β-dimethylaminoacrylate to ethyl trimesate, which is the end-product of the self condensation of ethyl formylacetate. This appears to be characteristic of the structure $R_2NCH{=}CH$—.[6]

Experimental

Raw Materials.—Alkyl β-alkoxyacrylates were supplied through the courtesy of Dr. W. J. Croxall of this Laboratory, and were prepared by the methods described by him.[5] The amines were commercial products used without purification.

General Procedure.—The following preparations are representative.

Ethyl β-Piperidinoacrylate.—To a mixture of ethyl β-ethoxyacrylate (57.6 g., 0.4 m.) and 20 g. of anhydrous potassium carbonate, heated on the steam-bath with stirring, piperidine (34 g., 0.4 m.) was added dropwise over a fifteen-minute period. The reaction mixture was heated on the steam-bath under reflux for four hours, filtered to remove potassium carbonate and distilled to yield 57.5 g. (79%) of ethyl β-piperidinoacrylate.

Ethyl β-Dimethylaminoacrylate.—To a mixture of ethyl β-ethoxyacrylate (144 g., 1 m.) and 50 g. of anhydrous potassium carbonate, contained in a flask equipped with gas inlet tube, stirrer and acetone–Dry Ice condenser. was added dimethylamine gas (45 g., 1 m.) at 25°. The mixture was stirred for several hours at room temperature, filtered to remove potassium carbonate and distilled. After removal of alcohol and unreacted ethyl β-ethoxyacrylate (31 g.) there was recovered 92 g. (53%) of ethyl β-dimethylaminoacrylate.

Hydrolysis of Ethyl β-Dimethylaminoacrylate.—Thirty grams of dilute hydrochloric acid (1:1) was added to ethyl β-dimethylaminoacrylate (21.5 g., 0.15 m.). The material formed a homogeneous solution which deposited an oily lower layer. After two weeks, crystals were present in this layer, and these were filtered off. The m. p. (132–135°) corresponded to that of triethyl trimesate and this was confirmed by a mixed m. p. with an authentic sample. Only a few grams of crystals were obtained; the remainder of the oil may have represented intermediate stages of condensation.

Acknowledgments.—To Dr. E. L. Stanley who directed the analytical work, and to Mr. E. J. Smialkowski for assistance in the experimental work.

Summary

A number of β-dialkylaminoacrylic esters have been prepared by the interchange reaction of β-alkoxyacrylic esters with secondary amines. The ease with which these reactions occur indicates a surprising degree of labilization by the single ester group.

PHILADELPHIA, PA. RECEIVED FEBRUARY 6, 1950

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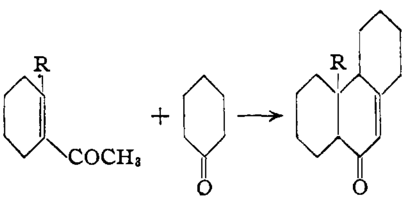
(6) Mannich and Davidsen, *Ber.*, **69B**, 2106 (1936).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Condensation of 1-Methyl-2-acetylcyclohexene with 1-Decalone, and with 1,5-Decalindione

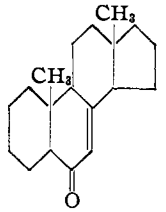
BY WILLIAM S. JOHNSON, JACOB SZMUSZKOVICZ[1] AND MAX MILLER[2]

The extension of the Robinson–Rapson synthesis[3]—typified by the base-catalyzed reaction between 1-acetylcyclohexene, I (R = H), and cyclohexanone to produce the ketododecahydrophenanthrene II (R = H)—to the production of fused ring systems containing the angular methyl group has been investigated by Huber,[4] who studied the condensation between 1-methyl-2-acetylcyclohexene, I (R = CH_3), and cyclohexanone. The product of this reaction was an oil, $\lambda_{max.}$ 238 mμ (in ether) (*E ca.* 2050), of expected composition which gave a semicarbazone in unspecified yield and on dehydrogenation with selenium afforded phenanthrene also in unspecified yield. From these observations Huber concluded that his product had the expected structure II (R = CH_3).

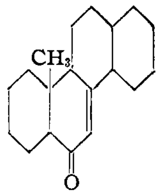


I II

On the basis of Huber's report, Bagchi and Banerjee[5] proposed the structure III for the product of the condensation of I (R = CH_3) with 8-methyl-4-hydrindanone, and Dimroth[6] similarly assigned the structure IV to the condensation product of I (R = CH_3) with 1-decalone. In the present paper we are reporting the results of some studies of condensations with 1-methyl-2-acetylcyclohexene, which force us to the conclusion that all of these structures II (R = CH_3), III and IV are open to question.



III



IV

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[1] Sterling-Winthrop Research Institute, and Wisconsin Alumni Research Foundation Postdoctoral Fellow 1948–1949; U. S. National Institute of Health Postdoctoral Fellow 1949–1950. On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

[2] Wisconsin Alumni Research Foundation Research Assistant 1949–1950.

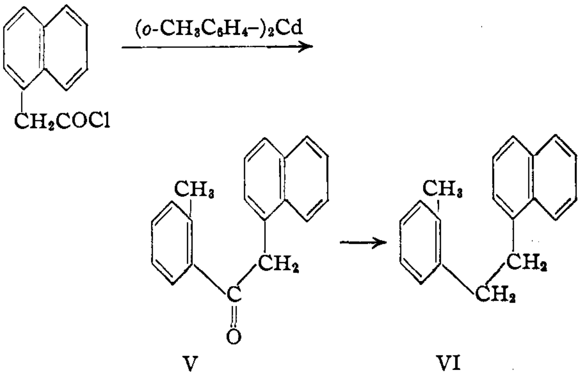
(3) Rapson and Robinson, *J. Chem. Soc.*, 1285 (1935); Crowfoot, Rapson and Robinson, *ibid.*, 757 (1936); Peak and Robinson, *ibid.*, 759(1936).

(4) Huber, *Ber.*, **71**, 725 (1938).

(5) Bagchi and Banerjee, *J. Ind. Chem. Soc.*, **23**, 397 (1946).

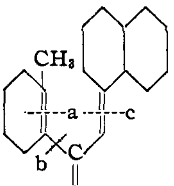
(6) Dimroth, *Angew. Chem.*, **59**, 215 (1947).

When 1-methyl-2-acetylcyclohexene and 1-decalone were allowed to condense in the presence of a mixture of potassium and aluminum *t*-butoxide, a high-boiling oil was produced in 37% yield. Although this material gave no ketone derivatives, the presence of the α,β-unsaturated carbonyl system was indicated by the ultraviolet absorption spectrum $\lambda_{\text{max.}}$ 248.5 mμ (*E* 6982). When this product was treated with lithium aluminum hydride, then dehydrated over potassium acid sulfate, and finally dehydrogenated over palladium-on-charcoal, there was no evidence of the presence of chrysene which would be the expected product from IV. Instead there was produced a crystalline hydrocarbon, $C_{19}H_{18}$ (isolated in 28% yield as the di-picrate) which was shown to be 1-(α-naphthyl)-2-(*o*-tolyl)-ethane (VI) by comparison with an authentic specimen prepared by the addition of di-(*o*-tolyl)-cadmium to 1-naphthylacetyl chloride followed by Wolff–Kishner reduction of the resulting ketone V, as depicted in the accompanying flow sheet.

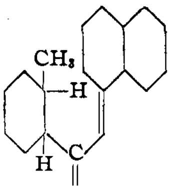


V VI

These observations suggest that the original condensation proceeded by an aldol condensation between the carbonyl group of 1-decalone and the reactive hydrogens of the acetyl group of I ($R = CH_3$) to produce the structure VII. Confirmation of this structure was afforded by ozonization experiments which yielded δ-acetylvaleric acid, $CH_3COCH_2CH_2CH_2CH_2COOH$ (by cleavage at points a and b) and 1-decalone (by cleavage at point c).



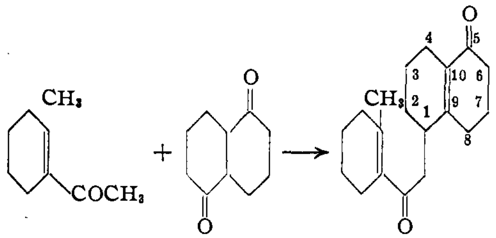
VII



VIII

It seems probable that the mechanism of the Robinson–Rapson reaction involves a Michael addition of the cyclic ketone to the α,β-unsaturated ketone followed by an intramolecular aldol condensation. In the present case the additional methyl group attached to the β-carbon of the α,β-unsaturated ketone system apparently inhibits the Michael addition so that an intermolecular aldol condensation occurs thus precluding cyclization.[7] The possibility that VII was formed from IV by a reversal of the Michael reaction seemed unlikely when it was found that 1-methyl-2-acetylcyclohexane condensed with 1-decalone just like the unsaturated ketone I ($R = CH_3$) giving what was undoubtedly VIII, as shown by the dehydrogenation sequence to give VI. The α,β-unsaturated carbonyl system was apparent from the absorption, $\lambda_{\text{max.}}$ 247 mμ (*E* 6800), which was similar to that of VII.[8]

The conclusion that Dimroth's product was indeed VII is valid provided the likely assumption is made that the different conditions employed by us (potassium *t*-butoxide instead of amyloxide) did not alter the course of the reaction. When aluminum *t*-butoxide, which is a good catalyst for the aldol condensation,[9] was also added to the reaction mixture, the condensation proceeded more cleanly, fewer tarry by-products being formed. The course of the reaction, however, did not appear to be altered by this modification as shown below in the decalindione study. The isolation of phenanthrene by Huber on dehydrogenation of his cyclohexanone condensation product suggests the presence of at least a small amount of cyclized material, but unfortunately no yield or experimental details were reported for this degradation.[9a]



IX X

The mole for mole condensation of I ($R = CH_3$) with 1,5-decalindione (IX) was also studied and found to give (with or without added aluminum *t*-butoxide) an oily product in better than 60% yield,[10] about half of which was obtained crystalline. This material, m. p. 66–67°, was shown to

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[7] It seems unlikely that a system VII would undergo an intramolecular Michael type of addition to give IV, because the formation of the necessary resonating anion involving the 2-position of the decalin nucleus, would concomitantly inhibit the polarizing effect of the carbonyl group on the double bond in the cyclohexane nucleus.

[8] The principal absorption of this type of dienone may be close to that of the eneone. *Cf.* for example the spectrum of 1,4-cholestadiene-3-one, $\lambda_{\text{max.}}$ 236 mμ (*E* 15,800), with that of 4-cholestene-3-one, $\lambda_{\text{max.}}$ 234 mμ (*E* 16,400); Dannenberg, *Abhandl. preuss. Akad. Wiss.*, **21**, 26 (1939). *Cf.* however, phorone and mesityl oxide.

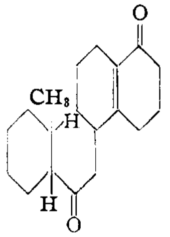
[9] Wayne and Adkins, THIS JOURNAL, **62**, 3401 (1940).

[9a] ADDED IN PROOF.—Dr. Richard B. Turner has kindly informed us that attempts to repeat the work of Huber have given a product which proved to consist largely of uncyclized material having a structure analogous to VII.

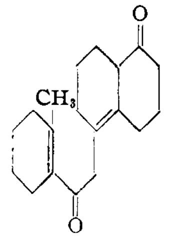
[10] The yield dropped to about 17% when the condensation was carried out by a procedure similar to Huber's (ref. 4).

have the structure X[11] as follows. The high extinction coefficient (E 19,950) of the ultraviolet absorption maximum at 249.5 mμ is approximately that expected from the sum of the E (*ca.* 13,820) for the octalone system as in compound XI (see below), and E (<6,500) for the other α,β-unsaturated carbonyl system as in I ($R = CH_3$).[12] The reduction–dehydration–dehydrogenation sequence (see above) yielded mainly VI, along with a small amount of a crystalline hydrocarbon which was identified as 1-methylchrysene by comparison with authentic material.[13] The product undoubtedly arose from some cyclization during the dehydrogenation treatment.[14] Ozonization of the condensation product gave δ-acetylvaleric acid, but no decalindione. It readily formed a monosemicarbazone having $\lambda_{\max.}$ 268 mμ (E 34,700) characteristic of an α,β-unsaturated semicarbazone, and hydrolysis of the derivative regenerated the original ketone, indicating that no bond shift occurred during semicarbazone formation. If the olefinic bonds were both conjugated with the exocyclic carbonyl group as in compound VII (which gives no semicarbazone), the isolated keto group in the decalin nucleus would have undoubtedly been involved in the semicarbazone reaction to give a product which would not be expected to absorb above 249 mμ. Of the two keto groups in X, it seems more likely from steric consideration that the semicarbazide would preferentially attack the one in the decalin nucleus. That such behavior is reasonable was shown by a study of the condensation product of 1-methyl-2-acetylcyclohexane and 1,5-decalindione. This substance, m. p. 68.8–69.7°, had a $\lambda_{\max.}$ 247.5 mμ (E 13,820), gave VI on dehydrogenation and, like X, readily formed a mono-α,β-unsaturated semicarbazone, $\lambda_{\max.}$ 268 mμ (E 30,530) which on hydrolysis regenerated the original ketone. In view of the fact that the corresponding product VIII in the 1-decalone series failed to form a semicarbazone, it follows from an argument analogous to that developed above for the structure of X, that this 69° product has the structure XI,[11] and the semicarbazone formation involves the keto group in the decalin nucleus.

The rearrangement of the olefinic bond which is formed as a result of the aldol condensation with 1,5-decalindione, is entirely reasonable in view of the well-known fact that α,β-unsaturated ketones having a hydrogen atom on the γ-carbon may undergo reversible rearrangement, particularly under the influence of alkali, to the β,γ-unsaturated ketone. In the present cases one of the two possible β,γ-tautomers of the expected product (analogous to VII) is represented by formula XII. With the bond thus placed in the decalin nucleus, this becomes also a β,γ-tautomer of the actual product X or XI, which is therefore probably produced by a second 3-carbon tautomeric shift. The possibility of the olefinic bond resting at the 4,10-instead of the 9,10-position of the decalin nucleus, accordingly, seems doubtful.



XI



XII

Experimental Part[15,16]

Condensation of 1-Methyl-2-acetylcyclohexene with 1-Decalone.—To a refluxing solution of 9.08 g. (0.0657 mole) of 1-methyl-2-acetylcyclohexene,[17] 10 g. (0.0657 mole) of 1-decalone (purified *via* the bisulfite addition compound; b. p. 240–241° at 740 mm.), and 32.4 g. of aluminum *t*-butoxide in 270 ml. of dry *t*-butyl alcohol was added dropwise with stirring to a solution of 3.85 g. of potassium in 100 ml. of dry *t*-butyl alcohol. After the addition was complete (one hour) the reaction mixture, which had turned to an orange color, was heated under reflux for an additional six hours, then cooled and poured onto a mixture of ice and 500 ml. of 20% sulfuric acid. The aqueous solution was saturated with salt, and extracted thoroughly with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, then with water, and dried over anhydrous sodium sulfate. Evaporation of the ether and *t*-butyl alcohol left an orange oil which was distilled through a 4-inch Vigreux column, yielding 7.6 g. of a mixture of starting materials, b. p. 81–106° (14 mm.) and 6.58 g. (37% of crude **1-methyl-2-(decahydro-1-naphthylideneacetyl)-1-cyclohexene** (VII), b. p. 150–156° (0.35 mm.)). The pale-yellow fraction boiling at 150–152° (0.35 mm.) was analyzed, $\lambda_{\max.}$ 248.5 mμ (E 6,982).

Anal. Calcd. for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.20; H, 10.20.

All attempts to form a semicarbazone or a 2,4-dinitrophenylhydrazone from this material failed.

Dehydrogenation of VII.—To a solution of 0.7 g. of lithium aluminum hydride in 100 ml. of dry ether was added 0.627 g. of the above condensation product in 50 ml. of dry ether, and the mixture was boiled under reflux for thirty minutes. After standing at room temperature overnight, water was added cautiously to decompose the excess hydride, and the mixture was then poured into ice and 60 ml. of 20% sulfuric acid. The product was taken up in ether, dried over anhydrous sodium sulfate and after

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(11) The alternate conjugated position for the double bond at 4,10 in the decalin nucleus has not been eliminated, but seems less probable.

(12) The low E value for I ($R = CH_3$) has been explained by Braude, Jones, Koch, Richardson, Sondheimer and Toogood, *J. Chem. Soc.*, 1890 (1949), as resulting from a steric inhibition of resonance. Such an effect should be even more pronounced in the more hindered system in question (see formula X).

(13) We are indebted to Professor W. E. Bachmann of the University of Michigan for supplying us with a sample of 1-methylchrysene prepared by the method of Bachmann and Struve, *J. Org. Chem.*, **5**, 416 (1940).

(14) *Cf.* Cook and Hewett, *J. Chem. Soc.*, 1098 (1933); Graebe and Bungener, *Ber.*, **12**, 1078 (1879); Ruzicka and Hösli, *Helv. Chim. Acta*, **17**, 470 (1934); Buu-Hoi and Hoan, *J. Org. Chem.*, **14**, 1023 (1949).

(15) All melting points are corrected for stem exposure.

(16) All ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer. Unless otherwise specified, 95% alcohol was employed as the solvent.

(17) Prepared from acetyl chloride and methylcyclohexene by the procedure of Ruzicka, Koolhaas and Wind, *Helv. Chim. Acta*, **14**, 1151 (1931).

evaporation of the ether, the yellow oily residue was heated at 170° with 0.65 g. of potassium bisulfate in a sublimation tube under nitrogen for fifteen minutes. Evaporative distillation at 110–115° (0.1 mm.) gave 0.51 g. of a pale yellow oil which was dehydrogenated with 0.3 g. of 30% palladium-on-carbon[18] at 320–360°. After heating for two hours the evolution of hydrogen was very slow. The product was separated from the catalyst by ether extraction, and then evaporatively distilled at 110–130° (0.05 mm.). Near the end of the distillation a small amount of solid material sublimed. After recrystallization once from benzene, then from toluene, it was obtained as colorless plates (3 mg.), m. p. 254.1–255°, undepressed on admixture with an authentic specimen of 1-methylchrysene (m. p. 255.6–256.6°).[13] On admixture with chrysene the m. p. was depressed to 243–246°.

The main product from the evaporative distillation was a yellow oil amounting to 0.240 g. (42% yield), which was treated with 0.44 g. of picric acid in 4 ml. of a saturated solution of picric acid in ethanol. The crude dipicrate which formed amounted to 0.45 g., m. p. 130–132°. Recrystallization from alcohol gave a product, m. p. 135.5–136°, which had a satisfactory analysis for C and H and which showed no m. p. depression on admixture with the specimen of VI prepared by an independent synthesis described below.

A sample of the picrate was decomposed by passing a solution in alcohol through a column of activated alumina. The oily eluate was crystallized from methanol giving colorless fluorescent plates, m. p. 53.2–54°, undepressed on admixture with the specimen of VI as described below. The ultraviolet absorption curves of the two hydrocarbons were likewise identical: $\lambda_{\max.}$ 225 mμ (*E* 86,200), 272 (8,760), 282.5 (9,620), 313.5 (1,208); $\lambda_{\min.}$ 247.5 mμ (*E* 39,600), 276.5 (8,000), 311.5 (1,095); inflections at 262.5–266 mμ (*E* 6,390), 290–293 (6,770), 335 (5,851).

The trinitrobenzene complex formed from the crystalline hydrocarbon was obtained from alcohol in the form of short yellow rods, m. p. 141–142°, undepressed on admixture with the trinitrobenzene complex of VI described below.

Synthesis of 1-(α-Naphthyl)-2-*o*-tolylethane (VI).—The Grignard reagent prepared from 0.294 g. of magnesium and 2.06 g. of *o*-bromotoluene in 40 ml. of dry ether was treated with 1.1 g. of cadmium chloride, and the mixture was allowed to reflux with stirring for two hours. A solution of 2.46 g. of α-naphthylacetyl chloride in 40 ml. of benzene was then added dropwise over a period of one hour at room temperature. The mixture was refluxed for an additional hour, and after standing overnight at room temperature decomposed with ice and hydrochloric acid and extracted with ether. The ether extracts were washed thoroughly with 2% sodium hydroxide solution, then with saturated salt solution, and finally dried over anhydrous sodium sulfate. Evaporation of the ether left an oil (3.44 g.) which was submitted to evaporative distillation at 0.05 mm. The fraction volatilizing at 120–150° amounted to 1.58 g. and was induced to crystallize from ether solution at −70°. This product, **1-naphthylmethyl *o*-tolyl ketone** (V), crystallized from methanol in the form of colorless prisms, m. p. 67.8–68.6° with softening at 67.2°. This material did not yield a semicarbazone by normal procedures.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.20. Found: C, 87.49; H, 6.33.

This substance had the following absorption characteristics: $\lambda_{\max.}$ 224 mμ (*E* 98,000), 273 (9,091), 278 (9,641), 282 (10,520), 312.5 (1,036); $\lambda_{\min.}$ 265 mμ (*E* 7,240), 274 (9,000), 279 (9,561), 311.5 (1,030); inflections at 238 mμ (*E* 13,550), 276–277 (9,260), 292.5 (7,944).

A 0.9-g. sample of the ketone was reduced according to the procedure of Huang–Minlon[19] by gently refluxing with 4.65 g. of 85% hydrazine hydrate and 0.65 g. of potassium hydroxide in 20 ml. of ethylene glycol. After one hour the condenser was removed and the solution allowed to evaporate until the temperature of the vapors rose to about 195°. The condenser was replaced, refluxing continued for two hours, then the mixture was cooled and poured into dilute hydrochloric acid. The aqueous solution was extracted with ether, the ether extracts washed with water and dried over anhydrous sodium sulfate. Evaporation of the ether gave 0.81 g. of a yellow oil which on crystallization from methanol afforded the hydrocarbon (VI) as colorless plates, m. p. 53.5–54.2°. This product gave no m. p. depression on admixture with the hydrocarbon which was obtained by dehydrogenation of X (described below) and which melted at 53.2–54° and had the analysis:

Anal. Calcd. for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.69; H, 7.42.

The **di-picrate** formed as described above crystallized from ethanol in the form of yellow rods, m. p. 134–135°. It gave no depression of the m. p. on admixture with the di-picrate which was obtained upon dehydrogenation of X (see below) and which melted at 135.5–136° and had the analysis:

Anal. Calcd. for $C_{31}H_{24}O_{14}N_6$: C, 52.84; H, 3.43; N, 11.93. Found: C, 53.14; H, 3.23; N, 11.88.

The ***bis*-trinitrobenzene complex** prepared as described above was obtained from alcohol as yellow rods, m. p. 141–142°.

Anal. Calcd. for $C_{31}H_{24}O_{12}N_6$: C, 55.36; H, 3.60. Found: C, 55.72; H, 3.93.

1-(α-Naphthyl)-2-*o*-tolylethylene.—A 40-mg. sample of the ketone V in 10 ml. of ether was reduced with a solution of 0.3 g. of lithium aluminum hydride in 50 ml. of ether. The crude oily carbinol, isolated as described above, was dehydrated by heating at 155-164° with 50 mg. of potassium bisulfate for ten minutes under nitrogen. Evaporative distillation at 130–160° (0.05 mm.) gave 29 mg. of colorless distillate which crystallized on standing, m. p. 64–68°. Recrystallization from methanol gave a colorless product, m. p. 68–72.4° softening at 63°, $\lambda_{\max.}$ 226 mμ (*E* 41,100), 309 (13,490), 314 (13,700); $\lambda_{\min.}$ 282 mμ (*E* 8,780), 310 (13,420).

Anal. Calcd. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.69; H, 6.86.

The **trinitrobenzene complex** was obtained from methanol in the form of yellow rods, m. p. 148–149.5°.

Anal. Calcd. for $C_{25}H_{19}O_6N_3$: C, 65.64; H, 4.19. Found: C, 65.63; H, 4.05.

Ozonization of VII.—A solution of 1.00 g. of the condensation product VII in 30 ml. of ethyl acetate at 0° was treated for fifteen hours with ozone produced by a U. S. Air ozonizer from oxygen flowing at a rate of 20 liters/hr. The solution was then added dropwise over a period of one hour to a boiling solution of 30% hydrogen peroxide (5 g.) containing 16 drops of concentrated sulfuric acid. The ethyl acetate distilled out of the mixture during the addition, leaving an aqueous solution which was saturated with salt and extracted thoroughly with ether. The ether extracts were washed with 5% potassium iodide solution, with 10% sodium thiosulfate solution, and then extracted with saturated sodium bicarbonate to remove acidic material. Evaporation of the remaining ether solution gave 0.215 g. of crude 1-decalone which gave a semicarbazone, m. p. 217–220°, in 83% yield. Recrystallization from ethanol raised the m. p. to 218.7–219.8° which was not depressed on admixture with an authentic sample of 1-decalone semicarbazone (m. p. 224.7–226.3°). The 2,4-dinitrophenylhydrazone was prepared directly from the semicarbazone,[20] and after recrystallization from ethanol melted at 227.5–228.5° alone or on admixture with an authentic sample of the derivative (m. p. 228–229.2°) prepared from 1-decalone.

The bicarbonate extracts were acidified with 6 *N* hydrochloric acid, saturated with salt, and extracted thoroughly with ether. After drying over anhydrous sodium sulfate the ether was evaporated leaving 0.373 g. of an oil which

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[18] Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).

[19] Huang-Minlon, This Journal, 68, 2487 (1946).

[20] *Cf.* Gutsche and Johnson, *ibid.*, 68, 2245 (1946).

was distilled at 10 mm. from powdered soft glass in a two-bulb flask. The colorless oily distillate (0.21 g.) was treated with semicarbazide hydrochloride (0.165 g.) and sodium acetate (0.165 g.) in dilute alcohol, and thus 0.245 g. of crude semicarbazone of δ-acetylvaleric acid was produced, m. p. 137–140° with previous softening. Recrystallization from dilute alcohol raised the m. p. to 142.4–143.6° which was not depressed on admixture with the authentic material described below.

δ-Acetylvaleric acid was prepared by ozonization of 2 g. of 1-methyl-1-cyclohexene (I, R = CH_3) in 40 ml. of acetic acid essentially as described above for the ozonization of VII. The crude acid amounted to 1.75 g. and partially solidified (the pure acid is reported to melt at 36.5°[21]). The semicarbazone prepared as described above was produced in 52% yield from the crude acid and after recrystallization from methanol melted at 142.8–143.6° (reported m. p. 144–146°[22]).

Condensation of 1-Methyl-2-acetylcyclohexane with 1-Decalone.—1-Methyl-2-acetylcyclohexane was prepared by the hydrogenation of 3.45 g. of I (R = CH_3) in 10 ml. of ethanol in the presence of 0.087 g. of 30% palladium-on-carbon[18] at room temperature and atmospheric pressure. The calculated volume of hydrogen was absorbed after agitation for three and one-half hours. Distillation of the product gave 3.3 g. of a mixture of stereoisomers, b. p. 81–82° (18 mm.).[23] Our product showed an extinction coefficient of only 133 at 248 mμ, indicating less than 3% of the α,β-unsaturated compound, and it was therefore considered satisfactory for use in synthesis.

The condensation of the above substance (1.75 g.) with 1-decalone (1.7 g.) was carried out just as described above for I (R = CH_3) in the presence of 6 g. of aluminum *t*-butoxide in 25 ml. of *t*-butyl alcohol, and 0.71 g. of potassium in 20 ml. of *t*-butyl alcohol. Evaporative distillation of the product at 130–140° (0.05 mm.) gave 1.11 g. (32% yield) of crude **1-methyl-2-(decahydro-1-naphthylideneacetyl)-cyclohexane (VIII)** which could not be crystallized and even after redistillation (evaporatively) did not give a satisfactory analysis probably due to the presence of some starting materials. Attempts to produce a semicarbazone or a 2,4-dinitrophenylhydrazone failed. The identity of this product, $\lambda_{max.}$ 247 mμ (*E* 6,800), was established, however, by dehydrogenation to VI according to the procedure described above for the dehydrogenation of VII. Thus from 0.21 g. of crude VIII there was obtained 0.205 g. (37% yield) of crude di-picrate, m. p. 130–132°, which melted at 135.5–136° after two recrystallizations and showed no m. p. depression on admixture with authentic material (see above). The free hydrocarbon VI was also produced from the picrate as described above. It melted at 53–54° alone or upon admixture with authentic VI.

Condensation of 1-Methyl-2-acetylcyclohexene with 1,5-Decalindione.—To a refluxing solution of 7.76 g. (0.056 mole) of I (R = CH_3),[17] 11.1 g. (0.067 mole) of *trans*-1,5-decalindione[24] (m. p. 167–168°), and 27.2 g. of aluminum *t*-butoxide in 350 ml. of dry *t*-butyl alcohol was added dropwise with stirring over a period of forty-five minutes, a solution of 3 g. of potassium in 80 ml. of dry *t*-butyl alcohol. As the yellow mixture was allowed to reflux for an additional five hours, a heavy colloidal precipitate formed. After standing overnight at room temperature, the mixture was poured into ice and 500 ml. of 20% sulfuric acid and worked up by extraction as described above in the 1-decalone series.

Upon chilling, the residue remaining after evaporation of most of the solvents deposited 1.58 g. of crystals of starting 1,5-decalindione which was removed by filtration and washed with a little cold ether. Evaporation of the combined filtrate and washings left 14.02 g. of yellow oil which was submitted to evaporative distillation. The more volatile fraction which came over at 100° (0.1 mm.) evidently consisted largely of starting materials and yielded an additional 0.35 g. of the crystalline dione. The main product came over at 125° (10^{-4} mm.) as a pale yellow oil weighing 9.76 g. (61% yield based on I, R = CH_3). Upon chilling to −70° with ether the product crystallized, giving a total of 5.60 g. of **1-methyl-2-(5-keto-1,2,3,4,5,6,7,8-octahydro-1-naphthylacetyl)-1-cyclohexene (X)**, m. p. 66–67° (soft at 65°). Recrystallization from dilute methanol gave colorless rods, m. p. 66–67°, $\lambda_{max.}$ 249.5 mμ (*E* 19,950).

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.74; H, 9.26.

The oil remaining after removal of the crystalline fraction gave the monosemicarbazone of X, m. p. 197.5–199°, in 85% yield according to the procedure described below.

The **mono-semicarbazone** of X was prepared by adding a saturated aqueous solution of semicarbazide hydrochloride (0.156 g.) and sodium acetate (0.16 g.) to a solution of crystalline X (0.4 g.) in 5 ml. of alcohol. After boiling for five minutes and standing at room temperature for twenty-four hours the solution deposited 0.33 g. of the derivative, m. p. 196–199° (dec.). A single recrystallization from alcohol gave pure material as colorless microcrystals, m. p. 197.5–199° (dec.), $\lambda_{max.}$ 268 mμ (*E* 34,700). This product deteriorated on standing.

Anal. Calcd. for $C_{20}H_{29}O_2N_3$: C, 69.94; H, 8.51. Found: C, 70.28; H, 8.44.

An additional 0.15 g. of monosemicarbazone, m. p. 196–199° (dec.), precipitated from the residue on longer standing.

A 0.1-g. sample of the pure monosemicarbazone was hydrolyzed by refluxing with 0.5 g. of oxalic acid in 5 ml. of water for one hour. The resulting oil crystallized on scratching and amounted to 0.075 g. (90% yield), m. p. 65–66°. Recrystallization raised the m. p. to 66–67°, $\lambda_{max.}$ 249.5 mμ (*E* 19,950). The m. p. was not depressed on admixture with the original sample of X described above.

The mono-**2,4-dinitrophenylhydrazone** of X was prepared in quantitative yield either from X or from the semicarbazone[20] by heating under nitrogen with the calculated amount of 2,4-dinitrophenylhydrazine in alcohol solution containing concentrated hydrochloric acid. Recrystallization from benzene–ethanol gave deep-red plates, m. p. 180.2–182°, $\lambda_{max.}$ 390 mμ (*E* 23,580) in chloroform.

Anal. Calcd. for $C_{25}H_{30}O_5N_4$: C, 64.36; H, 6.48. Found: C, 64.15, 64.08; H, 6.30, 6.41.

The mono-oxime was prepared by a procedure similar to that described above for the semicarbazone. The product crystallized from alcohol as colorless needles, m. p. 146–147°.

Anal. Calcd. for $C_{19}H_{27}O_2N$: C, 75.71; H, 9.03. Found: C, 75.94; H, 8.90.

Other Experiments on the Condensation of I (R = CH_3) with IX.—When 2.22 g. of the dione IX and 1.55 g. of I (R = CH_3) in 60 ml. of *t*-butyl alcohol was treated with a solution of 0.6 g. of potassium in 16 ml. of *t*-butyl alcohol as described above, the reaction mixture turned dark brown in color. Only about 0.1 g. of the dione was recovered, and evaporative distillation of the product at 160° (0.015 mm.) gave 2.45 g. of brown oil from which 1.06 g. of X, m. p. 55–65°, was obtained by crystallization at −70°. Two recrystallizations gave material m. p. 65–66°, undepressed on admixture with the sample of X described above. The non-crystalline residues gave only VI (isolated as the di-picrate) upon treatment by the reduction–dehydration–dehydrogenation sequence described above.

When the procedure of Huber[4] was followed using 0.97 g. of I (R = CH_3), 1.16 g. of IX, 30 ml. of pyridine and 0.34 g. of potassium in 2.3 ml. of isopropyl alcohol, the oily condensation product which evaporatively distilled at 150° (0.05 mm.), amounted to 0.35 g. (17% yield). The mono-semicarbazone melted at 198–199° (dec.), $\lambda_{max.}$ 268 mμ (*E* 30,800), and the mono-2,4-dinitrophenylhydrazone melted at 180–182°. No m. p. depression was

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[21] Derick and Hess, THIS JOURNAL, **40**, 537 (1918).

[22] Wallach, *Ann.*, **329**, 368 (1903).

[23] See Turner, THIS JOURNAL, **72**, 878 (1950).

[24] Hudson and Robinson, *J. Chem. Soc.*, 691 (1942). A modification of the English procedure developed in our laboratory by Gutsche and Banerjee will be reported in a forthcoming publication.

observed on admixture of these compounds with the corresponding derivatives produced from authentic X (see above).

When the condensation was conducted essentially as in the preceding experiment, but with potassium *t*-butoxide instead of isopropoxide a comparable yield (20%) of material having the same properties was produced.

It was shown that the aluminum *t*-butoxide alone does not promote the condensation, by treating a mixture of 0.97 g. of I (R = CH_3), 1.16 g. of IX and 20 ml. of pyridine with 5.1 g. of aluminum *t*-butoxide in 40 ml. of *t*-butyl alcohol for seven hours at room temperature and then for six hours at the boiling point. On working up the product, 1.05 g. (90%) of the crystalline decalindione (IX) was recovered.

Dehydrogenation of X.—A 1.54-g. sample of crude X was treated with 1 g. of lithium aluminum hydride as described for the dehydrogenation of VII (see above), and a portion (0.8 g.) of the oily reduction product was heated at 175–180° with 0.8 g. of potassium bisulfate in a sublimation tube for fifteen minutes under nitrogen. Evaporative distillation at 140–160° (0.1 mm.) gave 0.345 g. of yellow oil which was heated with 0.3 g. of 30% palladium-on-carbon[18] at 310–360°. After about three hours hydrogen evolution was very slow and the product was separated with ether and evaporatively distilled at 125° (0.1 mm.). Near the end of the distillation about 5 mg. of solid sublimed, which was recognized as 1-methylchrysene, m. p. 254.1–255°, after recrystallization from benzene and from toluene. The m. p. was not depressed on admixture with the authentic hydrocarbon,[13] but was depressed on admixture with chrysene. The main fraction (0.13 g. of oil) was converted to the di-picrate as described above. The yield of crude derivative was 0.34 g., m. p. 129–132°. After two recrystallizations, the m. p. was raised to 135.5–136° (see above for analytical data).

Decomposition of the picrate on a column of activated alumina (see above) yielded the hydrocarbon VI which crystallized from methanol in the form of fluorescent plates, m. p. 53.2–54° (see above for analytical data).

The trinitrobenzene complex was prepared from the crystalline hydrocarbon as described above. It crystallized from ethanol as short yellow rods, m. p. 141–142° (see above for analytical data).

Ozonization of X.—A solution of 0.75 g. of crystalline X in 20 ml. of acetic acid (distilled from potassium permanganate) was treated with ozone as above until the gas issuing from the reaction mixture rapidly liberated iodine from an acidified solution of potassium iodide, the treatment requiring about ten hours with a gas flow rate of about 10 liters/hour. Forty milliliters of water containing 1 ml. of concentrated hydrochloric acid was added to the reaction mixture which was then boiled under reflux for fifty minutes. The brown solution was neutralized with solid sodium bicarbonate and extracted with ether. Evaporation of the ether gave only 18 mg. of yellow oil which did not form a semicarbazone; thus there was no indication of any decalindione.

The aqueous layer was acidified with 6 *N* hydrochloric acid, saturated with salt, and extracted with ether. After drying over anhydrous sodium sulfate the ether was evaporated and the acetic acid removed by distillation at reduced pressure. The oily residue was distilled from a little powdered soft glass in a two-bulb flask yielding 0.325 g. of colorless oil (neut. equiv. 146). The semicarbazone, formed by the semicarbazide hydrochloride-sodium acetate method, amounted to 0.42 g., m. p. 136–138°. Repeated recrystallization from dilute alcohol gave small colorless crystals m. p. 144–145°, undepressed on admixture with the semicarbazone of δ-acetylvaleric acid described above.

Anal. Calcd. for $C_8H_{15}O_3N_3$: C, 47.75; H, 7.51. Found: C, 48.18; H, 7.30.

Condensation of 1-Methyl-2-acetylcyclohexane with 1,5-Decalindione.—The condensation was carried out as described above, using 1.7 g. of the same sample of 1-methyl-2-acetylcyclohexane that was employed in the 1-decalone condensation, 2.2 g. of the dione IX, 6 g. of aluminum *t*-butoxide in 40 ml. of *t*-butyl alcohol, and 0.7 g. of potassium in 20 ml. of *t*-butyl alcohol. The product was worked up as described above for the reaction of I (R = CH_3) with IX, the recovered IX amounting to 0.680 g. Evaporative distillation at 110° (0.05 mm.) gave a mixture of low boiling material from which an additional 0.31 g. of dione was isolated. Further evaporative distillation at 150–162° yielded 1.86 g. (53% yield) of oil which crystallized from ether at −70° giving 1.23 g. of **1-methyl-2-(5-keto-1,2,3,4,5,6,7,8-octahydronaphthylacetyl)-cyclohexane (XI)**, m. p. 68–69°. Recrystallization from alcohol gave colorless rods, m. p. 68.8–69.7°, $\lambda_{max.}$ 247.5 mμ (*E* 13,820).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.08; H, 9.42.

The **monosemicarbazone** formed rapidly with semicarbazide hydrochloride and pyridine in ethanol. The crude product, obtained in 82% yield, melted at about 226° with softening at 210°. After two recrystallizations from alcohol it was obtained as colorless plates, m. p. 227–228° (dec.).

Anal. Calcd. for $C_{20}H_{31}O_2N_3$: C, 69.53; H, 9.06. Found: C, 69.49; H, 9.19.

Attempts to produce a di-semicarbazone with excess reagent failed.

Hydrolysis of the monosemicarbazone with oxalic acid (see above) regenerated the crystalline diketone XI, m. p. 68.8–69.7°, undepressed on admixture with the original sample of XI.

The **mono-2,4-dinitrophenylhydrazone** was formed in quantitative yield directly from the semicarbazone (see above). The crude product melted at 203–204° (dec.) and after recrystallization from benzene–ethanol it was obtained as red needles, m. p. 203.9–205.1° (dec.).

Anal. Calcd. for $C_{25}H_{32}O_5N_4$: C, 64.08; H, 6.89. Found: C, 64.31; H, 6.91.

Dehydrogenation of XI.—A 0.3-g. sample of crude XI was treated with lithium aluminum hydride, then dehydrated over potassium bisulfate as described for VII above. Dehydrogenation of the oily product (0.22 g.) with 0.15 g. of 30% palladium-on-carbon,[18] yielded material which afforded 0.19 g. of the di-picrate of VI, m. p. 130.5–132.5°. Recrystallization gave a product, m. p. 135.5–136°, undepressed on admixture with the authentic material (see above). The free hydrocarbon, obtained by decomposition of the picrate on alumina, melted at 53–54°, and gave no m. p. depression on admixture with authentic VI (see above).

Summary

The alkoxide-catalyzed condensation of 1-methyl-2-acetylcyclohexene with 1-decalone gives mainly the product of a simple aldol condensation between the methyl group of the acetyl residue in the former and the keto group of the latter. There was no evidence of a ring closure as in the Robinson–Rapson synthesis. Analogous behavior was observed in the mole for mole condensation between 1-methyl-2-acetylcyclohexene and 1,5-decalindione.

It is concluded, therefore, that those structures —*viz.*, cyclized structures having the angular methyl group—assigned by previous workers to the condensation products of cyclic ketones with 1-methyl-2-acetylcyclohexene, are open to question, and more likely are represented correctly by structures analogous to those determined unequivocally in the present study.

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