[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Some Reactions of Δ^2-Cyclohexenone, Including the Synthesis of Bicyclo(2,2,2)-octanedione-2,6

BY PAUL D. BARTLETT AND G. FORREST WOODS[1]

According to the literature,[2-7] Δ^2-cyclohexenone is available by a variety of methods. In attempting to prepare a quantity of this ketone we obtained uniformly poor results with a number of the most promising methods previously described. The best method found was the dehydration at 310–320° of cyclohexanol-2-one-1 by activated alumina, a procedure not previously described. This yielded a mixture which on fractional distillation gave a 35% yield of Δ^2-cyclohexenone, characterized as described below. The other fractions were shown to contain phenol (identified as its tribromo derivative) and cyclohexanone (identified as the semicarbazone and 2,4-dinitrophenylhydrazone) in equal amounts, accounting for a further 40% of the starting material. Inasmuch as the original hydroxy ketone was shown to be pure by analysis, this cyclohexanone must have arisen along with the phenol by intermolecular hydrogen transfer between molecules of cyclohexenone on the catalyst.

The unsaturated ketone was obtained in 100-g. portions by careful fractionation under diminished pressure through a good modified Podbielniak column. The properties of the pure material are compared in Table I with those previously reported. The fact that our semicarbazone melts 10–11° higher than that reported by Kötz is probably a matter of the temperature scale employed, since on Kötz's scale cyclohexanone semicarbazone melted 12° below the point (167°) found by us and by others.

TABLE I

PROPERTIES OF Δ^2-CYCLOHEXENONE

	Our material	Ref. 3	Ref. 6	Ref. 7
B. p. (14 mm.)	61–63°	63°		
B. p. (760 mm.)	169–171°			
D_{18}		0.9668		
$n^{18}\text{D}$	1.4842	1.4796		
Semicarbazone m. p.	171–172°	161°	161°	161°
Oxime, m. p.	89–90°	75–76°		
2,4-Dinitrophenylhydrazone	163°			

Partly to settle any doubt of the structure and purity of our Δ^2-cyclohexenone, and partly to explore its synthetic possibilities, we have carried out a number of characterizing reactions.

A 10-g. sample of the unsaturated ketone with 0.10 g. of Adams platinum oxide catalyst absorbed 99% of the calculated hydrogen at a uniform rate in seventeen minutes, after which the absorption became extremely slow. The product was identified as cyclohexanone by its semicarbazone and 2,4-dinitrophenylhydrazone. The position of the double bond is shown by the diene and Michael reactions described below, as well as by oxidation with permanganate to glutaric acid (mixed m. p.). Aluminum isopropoxide reduces the ketone (1) to Δ^2-cyclohexenol (II),[8] identified through its phenylurethan, m. p. 106–107°.

From the reaction of Δ^2-cyclohexenone with diazomethane only a resin was obtained.

The addition of phenylmagnesium bromide to Δ^2-cyclohexenone is predominantly or wholly to the carbonyl group. The alcohol III was not isolated, hydrolysis of the Grignard addition product in the presence of ammonium chloride leading to a colorless liquid which on catalytic hydrogenation rapidly absorbed 90% of the calculated hydrogen for 2-phenylcyclohexadiene-1,3 (IV) and showed no reaction with semicarbazide or 2,4-dinitrophenylhydrazine hydrochloride. The diene was converted into diphenyl in 74% yield by heating with palladium–charcoal catalyst.

Δ^2-Cyclohexenone reacts sluggishly with dienes. With 2,3-dimethylbutadiene no reaction could be detected below 185°. From three days of heating in a sealed tube at 185–200° a 20% yield could be obtained of the addition product V, m. p. 62°. This product was identified only by analysis of its semicarbazone, which melted at 234° with decomposition.

---

(1) The original preparation of Δ^2-cyclohexenone described here was worked out by the junior author under the direction of the late Professor E. P. Kohler, who also directed the study of its reaction with diazomethane and with phenylmagnesium bromide.

(2) Kötz and Götz, *Ann.*, **358**, 183 (1908).

(3) Kötz and Grethe, *J. prakt. Chem.*, [2] **80**, 473 (1909).

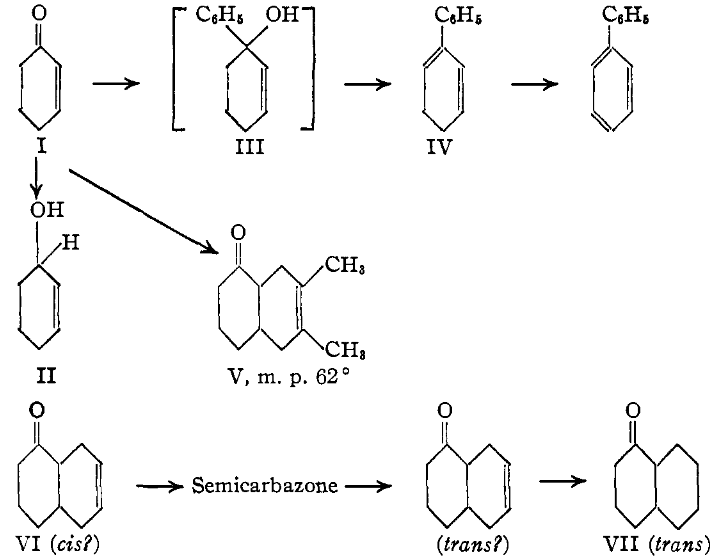
(4) Kötz, Blendermann, Mähnert and Rosenbusch, *Ann.*, **400**, 72 (1913).

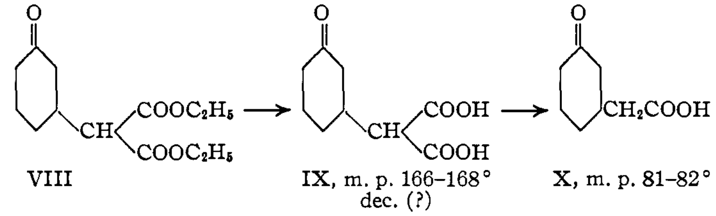
(5) Kötz and Richter, *J. prakt. Chem.*, **111**, 373 (1925).

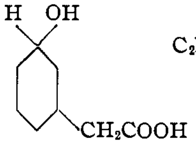
(6) Guillemonat, *Ann. Chim.*, **11**, 11 (1939); *Compt. rend.*, **205**, 67 (1937).

(7) Courtot and Pierron, *Bull. soc. chim.*, **45**, 286 (1929).

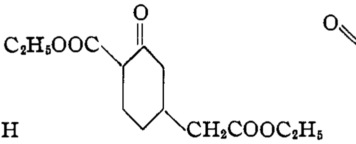
(8) Willstätter and Sonnenfeld, *Ber.*, **46**, 2957 (1913).



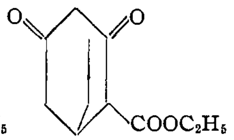




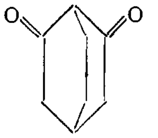
XI, m. p. 116–117°



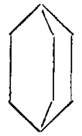
XII



XIII



XIV, m. p. 190–191°



XV, m. p. 168–169°

Butadiene, heated with Δ^2-cyclohexenone at 180–190° for three days, gave only 11% of a low-melting solid which could not be purified as such. It formed a semicarbazone, m. p. 240° (dec.), whose analysis was correct for the semicarbazone of VI. This semicarbazone was hydrolyzed and the steam distillate subjected to catalytic hydrogenation. From the resulting solution an oxime was prepared whose melting point (165.5–166.6°) and analysis corresponded to that of *trans-α*-decalone (VII).[9] Although the diene synthesis commonly leads to *cis*-ring union, the conditions of forming an oxime or semicarbazone are known to isomerize *cis*- into *trans-α*-decalone. It seems doubtful also whether Δ^6-octalone (VI) would escape *cis–trans* isomerization under the drastic conditions prevailing in the sealed tube in which it was prepared.

Dane and Eder[10] have recently reported a similar diene synthesis with Δ^2-cyclopentenone.

Ethyl malonate, with a small amount of sodium ethoxide in ethanol, adds smoothly to Δ^2-cyclohexenone at 0°, yielding cyclohexanone-3-malonic ester (VIII) in 90% yield. This ester yields a semicarbazone melting at 138–139°, and gives no color with ferric chloride. The latter fact rules out the structure XII, which might be anticipated from the formation and cleavage of the diketoester XIII. In the analogous condensation starting with 3-methyl-Δ^2-cyclohexenone, and employing more vigorous conditions, Farmer and Ross[11] obtained the homolog of XII and a cleavage product, but never the homolog of VIII, in striking contrast to the present case.

Many attempts were made to condense cyclohexanone-3-malonic ester by means of basic reagents to the diketo-ester XIII. With sodium ethoxide, sodamide, and with sodium in different solvents the chief product was always a tar. There was usually a small amount of liquid of the same boiling point as the starting material, which gave a coloration with ferric chloride but no copper derivative. This may have been starting material containing a small amount of XII. Only sodium *t*-amyloxide gave a small quantity of a crystalline solid melting at 198–199°, whose analysis and molecular weight corresponded to the formula $C_{14}H_{18}O_3$. It gave no ferric chloride test.

Cyclohexanone-3-malonic ester could be hydrolyzed with alkali to the acid IX, m. p. 166–168° (dec.), but never in satisfactory yield. This acid could be decarboxylated in 50% yield to cyclohexanone-3-acetic acid (X), m. p. 81–82°, which was also converted into the methyl ester

---

[9] Hückel, *Ann.*, **441**, 1 (1925).

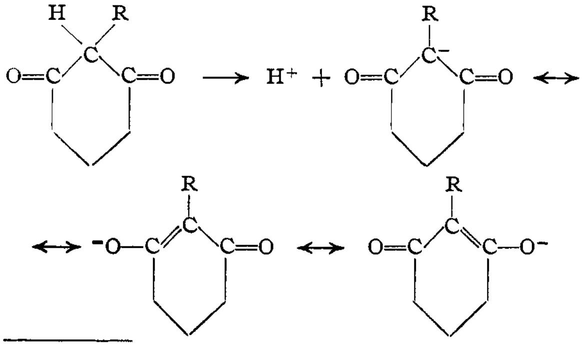
[10] Dane and Eder, *ibid.*, **539**, 207 (1939).

[11] Farmer and Ross, *J. Chem. Soc.*, **127**, 2358 (1925).

and its semicarbazone. Attempts to condense this methyl ester by bases to bicyclo[2,2,2]octanedione-2,6 (XIV) were unsuccessful.

When the crude cyclohexanone-3-malonic acid was recrystallized from acetic acid, the recovery was only 20–30%. From the mother liquors by evaporation and heating to decarboxylate, a small amount of a solid was obtained, melting at 116–117°. This product gave no semicarbazone, though its neutral equivalent was correct for the cyclohexanone-3-acetic acid, (X). The analysis corresponded to a hydrogenation product of X and indeed oxidation with dichromate and sulfuric acid converted the compound in 50% yield into cyclohexanone-3-acetic acid identical with that prepared by decarboxylation of the crystallized cyclohexanone-3-malonic acid. The structure XI, probably *trans*, is accordingly assigned to this by-product. It is difficult to account for the appearance of two hydrogen atoms in the treatment of the malonic ester and acid in any other way than by an intermolecular hydrogenation–dehydrogenation of the ring, induced this time by alkali or acid. The formation of phenol by the loss of malonic ester and hydrogen from the ring might provide a driving force for such a reaction. Such an irreversible process would help to explain the failure to obtain bicyclic products by the ester condensation.

Bicyclo[2,2,2]octanedione-2,6 (XIV) possesses the interesting structural feature of being a modified dihydroresorcinol in which enolization would constitute a violation of Bredt's rule.[12] Dihydroresorcinol and its simple derivatives are commonly completely enolized and possess very reactive hydrogen on the position between the two carbonyl groups. The activity of this hydrogen is currently explained as connected with the resonance in the negative ion remaining when the proton is removed:



If the central carbon atom is a bridge-head so that these double-bonded structures cannot contribute to the resonance, then not only will there be no enolic form of the diketone, but the hydrogen atom at the bridge-head will show less reactivity than any of the four hydrogen atoms in the α-position to a single carbonyl group.

Because of the theoretical interest attached to this diketone, we renewed our efforts to obtain it along other lines. Condensations with sulfuric acid and with liquid hydrogen fluoride failed, but it proved possible to obtain the diketone by passing the vapor of cyclohexanone-3-acetic acid (X) over alumina or, better, manganous oxide, at 300–325°. The results with manganous oxide were more reproducible than those with alumina. The best yields obtained were around 10% of white needles melting at 190–191° when recrystallized from benzene–hexane mixture. The analysis was correct for bicyclo[2,2,2]octanedione-2,6 (XIV), but the molecular weight in camphor was double and in bornyl chloride triple the calculated value. The compound showed marked volatility, consistent only with the C_8 formula. It gave a disemicarbazone, melting at 234–236° (dec.), which on Wolf–Kishner reduction yielded a very volatile hydrocarbon. After three sublimations this hydrocarbon melted at 168–169° in a sealed tube and its amount represented a 57% yield. Bicyclo[2,2,2]octane (XV) melts at 169–170° according to Alder and Stein,[13] and at 168° (cor.) according to Komppa.[14] From this it seems probable that our diketone actually has the structure of bicyclo[2,2,2]octanedione-2,6 (XIV) and that it is prone to associate in camphor and bornyl chloride. The model suggests the possibility of a mode of association involving eight hydrogen bonds per molecular pair.

The diketone gave no color with ferric chloride, no copper derivative, and showed no greater solubility in aqueous alkali than in pure water. In a Zerewitinoff determination it consumed two moles of methylmagnesium iodide and gave 0.15 mole of gas. It is thus non-enolic. It is not possible to say whether the gas originated from the hydrogen at the bridge-head or from one of the four hydrogens whose enolization is not prohibited.

Experimental

Δ^2-Cyclohexenone (I).—α-Chlorocyclohexanone was prepared according to the directions of Bartlett and

---

[12] Bredt, *Ann.*, **437**, 1 (1924).

[13] Alder and Stein, *ibid.*, **514**, 28 (1934).

[14] Komppa, *Ber.*, **68**, 1272 (1935).

Rosenwald.[15] Hydrolysis of the α-chlorocyclohexanone was accomplished using the quantities of α-chlorocyclohexanone, water and potassium carbonate recommended by Kötz and co-workers.[16] A mixture of 500 g. of α-chlorocyclohexanone, 2500 cc. of water and 1500 g. of potassium carbonate was stirred vigorously for eighteen hours using a nichrome wire stirrer. After filtering 460 g. (107%) of the calculated amount of solid α-hydroxycyclohexanone was obtained. This was recrystallized from alcohol–water to yield 327 g. (76%) of pure material.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.18; H, 8.77. Found: C, 63.00; H, 8.78.

A 500-cc. distilling flask was connected by a cork stopper to an electrically heated Pyrex tube (22 × 350 mm.) packed with activated alumina (no. 8 mesh). This system was connected through a suitable receiver and condenser to a source of vacuum. In a typical run, 350 g. of α-hydroxycyclohexanone was distilled at 15 mm. over the alumina heated to 310–320°. When all the α-hydroxycyclohexanone had passed through the alumina, requiring a time of four to six hours, the product was fractionally distilled at 14–15 mm. The forerun consisted of water and ketonic material, and that fraction boiling from 50–70° (14–15 mm.) was collected. The total higher boiling residue was returned to the catalytic dehydration apparatus and passed again over the alumina. This process was repeated until the residue was small enough to neglect. The following were obtained: (1) tarry material collected from the distilling flask of the catalytic apparatus (72 g.); (2) residue in the distilling flask from the final fractionation which consisted of phenol (44 g.); (3) water fraction containing some ketone (57 g.); (4) that material distilling in the range of 50–70° (14–15 mm.) (161.9 g.). Careful fractionation, using a good modified Podbielniak column, of fraction 4 combined with the ether extract of fraction 3 yielded 104 g. of Δ^2-cyclohexenone (b. p. 67–69° (22 mm.)), 13.2 g. of phenol as residue, and 59 g. of cyclohexanone (b. p. 57–59° (22 mm.)). The phenol (13.2 and 44 g.) was identified as the tribromo derivative (m. p. 95°) and gave no depression with an authentic sample in a mixed melting point determination. The cyclohexanone was converted into the semicarbazone (m. p. 165–166°) and the 2,4-dinitrophenylhydrazone (m. p. 153–154°), neither of which gave any depression in a mixed melting point determination with authentic samples.

Δ^2-Cyclohexenone prepared in the above manner boils at 61–63° (14 mm.), 67–69° (22 mm.), and at 169–171° (760 mm.) with slight decomposition. The semicarbazone melted at 171–172° with decomposition.

Anal. Calcd. for $C_7H_{11}ON_3$: C, 54.92; H, 7.18. Found: C, 54.84; H, 7.41.

Δ^2-Cyclohexenone oxime was prepared by adding 5 g. of Δ^2-cyclohexenone to 100 cc. of water containing 3.6 g. of hydroxylamine hydrochloride and 7 g. of sodium acetate. The oxime, purified by distillation and recrystallized from water, formed white needles melting at 89–90°.

Anal. Calcd. for C_6H_9ON: C, 64.88; H, 8.10. Found: C, 64.74; H, 8.08.

Δ^2-Cyclohexenone 2,4-dinitrophenylhydrazone prepared from 0.1 g. of Δ^2-cyclohexenone crystallized from alcohol–water in long orange needles melting at 163°.

Catalytic Hydrogenation of Δ^2-Cyclohexenone.—Hydrogenation of Δ^2-cyclohexenone was carried out using 10.0 g. of the ketone in 100 cc. of ethyl alcohol with 0.1 g. of platinum oxide as the catalyst at 25° and atmospheric pressure. After seventeen minutes 2610 cc. of hydrogen had been absorbed and after twenty minutes 2660 cc. (calcd.: 2660 cc. of hydrogen). The alcohol solution was filtered and fractionated yielding 9.2 g. (90%) of cyclohexanone boiling at 55–60° (12 mm.). The semicarbazone was prepared by treating 1 g. of the ketone with the calculated quantity of semicarbazide in alcohol. After warming, the solution was diluted with water until cloudiness occurred. The crystals so obtained were recrystallized from alcohol–ether and melted at 166°. No depression was obtained in a mixed melting point determination with an authentic sample of cyclohexanone semicarbazone.

Diene Reaction with Δ^2-Cyclohexenone.—(a) A mixture of 3.0 g. of Δ^2-cyclohexenone and 3.6 g. of 2,3-dimethylbutadiene was heated in a sealed tube at 185–200° for three days. From distillation of the product 1.1 g. (20%) of a white crystalline solid was obtained which melted at 62° and formed a semicarbazone melting at 234° with decomposition.

Anal. Calcd. for $C_{13}H_{21}ON_3$: C, 66.40; H, 8.93. Found: C, 66.34, 66.34; H, 8.81, 9.17.

(b) A mixture of 10 g. of Δ^2-cyclohexenone and 19 cc. of butadiene was heated in a sealed tube for seventy-two hours at 180–190°. Upon distillation 1.8 g. (11%) of a low melting solid was obtained which was converted into a semicarbazone melting at 240° with decomposition after recrystallization from alcohol.

Anal. Calcd. for $C_{11}H_{17}ON_3$: C, 63.78; H, 8.18. Found: C, 63.88; H, 8.02.

The free ketone obtained by steam distillation from 0.45 g. of the above semicarbazone was catalytically hydrogenated with 0.01 g. of platinum oxide upon addition of a small quantity of alcohol, absorbing 41 cc. (71% of the calculated amount) of hydrogen. The oxime of the product was prepared from this solution and recrystallized from alcohol–water mixture; melting point 165.5–166.5°.

Anal. Calcd. for $C_{10}H_{17}ON$: C, 71.87; H, 10.17. Found: C, 71.95; H, 10.14.

Another sample of ketone regenerated from the semicarbazone was converted into an oxime which melted at 153–155° and gave a 10° depression with the above hydrogenated oxime in a mixed melting point determination.

Reduction of Δ^2-Cyclohexenone to Δ^2-Cyclohexenol.—A solution of 9 g. of Δ^2-cyclohexenone in 140 cc. of isopropyl alcohol containing aluminum isopropoxide from 1.8 g. of aluminum was heated under a reflux condenser controlled so that the acetone could escape.[17] The product was worked up in the usual manner to yield 4.5 g. of Δ^2-cyclohexenol (49%) boiling at 85° (25 mm.). The Δ^2-cyclohexenol was identified as the phenylurethan which melted at 106–107° after recrystallization from alcohol. (Willstätter and Sonnenfeld[8] reported that Δ^2-cyclohexenol phenylurethan melted at 107°.)

---

[15] Bartlett and Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

[16] Kötz, Blendermann, Rosenbusch and Serringhaus, *Ann.*, **400**, 55 (1913).

[17] Lund, *Ber.*, **70**, 1520 (1937).

Anal. Calcd. for $C_{13}H_{15}O_2N$: C, 71.90; H, 6.90. Found: C, 71.96; H, 6.79.

Oxidation of Δ²-Cyclohexenone with Potassium Permanganate.—In 50 cc. of acetone 1 g. of Δ²-cyclohexenone was oxidized with 4.3 g. of powdered potassium permanganate. The product, 0.25 g. (25% of the calculated amount), was a white crystalline acid which melted at 95–96° after sublimation at greatly reduced pressure and several recrystallizations from benzene. This substance gave no depression in a mixed melting point determination with an authentic sample of glutaric acid.

Reaction of Δ²-Cyclohexenone with Phenylmagnesium Bromide.—To phenylmagnesium bromide prepared from 1.25 g. of magnesium and 7.60 g. of bromobenzene in 40 cc. of ether at 0° was added slowly 4.65 g. of Δ²-cyclohexenone in 40 cc. of ether. A half hour after all the Δ²-cyclohexenone had been added, the reaction mixture was worked up using dilute ammonium chloride solution. After extraction of the reaction mixture with ether, and removal of the ether, the product was subjected to distillation. A water-white liquid was obtained (7.5 g., 96% based on phenylcyclohexadiene) which boiled at 93° (3–4 mm.). This liquid would form no carbonyl derivative with semicarbazide in alcohol, nor with 2,4-dinitrophenylhydrazine hydrochloride.

The liquid was again distilled after a small quantity of acetic anhydride had been added to remove any tertiary alcohol. On catalytic hydrogenation with platinum oxide, 1 g. of this liquid absorbed 90% of the calculated quantity of hydrogen based on the structure of phenylcyclohexadiene.

Using 0.1 g. of palladium–charcoal catalyst, 0.75 g. of the liquid from the acetic anhydride treatment was dehydrogenated at 300–360° for five hours. The product was recrystallized from alcohol–water to yield 0.55 g. (74% of the calculated quantity) of a white solid melting at 68.5–69.5° alone and when mixed with authentic diphenyl.

Michael Reaction with Δ²-Cyclohexenone and Ethyl Malonate.—In a 1 l. flask fitted with a mercury-seal stirrer, thermometer and separatory funnel, were placed 300 cc. of anhydrous ethyl alcohol containing sodium alcoholate prepared from 0.2 g. of sodium and 150 g. of ethyl malonate. After the solution was chilled to below −5°, 87 g. of Δ²-cyclohexenone in 100 cc. of anhydrous alcohol was slowly added. After addition, the solution was allowed to warm to room temperature and stand for six hours. The product was worked up by removing excess alcohol under reduced pressure after destroying the sodium alcoholate with a little acetic acid, adding ether, and washing many times with water. After drying the ether solution, and removing the ether the residue was distilled from a modified Claisen flask with an electrically heated sidearm to yield 209 g. (90% of the theoretical quantity) of ethyl cyclohexanone-3-malonate, a water white liquid boiling at 135–137° (1–2 mm.). It formed a white crystalline semicarbazone melting at 138–139°.

Anal. Calcd. for $C_{14}H_{23}O_5N_3$: C, 53.69; H, 7.32. Found: C, 53.47; H, 7.22.

The ethyl cyclohexanone-3-malonate gave no color with ferric chloride in alcohol solution.

Reaction of Ethyl Cyclohexanone-3-malonate with Sodium *t*-Amyloxide.—To a mixture of sodium *t*-amyloxide, prepared from 3 g. of sodium wire, and 150 cc. of benzene heated under reflux was added slowly 14 g. of ethyl cyclohexanone-3-malonate in 50 cc. of benzene. The heating was continued for two hours after the addition of the ester. After cooling the solution was poured into dilute sulfuric acid, and then washed with water and dried. The benzene was removed under reduced pressure and the product dissolved in ether, washed again and dried. After removing the ether the product was distilled to yield starting material boiling at 150° (2–3 mm.) and 0.7 g. of material which solidified in the sidearm of the distilling flask. The solid after recrystallization from benzene–ligroin melted at 198–199°. This solid gave no color with ferric chloride in alcohol.

Anal.[18] Calcd. for $C_{14}H_{18}O_3$: C, 71.81; H, 7.69. Found: C, 71.52, 71.74; H, 7.79, 7.80. The molecular weight was 226 in freezing benzene.

Saponification of Ethyl Cyclohexanone-3-malonate.—(1) A solution of 40 g. of ethyl cyclohexanone-3-malonate and 300 cc. of water containing 15 g. of sodium hydroxide was heated under reflux for two hours at the end of which time another 15 g. of sodium hydroxide was added and heating continued for four more hours. After acidification with sulfuric acid the solution was extracted in a continuous ether extraction apparatus. The ether solution was dried and the residue distilled under greatly reduced pressure after the ether had been removed. Decarboxylation occurred and 8.1 g. of a water-white liquid distilled (35% of the calculated quantity) which, after recrystallization from benzene, melted at 81–82°.

(2) Under reflux, 30 g. of ethyl cyclohexanone-3-malonate was heated for eighteen hours in 300 cc. of methyl alcohol containing 15 g. of potassum hydroxide. The solid was filtered off and washed with methyl alcohol and then ether. The yield of the potassium salt of cyclohexanone-3-malonic acid was 24 g. (75%). The potassium salt was dissolved in a minimum of water and made neutral with sulfuric acid and then the calculated quantity of sulfuric acid added to release the cyclohexanone-3-malonic acid. The solution was extracted with ether and the product worked up as above to yield 5.3 g. (41%) of cyclohexanone-3-acetic acid.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.55; H, 7.68; equiv. wt., 156. Found: C, 61.43; H, 7.65; equiv. wt., 157.

One hundred twenty-five grams of crude cyclohexanone-3-malonic acid was dissolved in 300 cc. of hot acetic acid. After this had stood for two days, 24 g. of crystalline cyclohexanone-3-malonic acid was obtained. Recrystallization of 11 g. of this acid yielded 3.0 g. (27%) of cyclohexanone-3-malonic acid. The mother liquors were combined, the acetic acid removed under reduced pressure and the residue decarboxylated and distilled, all under greatly reduced pressure, to yield 32 g. of a liquid. Crystallization of this liquid from benzene yielded 11 g. of a solid acid which melted at 116–117°. This acid formed no semicarbazone.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.77; H, 8.85; equiv. wt., 158. Found: C, 60.62, 60.58; H, 8.91, 8.76; equiv. wt., 162.

Oxidation of 0.5 g. of this acid with 0.36 g. of potassium dichromate and 2 g. of sulfuric acid in 4 cc. of water yielded

---

[18] This analysis was performed by Mr. Lyon Southworth.

0.23 g. (46% of the calculated amount) of cyclohexanone-3-acetic acid after ether extraction, sublimation and recrystallization from benzene. This product melted at 80° and gave no depression in a mixed melting point determination with a sample of cyclohexanone-3-acetic acid obtained without attempted recrystallization from acetic acid.

By decarboxylation and distillation of 6 g. of the crystalline cyclohexanone-3-malonic acid 2.5 g. (53%) of cyclohexanone-3-acetic acid melting at 80–81° was obtained.

Methyl Cyclohexanone-3-acetate.—Seven grams of cyclohexanone-3-acetic acid was dissolved in 50 cc. of ether, and an excess of diazomethane in ether added. After removal of the ether the residue was distilled to yield 7.2 g. (94% of the calculated quantity) of water white methyl cyclohexanone-3-acetate boiling at 132–133° (9–10 mm.). This product formed a white crystalline semicarbazone which melted with decomposition at 163°.

Anal. Calcd. for $C_{10}H_{17}O_3N_3$: C, 52.88; H, 7.48. Found: C, 52.67; H, 7.22.

Bicyclo(2,2,2)octanedione-2,6.—A catalyst of manganous oxide was prepared by mixing five parts of manganous carbonate with six parts of plaster of paris, moistening and allowing the whole to set. The solid mass was broken up, and those particles which passed through a 20-mesh, and not a 30-mesh, screen were used. In a suitable apparatus, cyclohexanone-3-acetic acid was sublimed at a pressure of 1 mm. over a thin layer of catalyst which had just been heated to 400° and allowed to cool to 300°, and which was protected from air. A solid crystalline product was obtained which was recrystallized from benzene–hexane mixture and melted at 190–191°; yield: (a) 3 g. of cyclohexanone-3-acetic acid yielded 0.25 g. of the diketone, (9.4%); (b) 0.75 g. of cyclohexanone-3-acetic acid yielded 0.08 g. of the diketone, (12%).

Anal.[18] Calcd for $C_8H_{10}O_2$: C, 69.58; H, 7.24; mol. wt., 138. Found: C, 69.74, 69.53; H, 6.89, 7.32; mol. wt. (in camphor), 308, 306, 276; (in bornyl chloride) 401.

From 0.5 g. of this product 0.8 g. (88%) of a disemicarbazone was obtained which after recrystallization from alcohol–water melted at 234–236° with decomposition.

Anal. Calcd. for $C_{10}H_{16}O_2N_6$: C, 47.64; H, 6.34. Found: C, 47.76; H, 6.70.

A Zerewitinoff determination was made on the diketone to determine the number of carbonyl groups and active hydrogens. The reaction had to be carried out in a mixture of xylene and di-isoamyl ether: (1) weight of diketone, 0.0542 g.; (2) hydrogen evolution from Grignard reaction with diketone, 3.2 cc.; (3) volume of Grignard reagent used (1 cc. = 10.4 cc. of methane at 0° and 760 mm.), 2.54 cc.; (4) volume of methane given off after reaction and addition of water, 8.0 cc.; (5) a blank run using the quantity of xylene and di-isoamyl ether used in the above determination evolved 1.8 cc. of methane. (Therefore the figure 3.2 cc. (3) should be corrected to 1.4 cc.) Calculations: 3.92×10^{-4} mole of ketone required 7.84×10^{-4} mole of Grignard; observed was 7.25×10^{-4} mole consumed. The quantity of methane evolved from active hydrogen was 1.4 cc. (3.2 − 1.8 cc.) or 5.7×10^{-5} mole.

A solution of the diketone in alcohol gave no color with ferric chloride, nor could a copper derivative be obtained.

Bicyclo(2,2,2)octane.—A Wolff–Kishner reduction was carried out on 0.8 g. of bicyclo(2,2,2)octanedione-2,6 disemicarbazone in 3 cc. of alcohol containing sodium alcoholate from 0.3 g. of sodium. The product was worked up by steam distillation, and sublimed three times to yield 0.2 g. (57% of the calculated quantity) of a white crystalline material melting at 168–169°. This melting point value is in accord with the figure reported by Alder and Stein.[13]

Anal.[19] Calcd. for C_8H_{14}: C, 87.28; H, 12.72. Found: C, 88.24; H, 13.03.

Komppa[14] does not give any analytical data on the bicyclo(2,2,2)octane which he prepared. Alder and Stein[13] reported the following values: C, 85.9, 86.2, 86.1; H, 12.5, 12.5, 12.6.

Summary

Δ^2-Cyclohexenone has been prepared in 35% yield by the dehydration of cyclohexanol-2-one-1 over an alumina catalyst. It is accompanied by phenol and cyclohexanone. This unsaturated ketone has been characterized through its oxime, semicarbazone and 2,4-dinitrophenylhydrazone and by quantitative catalytic hydrogenation to cyclohexanone. It has been reduced by aluminum isopropoxide to Δ^2-cyclohexanol. With phenylmagnesium bromide it undergoes 1,2-addition and dehydration leading to phenylcyclohexadiene. Under vigorous conditions it adds butadiene and 2,3-dimethylbutadiene to give the corresponding octalones.

Malonic ester has been added to Δ^2-cyclohexenone, yielding cyclohexanone 3-malonic ester, which by hydrolysis yields the corresponding malonic acid, and this is decarboxylated to cyclohexanone-3-acetic acid. This acid has been cyclized by passage over hot manganous oxide to bicyclo[2,2,2]octanedione-2,6, a completely non-enolic β-diketone, whose structure was shown by a Wolff–Kishner reduction to bicyclo[2,2,2]octane.

CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 3, 1940

---

[19] Done by Arlington Laboratories, Arlington, Va.