Syntheses of γ-Ionone Analogues. III. Diels-Alder Reaction Involving a Mixture of 3, 4-Dimethyl-1, 3-pentadiene and 2, 3-Dimethyl-1, 3-pentadiene, and Some Derivatives from 2-Benzyloxymethyl-4, 5, 6-trimethylcyclohexa-1, 4-dienylmethanal

By Atsuaki ARAI and Iwao ICHIKIZAKI

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As described in a previous paper¹⁾, 2-methylene-4, 5-dimethylcyclohexylmethanol, an analogue of γ-cyclogeraniol, can be conveniently synthesized, in five steps, from a Diels-Alder adduct prepared by the condensation of 2, 3-dimethyl-1, 3-butadiene with 4-benzyloxy-2-butyn-1-al (I), $C_6H_5CH_2OCH_2C\equiv CCHO$. It is to be expected, therefore, that a similar condensation of 3, 4-dimethyl-1, 3-pentadiene (III) with I will yield 2-benzyloxymethyl - 3, 3, 4 - trimethylcyclohexa - 1, 4 - dienyl methanal (VI) and contribute an easy approach

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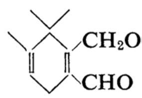
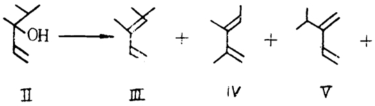
1) A. Arai and I. Ichikizaki, This Bulletin, 34, 1571 (1961).

to either 6-methyl-γ-cyclogeraniol or, further, to γ-irone itself.



VI

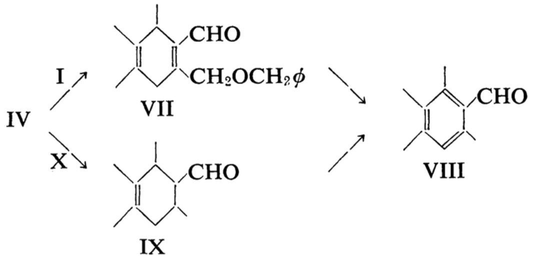
The studies under various conditions to prepare III revealed that the dehydration of 3, 4-dimethyl-1-penten-3-ol (II)[2,3] with potassium hydrogen sulfate afforded totally, in a 75% yield, a diene mixture containing III, 2, 3-dimethyl-1, 3-pentadiene (IV) and 2-isopropyl-1, 3-butadiene (V) in a ratio of approximately 18 : 21 : 53, with unkown three hydrocarbons of minor quantities.

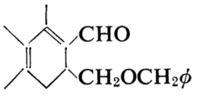


+ Three unknown hydrocarbons

The composition of these hydrocarbons scarcely changed during many dehydrations at 140~180°C. Since the effective separation of III from IV was particularly difficult even by careful fractionations through an efficient column, a mixture consisting of 37.5% III and 62.5% IV, b. p. 107.5~108°C/753 mmHg, n_D^{20} 1.4664, was employed for the Diels-Alder reaction in the early stage of this research.

When a benzene solution of the mixed diene in the presence of a little amount of hydroquinone was heated for 10 hr. at 155°C with I, a doubly unsaturated aldehyde, $C_{18}H_{22}O_2$, ν_{max}^{film} 2750 and 1670 cm^{-1}, was obtained in a 64% yield. The light absorption band (in ethanol) at 236 mμ (ε 5900) revealed that the unsaturated aldehyde contains an α, β- and an isolated unsaturated linkage. The quantitatively yielded phenylsemicarbazone was readily hydrolyzed by super heated steam in the presence of both phthalic and sulfric acids to be converted with the elimination of benzyl alcohol into 2, 3, 4, 6-tetramethylbenzaldehyde (VIII). The aldehyde VIII was also prepared from the sulfur dehydrogenation of 2, 3, 4, 6-tetramethyl-3-cyclohexenylmethanal(IX), which had been obtained in a 52% yield by a similar treatment of the same mixed diene with crotonaldehyde (X). Consequently, the structure of the adduct was reasonably concluded to be 2-benzyloxymethyl-4, 5, 6-trimethylcyclohexa-1, 4-dienylmethanal (VII). The aldehyde VII was readily converted by the action of diluted sulfuric acid into an isomer which was presumed to be 6-benzyloxymethyl-2, 3, 4-trimethylcyclohexa-1, 3-dienylmethanal (XI).





XI

All the results obtained above clearly indicated that only IV could participate in this reaction, that III could not practically react with the dienophiles, and, moreover, that a high degree of specificity was exhibited in the direction of the addition of IV to either I or X. And from the higher yield of VII than that expected, it was considered that III was partly isomerized to IV under the given conditions. In order to fully test the ability of III as a Diels-Alder diene, the authors employed for the reaction with X a specially enriched sample, b. p. 109.2~110°C/758 mmHg, n_D^{20} 1.4722, which had been confirmed to consist of 94.7% III, 5.3% IV and no other dienes; they then found that III was partly polymerized and mostly recovered after isomerizing to IV, whereas the addition product obtained in a slight yield was proved to consist largely of IX. On the other hand, a similar reaction at 125°C with a mixture, b. p. 106.3~106.6°C/760 mmHg, n_D^{20} 1.4634, containing 91.4% IV and 8.6% III, afforded IX in a 42% yield.

Naves[2], Nazarov[3] and their associates claimed that the Diels-Alder reaction between so-called 3, 4-dimethyl-1, 3-pentadiene and X gave an adduct which resulted directly from III itself as a main product, although as to the direction of the addition their conclusions were contradictory. It is still obscure, for the present, why the opinions about the Diels-Alder reaction involving III do not agree with one another; however, it should be emphasized that both the diene samples used by the European investigators, showing n_D^{20} 1.4560 and 1.4691 respectively, might be more heterogeneous and clearly more deficient in III than the one employed by the authors for the above test. Several problems concerning the diene III will be discussed in detail in a following paper.

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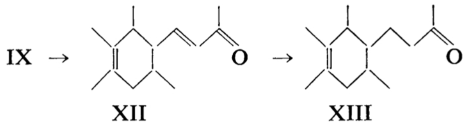
[2] Y. R. Naves and P. Ardizio, *Helv. Chim. Acta*, **31**, 2256 (1948).

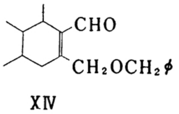
[3] I. N. Nazarov and M. V. Mavrov, *Zhur. Obshchei Khim.*, **29**, 1158 (1959).

The Diels-Alder adducts, VII and IX, gave several derivatives, some of which were proved to have an odor.

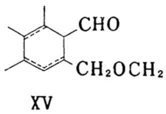
The aldehyde IX freshly regenerated from its phenylsemicarbazone afforded, on condensation with acetone, 4-(2′, 3′, 4′, 6′-tetramethyl-3′-cyclohexenyl)-but-3-en-2-one (XII) in an 82.2% yield. The catalytic hydrogenation of XII over platinum oxide catalyst gave, in an 81% yield, 4-(2′, 3′, 4′, 6′-tetramethyl-3′-cyclohexenyl)-butan-2-one (XIII). Both XII and XIII have a pleasant odor.



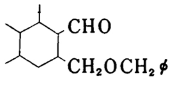
On the partial hydrogenation of VII in the presence of a palladium-calcium carbonate catalyst, when one mole of hydrogen was consumed, an α, β-unsaturated aldehyde XIV and appreciable amounts of an unconjugated unsaturated aldehyde XV were obtained, although the location of the double bond in the latter has not been confirmed. With a palladium-barium carbonate catalyst, after absorbing two moles of hydrogen, VII afforded 6-benzyl-oxymethyl - 2, 3, 4-trimethylcyclohexylmethanal (XVI). In the meanwhile, when hydrogenation was carried out under pressure in the presence of a Raney nickel catalyst, it afforded the saturated diol XVII in a yield of 73%.



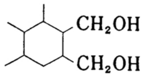
XIV



XV

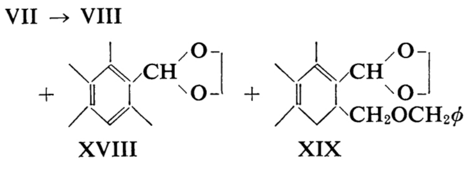


XVI

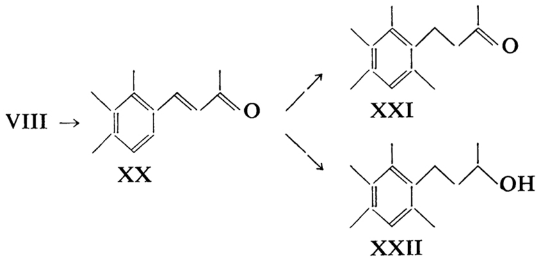


XVII

Treatment of VII with ethylene glycol[4] in the presence of p-toluenesulfonic acid gave VIII, the ethylene acetal XVIII and, in only a 3% yield, an acetal which was presumed to be XIX, an isomer of the desired acetal.



Finally, when VIII was condensed with acetone in the usual way 4-(2′, 3′, 4′, 6′-tetramethylphenyl)-but-3-en-2-one (XX), with a weak violet-like odor, was obtained in a 92% yield. On partial hydrogenation over platinum oxide catalyst XX afforded, in an excellent yield, 4-(2′, 3′, 4′, 6′-tetramethylphenyl)-butan-2-one (XXI), and, on further hydrogenation with a Raney nickel catalyst under pressure, it gave 4-(2′, 3′, 4′, 6′-tetramethylphenyl)-butan-2-ol (XXII).



Experimental[5]

3, 4-Dimethyl-1-penten-3-ol (II).—3, 4-Dimethyl-1-penten-3-ol (II) was prepared in an 85~89% yield by hydrogenation of 3, 4-dimethyl-1-pentyn-3-ol, b. p. 134.5°C/760 mmHg, n_D^{20} 1.4362 (lit.[3] b. p. 134~134.5°C/752 mmHg, n_D^{20} 1.4370), with a palladium-on-calcium carbonate catalyst. The carbinol II had b. p. 134.7~135°C/760 mmHg and n_D^{20} 1.4335 (lit.[3] b. p. 130.7~131°C/748 mmHg, n_D^{20} 1.4361).

Dehydration of 3, 4-Dimethyl-1-penten-3-ol (II) with Potassium Hydrogen Sulfate.—The carbinol II (77 g.) was stirred, drop by drop, into potassium hydrogen sulfate (fused, 20 g.) over a period of 7 hr. at 175~180°C under a nitrogen atmosphere and simultaneous distillation of the dehydration products through a 25 cm. Vigreux column. After separating the aqueous layer, the distillate was dried over calcium chloride, then simply redistilled through a 30 cm. column, and a fraction boiled at 82 to 108°C was collected. The yield was 43.7 g. (75%). There remained a brown tarry oil (ca. 10 g.) containing unchanged II in a distilling flask. Vapor phase chromatography at 90°C showed that the above fraction consists of six components containing 3, 4-dimethyl-1, 3-pentadiene (III), 2, 3-dimethyl-1, 3-pentadiene (IV) and 2-isopropyl-1, 3-butadiene (V) in a ratio of approximately 18 : 21 : 53, with three unknown hydrocarbons of minor quantities (Fig. 1).

The above fraction was carefully fractionated through a 100 cm. modified Todd fractionating column to give the following representatitive fractions :

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[4] E. I. Salmi, *Ber.*, **71**, 1803 (1938).

[5] All m. p.'s were determined on the Kofleir hot-stage and are uncorrected. The ultraviolet absorption spectra were determined with a Hitachi spectrophotometer model EPU-2A, while the infrared absorption spectra were obtained with a Perkin-Elmer model 112, a Kōken model DS-301 and a Nippon Bunkō model IR-S recording spectrophotometer using sodium chloride optics. Vapor phase chromatographic analyses were carried out with a Kotaki Super Fractioner model GU-21 using a 200 mm. × 8 mm. φ copper tube packed with Celite DM-13 A which was coated with Carbowax-4000.

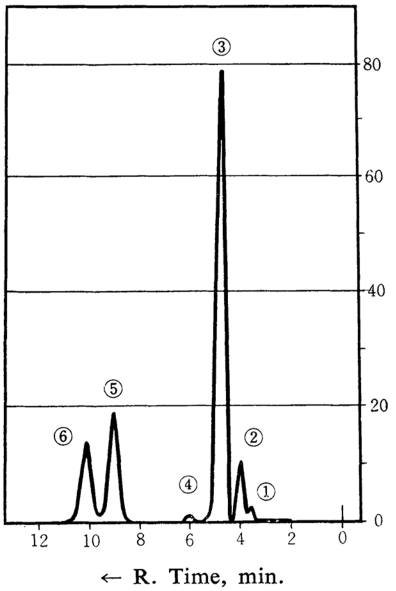

Fig. 1. Vapor phase chromatogram of the dehydration products of 3,4-dimethyl-1-penten-3-ol (II) with potassium hydrogen sulfate at 175~180°C.
①, ② and ④: Unknown hydrocarbons
③: 2-Isopropyl-1,3-butadiene (V)
⑤: 2,3-Dimethyl-1,3-pentadiene (IV)
⑥: 3,4-Dimethyl-1,3-pentadiene (III)

F. No.	B. p. °C/760 mmHg	n_D^{20}	Yield g.	Composition, % III	: IV	: V
3	86~87	1.4326	16.0			98
7	104~106	1.4552~1.4617	1.8	6	72	15
8	106~106.5	1.4635	2.9	7.5	85	4.5
9	106.5~107.5	1.4635~1.4660	2.5	17	82	
10	107.5~108.5	1.4664~1.4671	5.3	42	58	
11	108.5	1.4680	1.4	52	48	

The diene V was easily isolated from the other components after two redistillations through the same column, whereas III and IV could not be separated from each other even by the repeated redistillations. The enriched sample of III which was thus obtained had b. p. 109.2~110°C/758 mmHg and n_D^{20} 1.4722 and consisted of 94.7% III and 5.3% IV; that of IV had b. p. 106.3~106.6°C/760mmHg and n_D^{20} 1.4634 and was composed of 91.4% IV and 8.6% III.

Many dehydrations of II with potassium hydrogen sulfate carried out in the range at 140 to 180°C showed that the composition of the hydrocarbons was practically constant and did not change with the temperature.

A mixed diene consisting of 37.5% III and 62.5% IV, b. p. 107.5~108°C/753 mmHg, n_D^{20} 1.4664, which was easily obtained, was employed for the next Diels-Alder reactions.

2-Benzyloxymethyl-4,5,6-trimethylcyclohexa-1,4-dienylmethanal (VII).—A mixture of 4-benzyloxy-2-butyn-1-al (I) (34.8 g.), the mixed diene (20.2 g.) and benzene (30 ml.) was heated with a little hydroquinone for 10 hr. at 155°C under nitrogen in a glass bomb. Concentration of the reaction mixture under reduced pressure, followed by distillation, gave a small amount of unchanged I and a pale yellow oil (36.0 g.), b. p. 133~135°C/2.2×10^{-3} mmHg, n_D^{20} 1.5496. There remained a considerable amount of a dark-red resinous matter. In order to investigate the homogeneity of the above fraction, the 2,4-dinitrophenylhydrazone was directly prepared from the above fraction (0.34 g.), and the excess of water was added to the reaction mixture to precipitate any methanol-soluble materials. When the precipitate (0.36 g.) was dissolved in chloroform (1.5 ml.) and chromatographed on alumina (200 mm.×18 mm. ϕ) from benzene, a weak red-orange band at the top of the column and then a strong yellow-orange band were obtained. The lower zone afforded orange silk-like needles (270 mg.), m. p. 155~156°C, after being crystallized from ethanol-ethyl acetate.

Found: N, 12.42. Calcd. for $C_{24}H_{27}O_5N_4$: N, 12.44%.

The upper band gave red-orange needles (10 mg.), m. p. 128~129.8°C, after crystallization from methanol.

Found: N, 12.60%.

The phenylsemicarbazone was prepared from the above fraction (1.0 g.) in the usual manner, and an excess of water was added and allowed to stand overnight. The crystalline solid was collected and crystallized from ethanol to give colorless needles (1.27 g.) melting at 163~164°C, λ_{max}^{EtOH} 235 mμ (ε, 17700), 285 (32100), which could be converted into the 2,4-dinitrophenylhydrazone, m. p. 155~156°C, described above.

Found: N, 10.46. Calcd. for $C_{25}H_{29}O_2N_3$: N, 10.41%.

From the mother liquor, colorless needles (60 mg.) melting at 139 to 141°C were isolated.

Found: N, 10.38%.

The crude pale yellow oil mentioned above was twice redistilled carefully under nitrogen to afford VII as a pale yellow viscous liquid, b. p. 133~134°C/2×10^{-3} mmHg, n_D^{20} 1.5494. ν_{max}^{film} 2750, 1670 (CHO, conju.), 1640 (C=C, conju.), 1070 (C-O-C), 3025, 1502, 742 and 705 cm^{-1} (phenyl group). λ_{max}^{EtOH} 236 mμ (ε 5900).

Found: C, 79.80; H, 8.27. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%.

From the above fraction, only the 2,4-dinitrophenylhydrazone, m. p. 155~156°C, was obtained.

Treatment of the Aldehyde VII with Diluted Sulfuric Acid.—The aldehyde VII (0.3 g.), dissolved in a solution of concentrated sulfuric acid (0.2 ml.) in 80% aqueous methanol (2 ml.), was warmed at 60°C for 5 min. A saturated solution of potassium acetate in methanol was added dropwise to the cooled reaction mixture until the precipitation of potassium sulfate was completed. The mixture was filtered, and the filtrate was then concentrated and treated with a solution of phenylsemicarbazide (0.4 g.) in methanol (5 ml.). After this was kept overnight at room temperature, a solid derivative was collected and crystallized from 50% aqueous ethanol to yield what is believed to be the phenylsemicarbazone of 6-benzyloxymethyl-2, 3, 4-trimethylcyclohexa-1, 3-dienylmethanal (XI) (0.26 g.) as long needles, m. p. 167～169°C; this showed a marked depression in melting point on admixture with that of VII, m. p. 163～164°C.

Found: N, 10.37. Calcd. for $C_{25}H_{29}O_2N_3$: N, 10.41%.

2, 3, 4, 6-Tetramethyl-3-cyclohexenylmethanal (IX).—*a) From the Mixed Diene (b. p. 107.5～108°C/753 mmHg) and Crotonaldehyde (X).*—A mixture of mixed diene (16.2 g.), X (10.5 g.) and benzene (10 ml.) were heated with a small amount of hydroquinone for 7 hr. at 155°C in a 50 ml. glass bomb. After removal of the solvent, the residue was distilled to afford a colorless liquid (13.0 g.), b. p. 72～74.5°C/3.5 mmHg, n_D^{20} 1.4778.

Found: C, 79.16; H, 11.15. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

Treatment of the above fraction with the Brady reagent gave a yellow 2, 4-dinitrophenylhydrazone, m. p. 181～182°C, after crystallization from methanol.

Found: N, 16.16. Calcd. for $C_{17}H_{22}O_4N_4$: N, 16.18%.

From the mother liquor a small number of orange-yellow needles, m. p. 128.5～136°C, which have not been further investigated, were separated.

The phenylsemicarbazone obtained from the above fraction was crystallized from aqueous ethanol to give needles, m. p. 133～135°C, in a 62% yield.

Found: N, 14.23. Calcd. for $C_{18}H_{25}ON_3$: N, 14.04%.

From the mother liquor an appreciable amount of a crystalline solid melted at 115 to 121°C was separated.

The phenylsemicarbazone (6.7 g.) obtained above as the main product was mixed with *o*-phthalic acid (14 g.), ethylene glycol (6 ml.) and water (100 ml.), and distilled in steam. The distillate was extracted with ether, and the ether extract was then washed with a 10% aqueous sodium carbonate solution and with water, dried and evaporated. Distillation of the residue afforded the aldehyde IX (2.6 g., 68%), b. p. 61～63.5°C/1.5 mmHg, n_D^{20} 1.4795, which gave only 2, 4-dinitrophenylhydrazone melting at 181～182°C.

Found: C, 79.34; H, 11.08. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

b) From the Mixed Diene (b. p. 109.2～110°C/758 mmHg) and X.—A mixture of the mixed diene (2.5 g.), X (1.9 g.) and benzene (10 ml.) was heated with a small amount of hydroquinone for 30 hr. at 125°C in a 50 ml. glass bomb. After removal of the solvent, the residual oil was distilled through a 10 cm. Vigreux column to afford a considerable amount of fore-run consisting of the unchanged starting materials and an oil (0.3 g.), b. p. 71～73°C/3 mmHg, n_D^{20} 1.4796, whose vapor phase chromatogram showed that this fraction consisted mainly of IX and of an appreciable amount of some unknown components.

Found: C, 79.78; H, 11.12. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

From the vapor phase chromatography, it was shown that the fore-run obtained above contains the diene III and IV in the proportion of 1 : 5, besides unchanged crotonaldehyde (X).

When the same reaction mixture as above was heated for 6 hr. at 200°C, the compositions of product became more complicated. In all cases, a gummy matter, which on cooling solidified gradually to give a white amorphous polymer, softened at ca. 130°C.

c) From the Mixed Diene (b.p. 106.3～106.6°C/760 mmHg) and X.—A mixture of the mixed diene (2.5 g.), X (1.9 g.) and benzene (10 ml.) was heated with a small amount of hydroquinone for 12 hr. at 125°C in a 50 ml. glass bomb. After removal of the solvent, the residue was distilled through an 8 cm. Vigreux column under nitrogen to afford a fore-run consisting largely of the unchanged starting materials and a colorless oil (1.8 g.), b. p. 76～78°C/4 mmHg, n_D^{20} 1.4791. Redistillation gave pure IX (1.52 g.), b. p. 75.5°C/4 mmHg, n_D^{21} 1.4791. ν_{max}^{film} 2740, 1721 (CHO), 1468 (CH_2) and 1387 cm^{-1} (CH_3).

Found: C, 79.42; H, 11.12. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

Upon treatment with the Brady reagent, IX gave a yellow 2, 4-dinitrophenylhydrazone, m. p. 181～182°C, which showed no melting point depression on admixture with that prepared in a).

2, 3, 4, 6-Tetramethylbenzaldehyde (VIII).—*a) Acid Hydrolysis of the Phenylsemicarbazone of VII Melted at 163～164°C.*—A mixture of this derivative (7.0 g.), *o*-phthalic acid (7.0 g.), ethylene glycol (50 g.), concentrated sulfuric acid (15 g.) and water (50 ml.) was distilled in steam until no more organic materials passed over (7 hr. were required for this). The distillate (1300 ml.) was extracted with ether, and the ether extract was washed with water, dried over sodium sulfate and concentrated. Fractional distillation of the residual oil afforded a fore-run (0.6 g.), b. p. 49～55°C/1.2 mmHg, and 2, 3, 4, 6-tetramethylbenzaldehyde (VIII) (2.0 g., 69%) as a colorless oil, b. p. 92～94°C/1.2 mmHg, n_D^{20} 1.5482. ν_{max}^{film} 1709 (C=O), 867 cm^{-1} (pentasubstituted phenyl group). λ_{max}^{EtOH} 268.5 and 306 mμ (lit.[6] λ_{max}^{EtOH} 267 mμ (log ε, 4.00), 306 (3.32)).

Found: C, 80.75; H, 8.89. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

The semicarbazone crystallized from 50% aqueous methanol in the form of needles, melted at 189°C to a liquid which quickly solidified and then remelted at 259～260°C with partial decomposition. λ_{max}^{EtOH} 219 mμ (ε, 19200), 275 (12000).

Found: C, 65.72; H, 7.64; N, 19.12. Calcd. for $C_{12}H_{17}ON_3$: C, 65.72; H, 7.81; N, 19.16%.

The 2, 4-dinitrophenylhydrazone crystallized from ethanol-ethyl acetate in the form of orange-yellow needles, m. p. 222～223°C.

Found: C, 59.57; H, 5.15; N, 16.35. Calcd. for $C_{17}H_{18}O_4N_4$: C, 59.64; H, 5.30; N, 16.37%.

b) Sulfur Dehydrogenation of 2, 3, 4, 6-Tetramethyl-3-cyclohexenylmethanal (IX).—The aldehyde IX (3.3

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[6] N. J. Leonard and E. R. Blout, *J. Am. Chem. Soc.*, 72, 486 (1950).

g.) prepared in the method of c) was heated under reflux with sulfur (1.6 g.) at 220∼230°C under a nitrogen atmosphere until the evolution of hydrogen sulfide ceased (40 min. were required). The volatile materials were distilled under reduced pressure. The yellow distillate, b. p. 120∼130°C/8.2 mmHg, thus obtained, on further distillation under nitrogen through a 7 cm. Vigreux column, yielded 2,3,4,6-tetramethylbenzaldehyde (VIII) (1.0 g., 31%) which had b. p. 127°C/8.2 mmHg and n_D^{20} 1.5740. There remained black tarry materials (ca. 1.3 g.) in the distilling flask.

The semicarbazone crystallized from aqueous methanol in prisms melted at 187∼188°C to a liquid which rapidly solidified and then remelted at 259°C with partial decomposition; it gave no melting point depression on admixture with that prepared in a).

The 2, 4-dinitrophenylhydrazone prepared in the usual manner was chromatographed on alumina from benzene and crystallized twice from methanol-ethyl acetate to yield orange-yellow needles, m. p. 221∼222°C, which showed no melting point depression on admixture with that obtained in a).

4-(2′,3′,4′,6′-Tetramethyl-3′-cyclohexenyl)-but-3-en-2-one (XII).—The aldehyde IX (2.3 g.) regenerated from the phenylsemicarbazone described above in acetone (7.0 ml.) was added dropwise to a boiled solution of barium hydroxide (0.4 g.) in 80% aqueous acetone (20 ml.) and refluxed for 19 hr. After the bulk of the solvent had been removed, the residue was dissolved in ether. The ethereal solution was washed successively with 10% hydrochloric acid and water, dried over magnesium sulfate and evaporated. Distillation afforded the unsaturated ketone XII (2.35 g., 82.2%) as a colorless liquid with a pleasant odor, b. p. 98∼100°C/1.2 mmHg, n_D^{20} 1.4979. $\nu_{\max}^{\text{film}}$ 1680 (C=O), 1622 (C=C), 1257 (CH_3CO) and 984 cm^{-1} (-CH=CH-, *trans*).

Found: C, 81.63; H, 10.86. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75%.

The phenylsemicarbazone crystallized from ethanol in the form of feather-like needles, m. p. 149∼151°C.

Found: N, 12.33. Calcd. for $C_{21}H_{29}ON_3$: N, 12.38%.

The 2, 4-dinitrophenylhydrazone crystallized from ethanol-ethyl acetate in the form of ruby-red needles, m. p. 141∼142°C.

Found: N, 14.51. Calcd. for $C_{20}H_{26}O_4N_4$: N, 14.50%.

4-(2′, 3′, 4′, 6′-Tetramethyl-3′-cyclohexenyl)-butan-2-one (XIII).—The ketone XII (1.45 g.) in ethyl acetate (40 ml.) was hydrogenated at ordinary pressure in the presence of a platinum oxide catalyst (50 mg.) until one molar equivalent (170 ml. at 20°C) of hydrogen had been absorbed. Removal of the catalyst and solvent, followed by distillation of the residue, afforded XIII (1.18 g., 80.5%) as a colorless liquid with a pleasant odor, b. p. 97∼99°C/1.5 mmHg, n_D^{20} 1.4769.

Found: C, 80.50; H, 11.77. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61%.

The semicarbazone crystallized from 40% aqueous methanol in the form of needles, m. p. 152.5∼153.5°C.

Found: C, 68.00; H, 10.09; N, 15.76. Calcd. for $C_{15}H_{27}ON_3$: C, 67.88; H, 10.26; N, 15.83%.

The 2, 4-dinitrophenylhydrazone crystallized from ethanol-ethyl acetate in the form of bright yellow prisms, m. p. 150∼150.5°C.

Found: C, 61.57; H, 7.11; N, 14.60. Calcd. for $C_{20}H_{28}O_4N_4$: C, 61.84; H, 7.27; N, 14.42%.

2-Benzyloxymethyl-4, 5, 6-trimethyl-1-cyclohexenylmethanal (XIV).— The aldehyde VII (5.4 g.) in ethanol (10 ml.) was hydrogenated in the presence of a palladium-on-calcium carbonate catalyst (2.5% Pd, 2.0 g.) until 1.1 mol. equivalents (508 ml. at 8°C and 754 mmHg) of hydrogen had been absorbed. Removal of the catalyst and solvent, followed by distillation of the residue, afforded a pale yellow liquid (3.6 g.), b. p. 124∼126°C/9×10^{-3} mmHg, n_D^{20} 1.5388.

Found: C, 78.71; H, 8.72. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88%.

The phenylsemicarbazone crystallized from ethanol in the form of needles, m. p. 173.5∼174.5°C. $\lambda_{\max}^{\text{EtOH}}$ 232 mμ (ε 29400), 292 (22200).

Found: N, 10.46. Calcd. for $C_{25}H_{31}O_2N_3$: N, 10.36%.

The crude 2,4-dinitrophenylhydrazone prepared directly from the above hydrogenation product (0.4 g.) in the usual manner was chromatographed on alumina from benzene. The lower, main red-orange zone gave the 2,4-dinitrophenylhydrazone of XIV as orange-red needles, m. p. 164∼165°C (0.33 g.), after recrystallization from ethanol-ethyl acetate.

Found: N, 12.52. Calcd. for $C_{24}H_{28}O_5N_4$: N, 12.38%.

The upper, slight yellow band yielded, after being crystallized from ethanol-ethyl acetate, a 2, 4-dinitrophenylhydrazone (10 mg.), m. p. 193∼194°C, which is believed to be that of 6-benzyloxymethyl-2, 3, 4-trimethylcyclohexenylmethanal (XV), although the location of the double bond has not been determined.

Found: N, 12.38%.

6-Benzyloxymethyl-2, 3, 4-trimethylcyclohexylmethanal (XVI).—The aldehyde VII (2.70 g.) in ethanol (20 ml.) was hydrogenated at one atmosphere in the presence of a palladium-on-barium carbonate catalyst (2.5% Pd, 1.0 g.) until 2.05 mol. equivalents (470 ml. at 9.5°C) of hydrogen had been absorbed. Removal of the catalyst and solvent, followed by distillation of the residue, afforded the saturated aldehyde XVI (2.10 g., 76.6%) as a colorless liquid, b. p. 115∼117°C/5×10^{-3} mmHg, n_D^{20} 1.5290. $\nu_{\max}^{\text{film}}$ 2710, 1724 (CHO), 1099 (C-O-C), 741 and 703 cm^{-1} (mono-substituted phenyl group).

Found: C, 78.74; H, 9.29. Calcd. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55%.

The phenylsemicarbazone crystallized from ethanol in the form of fine needles, m. p. 134∼135°C. $\lambda_{\max}^{\text{EtOH}}$ 248 mμ (ε 28400).

Found: N, 10.47. Calcd. for $C_{25}H_{33}O_2N_3$: N, 10.31%.

The 2, 4-dinitrophenylhydrazone crystallized from ethyl acetate in the form of orange-yellow needles, m. p. 105°C.

Found: N, 12.54. Calcd. for $C_{24}H_{30}O_5N_4$: N, 12.33%.

1, 2 - Bishydroxymethyl - 3, 4, 5 - trimethylcyclohexane (XVII).—The aldehyde VII (2.7 g.) in ethanol (30 ml.) was hydrogenated in the presence of a Raney nickel catalyst (1.0 g.) for 4 hr. at 150°C and 195 kg./cm^2. After the catalyst had been removed, the filtrate was again hydrogenated with a palladium-on-charcoal catalyst (5% Pd, 1.0 g.) for 2 hr. at 130°C and 150 kg./cm^2. Removal of the catalyst and solvent, followed by distillation of the residue, gave the diol XVII (1.36 g., 73%), b. p. 113~115°C/4$\times 10^{-3}$ mmHg, n_D^{25} 1.4860. ν_{max}^{film} 3333 and 1054 cm^{-1} (OH).

Found: C, 71.32; H, 11.75. Calcd. for $C_{11}H_{22}O_2$: C, 70.29; H, 11.90%.

The bisphenylurethane crystallized from benzene-ethyl acetate in the form of needles, m. p. 173°C.

Found: C, 67.88; H, 7.59; N, 6.42. Calcd. for $C_{25}H_{32}O_4N_2 \cdot H_2O$: C, 67.85; H, 7.75; N, 6.33%.

Attempted Acetalation of 2-Benzyloxymethyl-4, 5, 6-trimethylcyclohexa-1, 4-dienylmethanal (VII) with Ethylene Glycol.—A mixture of the aldehyde VII (13.5 g.), ethylene glycol (15 g.), *p*-toluenesulfonic acid (0.25 g.) and benzene (60 ml.) was heated under reflux in an oil bath at a temperature of 120°C for 4 hr. with an azeotroper. The reaction mixture was cooled and the benzene layer separated. The ethylene glycol layer was extracted with benzene. The combined benzene solution was washed with a 10% aqueous sodium carbonate solution and with water, dried over sodium sulfate and evaporated. The residue was fractionated through a 7 cm. Vigreux column to give three representative fractions: i) 2, 3, 4, 6-Tetramethylbenzaldehyde (VIII) (3.3 g., 40.0%), b. p. 106~107°C/2.2 mmHg, n_D^{20} 1.5482, whose infrared spectrum was identical with that of the authentic VIII described above.

Found: C, 81.34; H, 8.77%.

ii) 2, 3, 4, 6 - Tetramethylbenzaldehyde ethylene acetal (XVIII) (1.0 g., 17%), a colorless oil, b. p. 123~125°C/2.2 mmHg, which solidified quickly to give prisms melting at 58°C after being crystallized from petroleum ether.

Found: C, 75.32; H, 8.69. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%.

Treated with the Brady reagent, XVIII gave 2, 4-dinitrophenylhydrazone, m. p. 221°C, which showed no melting point depression on admixture with that of VIII.

iii) 6-Benzyloxymethyl-2, 3, 4-trimethylcyclohexa-1, 3-dienylmethanal ethylene acetal (XIX) (0.5 g., 3%), a pale yellow viscous oil, b. p. 147~150°C/2 $\times 10^{-2}$ mmHg, n_D^{20} 1.5630.

Found: C, 76.20; H, 8.30. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34%.

4-(2′, 3′, 4′, 6′ - Tetramethylphenyl)-but-3-en-2-one (XX).—The aldehyde VIII (1.0 g.) in acetone (5 ml.) was added dropwise to a boiled 80% aqueous acetone (10 ml.) containing barium hydroxide (0.2 g.), and the resultant mixture was refluxed for 21 hr. The cooled reaction mixture was neutrallized with 1 N hydrochloric acid and concentrated under reduced pressure. The pale yellow crystalline residue (1.25 g.) was crystallized from 80% aqueous methanol to give the unsaturated ketone XX (1.15 g., 92.2%) as colorless fine long needles with a weak violet-like odor, m. p. 80°C. ν_{max}^{KBr} 1658 (C=O, conju.), 1611 (C=C, conju.), 1255 (CH_3CO), 1004 (-CH=CH-, *trans*) and 878 cm^{-1} (penta-substituted phenyl group). λ_{max}^{EtOH} 218 mμ (ε 20500), 295 (11700).

Found: C, 82.88; H, 9.08. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

The semicarbazone crystallized from ethanol-ethyl acetate in leaflets, m. p. 225~226°C (partly decomp.). λ_{max}^{EtOH} 286 mμ (ε 31000).

Found: C, 69.27; H, 8.25; N, 16.05. Calcd. for $C_{15}H_{21}ON_3$: C, 69.46; H, 8.16; N, 16.21%.

The 2, 4-dinitrophenylhydrazone crystallized from ethanol-ethyl acetate in the form of dark-red prisms, m. p. 174~175°C.

Found: N, 14.58. Calcd. for $C_{20}H_{22}O_4N_4$: N, 14.65%.

4-(2′, 3′, 4′, 6′ - Tetramethylphenyl) - butan - 2 - one (XXI).—The ketone XX (50.6 mg.) in ethanol (20 ml.) was hydrogenated in the presence of a platinum oxide catalyst (30 mg.) until 1.05 mol. equivalents (5.9 ml. at 10°C and 754 mmHg) of hydrogen had been absorbed. Removal of the catalyst and solvent, followed by recrystallization of the residual solid from petroleum ether, gave the ketone XXI (47.0 mg., 93%) as colorless needles, m. p. 62.5~63.5°C.

Found: C, 82.54; H, 9.90. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87%.

The 2, 4-dinitrophenylhydrazone crystallized from ethanol-ethyl acetate in the form of yellow needles, m. p. 166~167°C.

Found: C, 62.12; H, 6.26. Calcd. for $C_{20}H_{24}O_4N_4$: C, 62.48; H, 6.29%.

4 - (2′, 3′, 4′, 6′ - Tetramethylphenyl) - butan - 2 - ol (XXII).—The ketone XX (0.7 g.) in ethanol (50 ml.) was hydrogenated in the presence of a Raney nickel catalyst (1.2 g.) for 1.5 hr. at 120~130°C and 110 kg./cm^2 in a 100 ml. autoclave. Removal of the catalyst and solvent, followed by crystallization of the residue from methanol, yielded the carbinol XXII (0.66 g., 92.6%) as colorless needles, m. p. 79°C. ν_{max}^{KBr} 3356, 1089 (OH), 867 and 857 cm^{-1} (penta-substituted phenyl group).

Found: C, 80.75; H, 10.74. Calcd. for $C_{14}H_{22}O$; C, 81.50; H, 10.75%.

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