haury, U. S. Patent 2,225,542.

(17) Wingfoot Corp., U. S. Patent 2,256,149.

(18) Porter, *Chem. Eng.*, **54**, 102 (1947).

(19) Weizmann, British Patent 569,373; *C. A.*, **41**, 5545 (1947).

(20) Carter, U. S. Patent 1,896,161.

(21) Conaway, U. S. Patent 1,967,225.

(22) H. J. Hagemeyer of this Laboratory (private communication) by the reaction of methyl ethyl ketone, formalin and dimethylamine hydrochloride, obtained a product having an n^{20}_D value of 1.4235, which is considered correct for methyl isopropenyl ketone.

perienced with the formation of a white, insoluble polymer which would completely plug and break the glass distilling column unless it was removed as soon as it began to form. The polymer usually appeared at the bottom of the packed column toward the end of the distillation of the ethyl vinyl ketone fraction, and was probably due to the presence of some higher boiling, divinyl component which has not been identified.

Proof that the Vapor-Phase Reaction of Methyl Ethyl Ketone and Formaldehyde Leads to Formation of both Unsaturated Ketones.—The above fractions of the product of the vapor-phase reaction of methyl ethyl ketone and formaldehyde were compared with authentic methyl isopropenyl ketone and ethyl vinyl ketone by relating the properties of the compounds themselves and the properties of their derivatives. The relationships are shown in Tables II and III.

TABLE II

MIK PROPERTIES AND DERIVATIVES

Source	Vapor-phase, MEK + CH_2O	Authentic
2,4-Dinitrophenylhydrazine deriv.	M. p. 180.3–181.2°	M. p. 184–186°
	Identical X-ray patterns	
Semicarbazide deriv.	M. p. 172.6–173.4°	M. p. 172.6–173.5°
	Mixed m. p. 172.3–173.9°	
	Identical X-ray patterns	
Iodoform test	Positive	Positive
n^{20}_D	1.4235	1.4235
d^{20}_4	0.8529	0.8521

Treatment of methyl isopropenyl ketone with aniline at room temperature resulted in formation of an adduct which was an oil. This is in contrast to the solid adduct formed from ethyl vinyl ketone and aniline.

Four fractions of the crystalline product obtained by reaction of 2,4-dinitrophenylhydrazine with authentic methyl isopropenyl ketone showed apparently different solubility and melting point behavior, but they gave X-ray diffraction patterns which were identical with each other and with that of one of three derivatives of a fraction of methyl ethyl ketone–formaldehyde reaction product which also contained ethyl vinyl ketone.

TABLE III

EVK PROPERTIES AND DERIVATIVES

Source	Vapor-phase, MEK + CH_2O	Authentic
2,4-Dinitrophenylhydrazine deriv.	(a) —	M. p. 128.8–129.0°
	Identical X-ray patterns	
	(b) —	M. p. 166–166.5°
	Identical X-ray patterns	
Aniline adduct	M. p. 56.3–56.7°	M. p. 56.5–57.0°
	Identical X-ray patterns	
	Mixed m. p. 56.0–56.7°	
Iodoform test	Negative	Negative
n^{20}_D	1.4180–1.4185	1.4180–1.4185, 1.4192

Despite the apparent identity with the authentic product, the purest ethyl vinyl ketone obtained by the vapor-phase synthesis contained some methyl isopropenyl ketone, as evidenced by the study of some derivatives.

Three products were obtained by treatment with 2,4-dinitrophenylhydrazine of a fraction of the vapor-phase product which, on the basis of its refractive index value of 1.4185, was considered to be pure ethyl vinyl ketone. One of the products gave an X-ray pattern identical with that of the low-melting derivative from known ethyl vinyl ketone. The second derivative gave an X-ray pattern identical with that of the high-melting derivative of known ethyl vinyl ketone. The third, as stated above, gave a pattern identical with those obtained from known methyl isopropenyl ketone.

Two separate and distinct 2,4-dinitrophenylhydrazine derivatives were obtained from the authentic ethyl vinyl ketone. One was easily soluble in ethanol and was crystallized from this solvent. The other derivative was insoluble in ethanol and difficultly soluble in chloroform and acetone. The former derivative had a considerably lower melting point and a lower nitrogen content than the latter.

Polymerization.—Peroxide-catalyzed mass polymerizations were run on the two authentic monomers and on mixtures of the two. Polymethyl isopropenyl ketone was clear, colorless and hard. Polyethyl vinyl ketone was clear, slightly yellow and quite soft, and formed at a much faster rate than its isomer. In copolymerizations it was observed that the higher the ethyl vinyl ketone content of the monomer mixture, the faster was the polymerization rate and the softer was the product.

Experimental[23]

Direct Preparation of Ethyl Vinyl Ketone.—Propionyl chloride (400 g., 4.3 moles) was added slowly to a stirred mixture of carbon disulfide (2000 g.) and anhydrous aluminum chloride (575 g., 4.3 moles). The mixture was cooled to about 0° with stirring and dry ethylene was passed into the mixture for about seven hours. The mixture was next warmed on a water-bath to 40–45°, until the initial brisk evolution of hydrogen chloride had diminished, then allowed to stand overnight. The residue was then poured onto ice; this treatment decomposed the aluminum chloride complex and gave a liquid, two-phase system. The organic layer was washed with dilute hydrochloric acid, water, then dilute sodium bicarbonate solution until an alkaline reaction was obtained. The bulk of the carbon disulfide was removed by distillation through a short, packed column at normal pressure. Water was added to the residue and the mixture was distilled at 150 mm. through a short stillhead. Redistillation of the two-phase distillate through a fractionating column at normal pressure gave ethyl vinyl ketone as the water azeotrope, boiling at 83.1–83.3°[24] (740 mm.). Another distillation

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[23] The authors are indebted to Mr. Douglas C. Sievers for the analyses made in connection with this work and to Dr. Wilbur I. Kaye for the preparation and evaluation of the X-ray diffraction patterns.

[24] All melting points and boiling points are uncorrected, unless otherwise specified.

gave the dry ethyl vinyl ketone, b. p. 102.2° (740 mm.); $n^{20}D$ 1.4192; d^{20}_4 0.8468. The yield was 80 g. (22%). Ethyl vinyl ketone is a water-white liquid with a pronounced odor and lachrymatory action. At room temperature it dissolves about 3% of water.

Preparation of Ethyl β-Chloroethyl Ketone.—A mixture of 300 g. (3.24 moles) of propionyl chloride, 453.6 g. (3.40 moles) of anhydrous aluminum chloride and 1000 ml. of nitrobenzene was cooled to 0°. Ethylene was then added with stirring at 5.0–6.5° for five hours. The reaction mixture was then poured into a mixture of 10% hydrochloric acid and ice. After decomposition of the aluminum chloride complex, the organic layer was quite milky; it was washed with 10% hydrochloric acid until it no longer gave a flocculent precipitate with ammonium hydroxide, and was then separated. The washings were extracted with chloroform, and the combined product and extract was distilled under reduced pressure in the presence of 150 ml. of diethylaniline to neutralize any hydrochloric acid which was liberated during the low-temperature distillation. About 200 ml. of crude chloroketone was collected at 33° (2 mm.).

The combined chloroketone from two runs was refractionated through a 48-in. silvered, vacuum-jacketed column, of 1.5 in. (i. d.), and packed with 8-mm. glass Raschig rings. The mixture distilled at 39–40° (4.5 mm.) for two hours, when hydrogen chloride suddenly was liberated; ethyl vinyl ketone was formed simultaneously. The distillation was stopped and 25 ml. of diethylaniline was added to the residue in the base heater. The distillation was continued, and the product was collected at 32.3–33.3° (2.5 mm.); $n^{20}D$ 1.4361. The yield was 352.5 g. (45%) of a slightly yellow liquid with a not unpleasant odor.

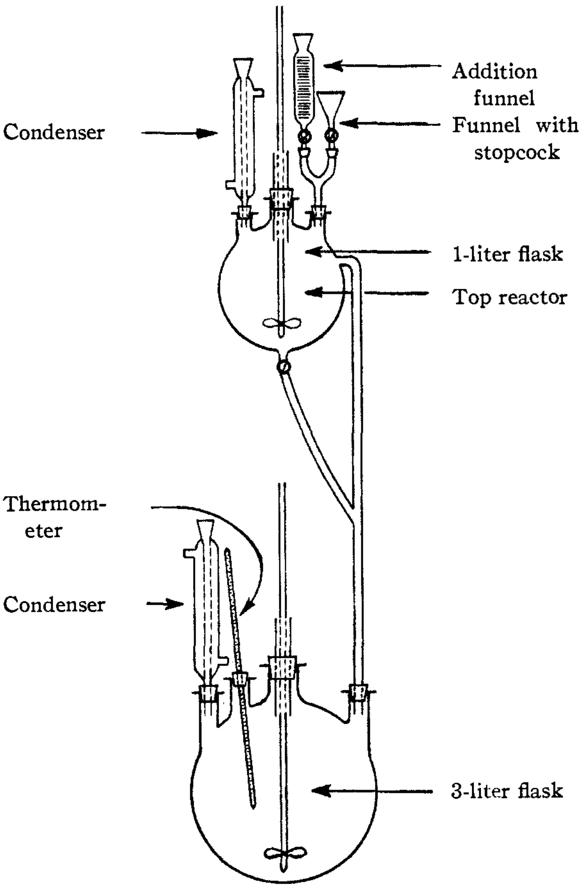

Fig. 2.—Apparatus.

Anal. Calcd. for C_6H_9OCl: Cl, 29.2. Found: Cl, 28.5.

The substitution of chloroform for nitrobenzene resulted in a more easily-handled reaction mixture.

Dehydrohalogenation of Ethyl β-Chloroethyl Ketone.—A mixture of 60 g. of distilled chloroketone and 300 g. of diethylaniline was heated rapidly in a one-liter flask fitted with a thermometer and a still-head, leading to a condenser and a receiver cooled with Dry Ice and acetone. At 160° a violent reaction took place; 60 ml. of distillate was collected. In several runs, a total of 385 ml. of distillate was collected from 352.5 g. of chloroketone.

No ethyl vinyl ketone was produced when 200 g. of chloroketone was fed slowly and continuously below the surface of 2000 ml. of diethylaniline which was maintained at 180°.

Vacuum Fractionation of Crude Ethyl Vinyl Ketone.—The 385 ml. of crude ethyl vinyl ketone from the dehydrohalogenation described above was distilled under reduced pressure in the presence of 300 ml. of distilled water. In addition to about 100 ml. of ethyl chloride, an ethyl vinyl ketone–water fraction boiling at 21–25° (50 mm.) was obtained, of which the upper, non-aqueous layer amounted to 165 ml. This represented a yield from the chloroketone of approximately 57%, and from propionyl chloride of about 25%.

An attempt was made to refractionate an ethyl vinyl ketone fraction, obtained by diethylaniline dehydrohalogenation and with an $n^{20}D$ value of 1.4171, at atmospheric pressure. A polymerization inhibitor ("M. U. F.," Naugatuck Chemical Co.) was added prior to fractionation. Distillate was collected at b. p. 101.1–101.3° (732.8 mm.) for a short time, until the residue became very viscous and began to decompose; the product had an $n^{20}D$ value of 1.4168, indicating little change from the original material.

Preparation of Methyl Isopropenyl Ketone from Acetone and Acetylene.—(a) **Dimethylethinylcarbinol.**—To a solution of 10 parts of acetone and 8 parts of water (by volume) was added solid potassium hydroxide, using 25 g. for each liter of water. This solution was agitated with acetylene in an autoclave at 300 p. s. i. and at 100°. After six hours, the mixture was cooled and treated with sodium bicarbonate. The organic layer was salted out with sodium chloride, separated and fractionally distilled. Yields of 85% were realized. The dimethylethinylcarbinol-water azeotrope boiled at 58° (203 mm.). The dry product boiled at 56° (97 mm.) and at 69.5° (198 mm.); $n^{20}D$ 1.4211; d^{20}_4 0.8614.

(b) **Preparation of Dimethylacetylcarbinyl Acetate.**—The conditions described here for this reaction resulted in higher yields than those described previously.[15]

For this reaction a two-stage reactor system was arranged as shown in Fig. 2. In this operation the acetic acid and catalyst were treated with the dimethylethinylcarbinol in the top reactor and then the incompletely reacted mixture was dropped into the lower reactor, where fresh acetic acid and catalyst were added and the reaction completed.

In the top reactor was placed 110 ml. of a solution of 37 g. of mercuric acetate in 555 g. of glacial acetic acid. This material was heated to 70°, and the addition of dimethylethinylcarbinol was begun at a slow rate. No reaction was apparent, so the temperature was raised to 95° and 110 ml. more of the mercuric acetate solution in acetic acid was added. Then 150 ml. of the carbinol was added slowly. After an elapsed time of eighty minutes, the reaction mixture was run into the lower reactor, where it was held at 95°. After forty-five minutes, 110 ml. more of the mercuric acetate solution was added to the top reactor and heated to 70°. On starting the addition of the carbinol, reaction began at once and the temperature rose above 100°. The flask was cooled by an air blast. The reaction mixture assumed a light reddish-purple color. The carbinol was added at a rate such that the temperature was maintained at 90–95°. After 220 ml. of the carbinol had been added, the solution was run into the lower reactor. This process was repeated until all the dimethylethinylcarbinol (621 g., 7.4 moles) and mercuric acetate solution (37 g. of mercuric acetate in 555 g. of acetic acid) had reacted in the top reactor. The temperature of the lower reactor was maintained at 95°.

After a total elapsed time of four and one-third hours, a solution of 22.2 g. of mercuric acetate in 185 g. of acetic acid was added to the lower reactor. There was no rise in temperature, so the heating mantle was removed. Four hours thereafter, the temperature had dropped to 75°. Stirring was continued for sixteen hours more without addition of heat. The total weight of reaction mixture was 1419 g. On fractional distillation at reduced pressure, 90 g. of dimethylethinylcarbinol (b. p. 56° at 97 mm.) and 373 g. of acetic acid were recovered. There was obtained 896 g. of dimethylacetylcarbinyl acetate, b. p. 75° (20 mm.), 83° (30 mm.), 93° (50 mm.), $n^{20}\text{D}$ 1.4180. The conversion was 84.2% and the yield was 98.5%, based on the carbinol used.

(c) **Pyrolysis of Dimethylacetylcarbinyl Acetate to Methyl Isopropenyl Ketone.**—The pyrolysis step was carried out in a Pyrex tube filled with Pyrex chips. The pyrolysis temperature was maintained at 485°. Nitrogen was fed at the rate of 0.26 cu. ft. per hr. A contact time of 8.4 seconds was maintained. From 500 g. of dimethylacetylcarbinyl acetate 285 g. of methyl isopropenyl ketone was obtained. The yield of product boiling at 38° (85 mm.), ($n^{20}\text{D}$ 1.4235), (d^{20}_4 0.8521) was 97.8% of the theoretical amount. It was much less lachrymatory than ethyl vinyl ketone.

(d) **Methyl Isopropenyl Ketone by Hydration of Isopropenylacetylene.**—In a one-liter, three-necked flask fitted with a centrifugal stirrer, a thermometer and a condenser, was placed a mixture of 540 g. of acetic acid, 162 g. of water and 40 g. of mercuric acetate. During a period of three and one-half hours, 221 g. of isopropenylacetylene was fed into the flask through a spray nozzle in the bottom of the flask. The temperature was maintained at 75–85°. On distillation, 92.7 g. of methyl isopropenyl ketone was obtained and 141 g. of unreacted isopropenylacetylene was recovered. This represented a conversion of 33% and a yield of 91%.

Procedure for Vapor Phase Reaction of Methyl Ethyl Ketone and Formaldehyde and Treatment of the Product.—The vapor-phase reaction between methyl ethyl ketone and formaldehyde was carried out in the following manner. The methyl ethyl ketone and formaldehyde (as formalin) were mixed in the molar ratio of 4 to 1. The mixture was vaporized, then passed through a Johns-Manville type 10X catalyst (magnesium silicate containing 10% chemically combined PbO) at 290–310°. The space velocity, calculated for this reaction temperature, was maintained at about 1000. The product was stabilized with hydroquinone.

The formaldehyde was first removed by extractive distillation of the crude product with water in a packed column under reduced pressure (160 mm.). The pressure was reduced gradually as the base heater temperature rose, to keep the temperature below 50°. The distillate consisted of water, methyl ethyl ketone and unsaturated ketones. The ketone mixture was salted out with sodium chloride and dried with calcium chloride.

The dry ketone mixture was then treated with a polymerization inhibitor and distilled at from 70 to 40 mm. pressure, depending on the base heater temperature, which was kept below 25°. This part of the purification process was controlled by taking frequent refractive index readings at 20° (1.379 for methyl ethyl ketone). The removal of the methyl ethyl ketone was evidenced by a rise in the refractive index and a necessary lowering of the distillation pressure to maintain the base-heater temperature below 25°.

The methyl isopropenyl ketone was next removed, as indicated by a gradual rise of the refractive index of the distillate to about 1.420. The refractive index values started decreasing as the ethyl vinyl ketone component started coming over. Although the reason is not clear, refractive index values as low as 1.417 were obtained at this stage of the distillation. When the base heater temperature would no longer stay below 25° (10 mm.) the distillation was stopped.

It was the practice to combine the fractions from several distillations, like the one described above, as shown in Table IV.

TABLE IV

Composition	$n^{20}\text{D}$ range	Approximate boiling range, °C.
MEK to MIK	1.380–1.410	13 (43 mm.) to 13 (22 mm.)
MIK	1.410–1.421	13 (22 mm.) to 14 (18 mm.)
MIK to EVK	1.421–1.419	14 (18 mm.) to 14.5 (18 mm.)
EVK	1.419–1.417	14.5 (18 mm.) to 12.5 (11 mm.)

These and all other unsaturated ketone fractions were stored in a Dry Ice-chest. When enough of any one composite sample was accumulated, it was distilled, as before, to yield another series of fractions of varying refractive indices, each fraction then being added to the proper composite sample. In this way, quantities of relatively pure methyl isopropenyl ketone and ethyl vinyl ketone were accumulated. These latter composites could then be distilled to obtain samples approaching complete purity. A reasonable refractive index range ($n^{20}\text{D}$) for methyl isopropenyl ketone was considered to be 1.4230 to 1.4235 and, for ethyl vinyl ketone, 1.4180 to 1.4185.

The column used for the purification process consisted of two 48-in. × $1^1/_2$-in. (i. d.) silvered, vacuum-jacketed columns placed end to end and packed with 8 × 8 mm. glass Raschig rings. The oversized packing was considered necessary to reduce the pressure drop through the column. The still head was a total condensation-variable takeoff type, using a Dry Ice–acetone mixture for cooling. Reflux ratios varied from 100-1 to 50-1.

Preparation of 2,4-Dinitrophenylhydrazine Derivatives.—(a) **Authentic Methyl Isopropenyl Ketone.**—A saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid was prepared, allowed to stand for a week, then filtered.

A solution of 10 ml. of methyl isopropenyl ketone (b. p. 38.5° at 87.5 mm.) in 20 ml. of 95% ethanol was added to a liter of the above solution. The crude product obtained was boiled with ethanol and filtered. The first crop of crystals from the filtrate melted at 179–181°. The mother liquor was concentrated and cooled to obtain a second crop melting at 171–176°.

The product remaining undissolved in the initial boiling with ethanol was crystallized from chloroform. The first crop of crystals melted at 184–186° (189.5–191.5° cor.).

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: N, 21.21. Found: N, 21.29 (Dumas).

The mother liquor was concentrated and cooled to obtain a second crop melting at 179–181°.

The X-ray diffraction patterns of all four fractions were identical.[25]

(b) **Vapor-Phase Methyl Isopropenyl Ketone.**—A solution of 5 ml. of methyl isopropenyl ketone ($n^{20}\text{D}$ 1.4235) in 10 ml. of 95% ethanol was treated with the 2,4-dinitrophenylhydrazine solution described above. The crude product was worked up as described in (a). The first and second crops of crystals from ethanol melted at 179–184° and 171–173°, respectively. The first and

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(25) X-Ray diffraction patterns were not microphotometered, nor were they originally photographed for the purpose of obtaining the most accurate "*d*" values, but for the purpose of comparison. This led to some discrepancy in measured "*d*" values, although the patterns superimposed nicely. The intensities were measured by eye only. Patterns of derivatives of known compounds were taken with unfiltered radiation from a copper target tube. Patterns of the derivatives of the unknown ketones were taken with filtered radiation from a copper target tube.

second crops from chloroform melted at 179–186° and 183–185°.

(c) **Authentic Ethyl Vinyl Ketone.**—A solution of 10 ml. of ethyl vinyl ketone ($n^{20}\text{D}$ 1.4183), in 25 ml. of ethanol was added dropwise to a liter of the 2,4-dinitrophenylhydrazine solution. The precipitate was nonhomogeneous. One portion was soluble in ethanol and was recrystallized from this solvent. It melted at 128.8–129.0°. It probably was the adduct to the olefinic linkage.

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: N, 19.85. Found: N, 19.44 (Dumas).

The other portion was insoluble in ethanol, but was soluble with difficulty in chloroform and in acetone. After recrystallization from chloroform, it melted at 166–166.5°, with shrinkage at 164°. It probably was the 2,4-dinitrophenylhydrazone or the isomeric pyrazoline-type compound.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: N, 21.21. Found: N, 21.80 (Dumas).

(d) **Vapor-Phase Ethyl Vinyl Ketone.**—A solution of 10 ml. of a fraction having $n^{20}\text{D}$ 1.4185, isolated from the methyl ethyl ketone–formaldehyde reaction product, was added to a liter of the 2,4-dinitrophenylhydrazine solution, as described above. The precipitate was extracted with hot ethanol and the soluble portion was recrystallized from the same solvent. The purified product (I) gave an X-ray diffraction pattern identical with that of the lower-melting derivative from authentic ethyl vinyl ketone.

The alcohol-insoluble portion was recrystallized several times from chloroform and from acetone successively, and was finally separated into two fractions. One of these (II) gave an X-ray diffraction pattern which was identical with that of the higher-melting derivative from authentic ethyl vinyl ketone. The other fraction (III) gave an X-ray diffraction pattern which was identical with those of the four fractions of the product from authentic methyl isopropenyl ketone, which were all the same. Compound III melted at 180.3–181.2° and was analyzed for nitrogen.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: N, 21.21. Calcd. for $C_{12}H_{14}N_4O_5$: N, 19.85. Found: N, 20.61 (Dumas).

Preparation of Semicarbazide Derivatives.—(a) **Authentic Methyl Isopropenyl Ketone.**—The semicarbazide derivative was prepared by treatment of the ketone in dilute alcohol with a solution of semicarbazide hydrochloride buffered with sodium acetate. The product was crystallized from water and melted at 172.6–173.5 (cor.).

Anal. Calcd. for $C_6H_{11}N_3O$: N, 29.79. Found: N, 29.79 (Dumas).

(b) **Vapor-Phase Methyl Isopropenyl Ketone.**—This derivative was prepared from a product having $n^{20}\text{D}$ 1.4235 and $d^{20}{}_4$ 0.8529. It was crystallized from water and melted at 172.6–173.4° (cor.).

Anal. Calcd. for $C_6H_{11}N_3O$: N, 29.79. Found: N, 30.03 (Dumas).

A mixed melting point determination gave a value of 172.3–173.9° (cor.). The X-ray diffraction patterns were identical.

(c) **Authentic Ethyl Vinyl Ketone.**—On treatment of ethyl vinyl ketone in a similar way, no derivative formed. On continued standing, polymerization apparently occurred.

Hydrogenation.—(a) **Methyl Isopropyl Ketone from Authentic Methyl Isopropenyl Ketone.**—Two moles (168 g.) of authentic methyl isopropenyl ketone, diluted to 400 ml. with ethanol, was placed in an 800-ml. steel rocking autoclave. Approximately 4 g. of Raney nickel was added; an amount of hydrogen calculated to be 1.1 moles was then placed in the autoclave under 1080 p. s. i. After eight and one-half hours of agitation at 20–32° the pressure had dropped to 20 p. s. i. The mixture was filtered and fractionally distilled. After removal of the ethanol there was obtained 56 g. of a fraction boiling up to 55° (236 mm.), of which 87% was methyl isopropyl ketone. The second fraction, consisting of 84 g., boiled at 56° (238 mm.), $n^{20}\text{D}$ 1.3883, $d^{20}{}_4$ 0.8035. The residue was a mixture of 17.5 g. of methyl isopropyl ketone and 5 g. of methylisopropylcarbinol.

A 2,4-dinitrophenylhydrazone prepared from the second fraction melted at 124.7°. The X-ray diffraction pattern was correct for that of the corresponding derivative of known methyl isopropyl ketone.

(b) **Methylisopropylcarbinol from Authentic Methyl Isopropenyl Ketone.**—One mole (84 g.) of methyl isopropenyl ketone was treated with 2.5 g. of Universal Oil Products Company nickel catalyst and diluted to approximately 150 ml. with ethanol. The hydrogenation was carried out in the 800-ml. steel autoclave, using a hydrogen pressure of 1500 p. s. i. for four hours at 80°.

The mixture was filtered and fractionally distilled at 733.8 mm. pressure. The first fraction, after removal of the ethanol, was collected up to 111° and amounted to 21 g. The second fraction boiled at 111–115° and amounted to 58.9 g. ($d^{20}{}_4$ 0.8162, $n^{20}\text{D}$ 1.4098).

The α-naphthylurethan of the second fraction melted at 112.8°.

Anal. Calcd. for $C_{16}H_{19}NO_2$: N, 5.45. Found: N, 5.30.

A similar derivative was prepared from authentic methylisopropylcarbinol, which was made from acetaldehyde and isopropyl bromide by the Grignard reaction. It melted at 112.0°.

Anal. Calcd. for $C_{16}H_{19}NO_2$: N, 5.45. Found: N, 5.48.

The mixed melting point value was 112.1°.

(c) **Diethylcarbinol from Authentic Ethyl Vinyl Ketone.**—Approximately two moles of authentic ethyl vinyl ketone diluted to about 400 ml. with ethanol was hydrogenated at 70° for four hours under a pressure of 2000 p. s. i., with 5 g. of Raney nickel catalyst. The reduction was conducted in the 800-ml. rocking autoclave. The reaction mixture was filtered and fractionally distilled at 731.6 mm. pressure. After removal of the ethanol and an intermediate fraction there was obtained the diethylcarbinol fraction, boiling at 112–113°.

The phenylurethan of the product, crystallized from petroleum ether, melted at 48.9–49.5° (cor.), which is correct for this compound.

The 3,5-dinitrobenzoate of the product melted at 98.6°. A similar derivative of commercial diethylcarbinol (Sharples Chemical Company) melted at 97.4°. The mixed melting point value was 98.2°.

Aniline Adducts.—(a) **Authentic Methyl Isopropenyl Ketone.**—To 73.7 g. (0.88 mole) of authentic methyl isopropenyl ketone was added 81.5 g. (0.88 mole) of aniline. After standing for sixteen hours at room temperature the mixture was clear, amber and viscous. No odor of either reactant was noticeable. The mixture stood for two weeks before being distilled. The product distilled at 72° (50 microns).

Anal. Calcd. for $C_{11}H_{15}NO$: N, 7.92. Found: N, 8.00.

(b) **Authentic Ethyl Vinyl Ketone.**—To 10 ml. of aniline was added 10 ml. of authentic ethyl vinyl ketone. After standing one day at room temperature about half of the mixture had solidified. On the fifth day the crystals were removed and recrystallized several times from alcohol. The product melted at 56.5–57.0°. Infrared examination showed carbonyl absorption.

Anal. Calcd. for $C_{11}H_{15}NO$: N, 7.92. Found: N, 8.07.

(c) **Vapor-Phase Ethyl Vinyl Ketone.**—To 507 g. of a composite of fractions of the methyl ethyl ketone–formaldehyde reaction product having an $n^{20}\text{D}$ range of 1.4085 to 1.4195 were added 300 g. of aniline and 500 ml. of toluene. After standing one day at room temperature, the mixture was distilled. After removal of 208 g., b. p. 15.3–17.6° (30.5–22.5 mm.), $n^{20}\text{D}$ 1.4183 and 122 g., b. p. 11.8–15.4° (20.5–18 mm.), $n^{20}\text{D}$ 1.4339, the residue was

TABLE V

Number	EVK	1	2	3	4	5	6	7	8	9	MIK
% MIK in monomer mixture	0	10.47	20.49	29.37	39.91	50.25	60.24	70.41	80.50	89.43	100
n^{20}_D	1.4182	1.4189	1.4195	1.4200	1.4204	1.4210	1.4214	1.4220	1.4225	1.4230	1.4233
d^{20}_{20}	0.8497	0.8498	0.8504	0.8503	0.8508	0.8522	0.8524	0.8532	0.8537	0.8539	0.8541
Days to form solid polymer	1	1	1	2	3	2	4	4	5	6	6
Degree of yellow color (relative)	1	1	2	3	4	5	4	3	2	1	1
Rockwell hardness (15X)		Too soft to test			69.7	82.5	90.0	92.1	92.8	93.0	94.5

set aside at Dry Ice temperature overnight. A considerable quantity of a white, crystalline solid separated; a portion, crystallized from absolute ethanol, melted at 56.3–56.7°. The mixed melting point value was 56.0–56.7°.

Polymerization.—A series of mixtures of the two authentic monomers was prepared for refractive index and density determinations. To 10 ml. of each mixture was added 0.1 ml. of a commercial 30% solution of acetyl peroxide in dimethyl phthalate. The reactions were run in sealed ampoules at 40°. The results are presented in Table V.

Summary

The syntheses of authentic ethyl vinyl ketone and methyl isopropenyl ketone by independent routes have been described.

By comparison of the properties of these products with those of the purified materials isolated from the catalytic vapor phase reaction of methyl ethyl ketone and formaldehyde, it has been established that the vapor-phase reaction leads to the formation of both ketones.

The physical properties of the ketones and of some of their derivatives have been described.

KINGSPORT, TENNESSEE RECEIVED FEBRUARY 16, 1948

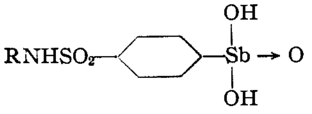
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Preparation of Aromatic Stibonic Acids of Certain Benzenesulfonamides

BY ROBERT D. ENGLERT[1] AND ORVILLE J. SWEETING

In connection with work in this Laboratory on the chemotherapy of Schistosomiasis it was of interest to prepare for test pure samples of stibonic acids derived from certain sulfonamides: sulfanilamide, sulfathiazole, sulfapyridine, and sulfadiazine. For the tests of biological activity, it was necessary to obtain the stibonic acids free from extraneous toxic antimony compounds such as the oxides.

The structure of these compounds in the solid state, all of which melt at high temperatures, has been explained in terms of polymers associated through hydrogen bonding,[2] but for simplicity these compounds may be formulated as follows, I representing the acid and II the corresponding hydrated form, in which R represents hydrogen or the 2-thiazolyl, 2-pyridyl, or 2-pyrimidyl radical.



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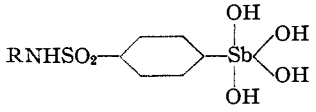

II

Two methods of synthesis have been used, with concordant results: decomposition of the aryldiazonium fluoborate salts in a manner similar to that used for preparing aromatic arsonic acids,[3] and a modified Scheller reaction.[4]

In many cases it has been found that different preparations of the same stibonic acid give inconsistent analyses when purified by double precipitation methods from alkaline solution by addition of strong acid; it was for this reason that the pyridinium arylchloroantimonates,[5] $[ArSbCl_5]^-[C_5H_5NH]^+$, were recrystallized from a solvent of mixed hydrochloric acid and ethanol. This procedure gave quite pure aromatic stibonic acids except with the product from sulfapyridine. The latter acid was purified only with difficulty, since the pyridine nucleus of the stibonic acid no doubt retains some antimony.

Experimental Part

Melting points were observed with a Fisher-Johns melting point apparatus and are uncorrected unless otherwise stated. Analyses for antimony were done by a micro titration with standard potassium bromate solution and for chloride by the micro Volhard method, using 5- to 10-mg. samples of the stibonic acid.

Preparation of an Aromatic Stibonic Acid *via* the Diazonium Fluoborate.—Diazonium fluoborates have not been extensively used for the preparation of organic arsenical and antimonial compounds. In many instances, however, the fluoborates are advantageous to use instead of other diazonium compounds since their stability toward heat results in diminished tendency to form undesirable products.[6] It was therefore thought advisable to investi-

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[1] Fellow in Chemistry at the Chemical Foundation Laboratory, by grant from the U. S. Public Health Service.

[2] Doak, THIS JOURNAL, **68**, 1991 (1946).

[3] Ruddy, Starkey and Hartung, *ibid.*, **64**, 828 (1942); Hamilton and Morgan in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 419.

[4] Scheller, British Patent 261,026 (1925) [*C. A.*, **21**, 3371 (1927)]; French Patent 624,028 [*Chem. Zentr.*, **98**, II, 2229 (1927)]; Doak, THIS JOURNAL, **62**, 167 (1940).

[5] Doak and Steinman, *ibid.*, **68**, 1987 (1946).

[6] See Hamilton and Morgan, ref. 3.