Leaf Alcohol. (XV)

Leaf Alcohol Reaction

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Evidence was provided by syntheses through unequivocal routes for the structures of both 2-propyl-5-ethylbenzyl- and 2-ethyl-5-methylbenzyl alcohols, the leaf alcohol reaction products from leaf alcohol and *n*-pent-3-en-1-ol respectively.

Reaction mechanism was proposed on the basis of a model reaction with crotonaldehyde which on stepwise treatments with bases gave 2-methylbenzyl alcohol *via* a cyclodiene intermediate, *o*-dihydrotolualdehyde. 2-Propyl-5-ethylbenzyl alcohol, having a lemon-like aroma characteristic of manufactured black tea, was suspected to have been enzymatically formed from leaf alcohol or aldehyde in fresh tea leaves during fermentation process and an attempted search for this compound in the essential oil obtained by steam distillation of manufactured black tea was made, but its existence has not so far been confirmed.

I. INTRODUCTION

In an earlier work, one of the present authors reported that leaf alcohol, 3-*cis*-hexen-1-ol, when refluxed with metallic sodium at 160-170°, gave a liquid substance boiling at 240° and having a lemon-like flavor, which was tentatively assumed as being 3-propyl-nona-3, 6-dien-1-ol or 3-propyl-non-3-en-1-ol[1].

The structural elucidation of this compound was not taken up again until the postwar time, but has since been prosecuted in this laboratory with some measure of success. In recent works,[2,3,4] it was revealed that this alcohol resisted catalytic hydrogenation and faded neither potassium permanganate solution nor bromine at room temperature, contrary to what was expected from the aliphatic diene structure previously assumed. The UV-absorption at 268 $m\mu$ and the IR-absorption bands characteristic of 1,2,4-substituted benzene nucleus suggested that this compound should have resulted from aromatization reaction of the starting leaf alcohol. Consistently, this compound upon oxidation with boiling potassium permanganate solution afforded trimellitic acid in a good yield. Based on these facts, the 2-propyl-5-ethylbenzyl alcohol structure was tentatively deduced to this compound and this was confirmed by unequivocal synthetic evidence as will be detailed in the succeeding section. This alcohol was also obtained from 3-*trans*-, 2-cis-, 2-*trans*-hexen-1-ols as well as from leaf aldehyde, 2-*trans*-hexen-1-al, under exactly the same reaction conditions. Furthermore, in the extention of this reaction to the lower homologs such as 3-cis, *trans*-penten-1-ol and 2-*trans*-buten-1-ol, the aromatization was also effected, 2-ethyl-5-methylbenzyl- and 2-methylbenzyl alcohols having been obtained from the respective starting olefinic alcohols.
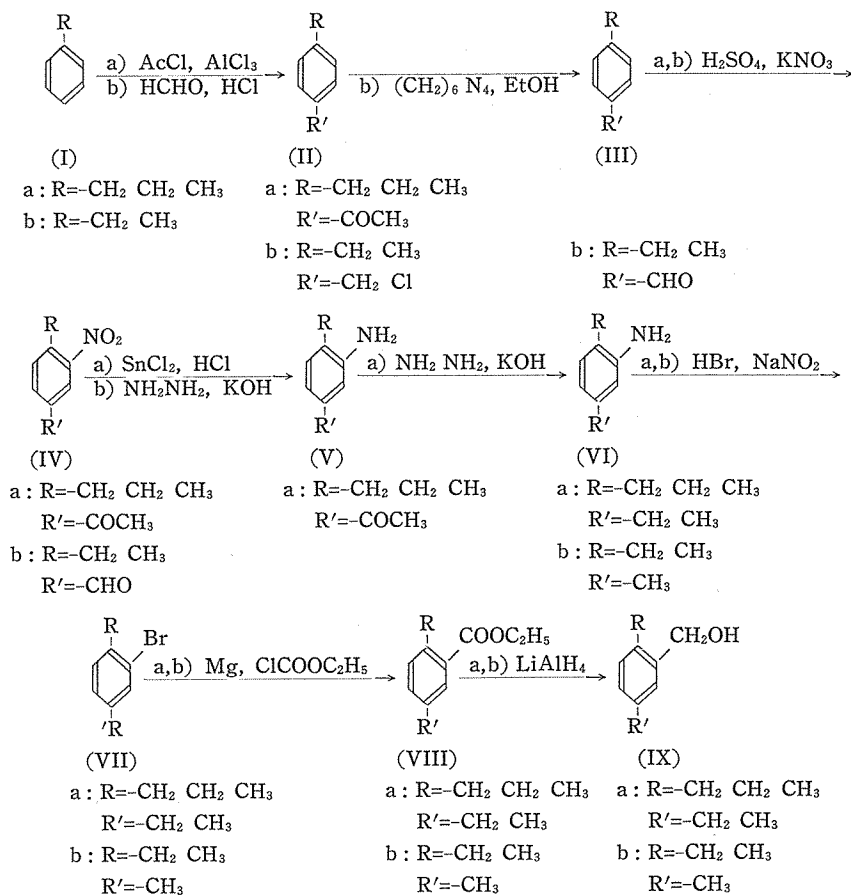
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This aromatization reaction originally found with leaf alcohol seemed to be generalized to the aliphatic α, β- and β, γ-unsaturated alcohols and aldehydes and hence was designated as *leaf alcohol reaction*. Besides the substituted benzyl alcohol, saturated fatty acids and alcohols in considerable yields and a Guerbet reaction product in minor quantity have been detected in the reaction products[5].

II. SYNTHESES OF 2-PROPYL-5-ETHYLBENZYL- AND 2-ETHYL-5-METHYLBENZYL ALCOHOLS

2-Propyl-5-ethylbenzyl- and 2-ethyl-5-methylbenzyl alcohols, both the leaf alcohol reaction products from the respective olefinic alcohols or aldehydes, were synthesized by the following eight-stage schemes and the identity with those from the leaf alcohol reactions was obtained, thereby establishing the previous deduction.

In the first stage of the scheme, the Friedel-Crafts acetylation[6] of *n*-propylbenzene (I-a) gave the desired *p*-propylacetophenone (II-a) which was found to be contaminated by a considerable amount of *o*-isomer. The purification of II-a was carried out by repeated recrystallizations of its semicarbazone followed by careful rectifications through an effective column of the regenerated ketone, the purity of which being checked by means of vapor phase chromatography[7].

R
a) AcCl, AlCl₃ → R, R' b) (CH₂)₆N₄, EtOH → R, R' a,b) H₂SO₄, KNO₃ →
b) HCHO, HCl

(I)
(II)
(III)

a : R=-CH₂ CH₂ CH₃   a : R=-CH₂ CH₂ CH₃
b : R=-CH₂ CH₃   R'=-COCH₃
                            b : R=-CH₂ CH₃   b : R=-CH₂ CH₃
                               R'=-CH₂ Cl   R'=-CHO

R, NO₂
a) SnCl₂, HCl → R, NH₂ a) NH₂ NH₂, KOH → R, NH₂ a,b) HBr, NaNO₂ →
b) NH₂NH₂, KOH

R'
(IV)   R'
              (V)   R'
                           (VI)

a : R=-CH₂ CH₂ CH₃   a : R=-CH₂ CH₂ CH₃   a : R=-CH₂ CH₂ CH₃
   R'=-COCH₃   R'=-COCH₃   R'=-CH₂ CH₃
b : R=-CH₂ CH₃   b : R=-CH₂ CH₃
   R'=-CHO   R'=-CH₃

R, Br
a,b) Mg, ClCOOC₂H₅ → R, COOC₂H₅ a,b) LiAlH₄ → R, CH₂OH

'R   R'   R'
(VII)   (VIII)   (IX)

a : R=-CH₂ CH₂ CH₃   a : R=-CH₂ CH₂ CH₃   a : R=-CH₂ CH₂ CH₃
   R'=-CH₂ CH₃   R'=-CH₂ CH₃   R'=-CH₂ CH₃
b : R=-CH₂ CH₃   b : R=-CH₂ CH₃   b : R=-CH₂ CH₃
   R'=-CH₃   R'=-CH₃   R'=-CH₃

This procedure was repeated until the melting point of the semicarbazone reached 186-7° and the ketone regenerated therefrom showed a single peak in v.p.c.

The p-ethylbenzaldehyde (III-b) was obtained by Blanc chloromethylation of ethylbenzene (I-b) followed by Sommelet conversion of the resulting p-ethylbenzylchloride (II-b). This product was found to be contaminated by a considerable amount of isomers. The purification of (III-b) was carried out by recrystallization of its semicarbazone. This recrystallization were repeated until the melting point of the semicarbazone reached 202-3° and the p-ethylbenzaldehyde (III-b) regenerated therefrom showed a single peak in v.p.c.. The nitration of p-ethylbenzaldehyde (III-b) gave the desired 3-nitro-4-ethylbenzaldehyde (IV-b) which was found to be contaminated by some amount of isomers, but this contamination was eventually eliminated in the succeeding several processes, as was shown at the stage of 3-bromo-4-ethyltoluene (VII-b) which showed a single peak in v.p.c..

The nitration of II-a and III-b in a usual way yielded the corresponding nitrocompounds IV-a and IV-b, in which the nitro group was orientated to m-position relative to the originally present carbonyl-substituent. The amino-ketone (V-a) which resulted from the stannous chloride reduction of the nitro-compound, was then subjected to Wolff-Kishner reduction with hydrazine and potassium hydroxide to give the dialkyl-substituted aniline (VI-a). The nitro-aldehyde (IV-b) was reduced with hydrazine directly to give 2-ethyl-5-methylaniline (VI-b). Bromine was introduced by Gattermann diazonium exchange into the aromatic nuclei and the resulting bromobenzenes (VII-a, b) were converted *via* Grignard compounds into the corresponding benzoates (VIII-a, b).

In the final stage of the routes, the lithium aluminum hydride reduction of ethyl 2-propyl-5-ethylbenzoate (VIII-a) and ethyl 2-ethyl-5-methylbenzoate (VIII-b) afforded 2-propyl-5-ethylbenzyl alcohol (IX-a) and 2-ethyl-5-methylbenzyl alcohol (IX-b) respectively. The identity of these alcohols with respective specimen obtained from the leaf alcohol reactions of hexenol and pentenol was obtained by the direct and spectral comparisons as well as by the mixed melting point comparison of their 3,5-dinitrobenzoates.

EXPERIMENTAL

4-n-Propylacetophenone (II-a). To a mixture of n-propylbenzene (60 g., 0.5 mole) and powdered aluminum chloride (66 g., 0.5 mole), acetyl chloride (78 g., 1 mole) was slowly added under stirring. The reaction mixture was kept at 12°. When the evolution of HCl ceased, the reaction mixture was poured into ice-water and extracted with ether and the ethereal solution was distilled to give 58 g. (71.4%) of 4-n-propylacetophenone. b.p. 95°/2mm., n_D^{20} 1.5215 ; semicarbazone, m.p. 186-7°.

Purification of 4-n-propylacetophenone : After three recrystallizations of crude 4-n-propylacetophenone semicarbazone from benzene, the melting point was elevated to 186-7°. This was saponified with dil. sulfuric acid and the regenerated ketone was distilled through an effective column to give pure 4-n-propylacetophenone which indicated a single peak in v.p.c..

3-Nitro-4-propylacetophenone (IV-a). To 100 g. (1 mole) of conc. sulfuric acid previously cooled in ice-bath, were added in small portions under stirring,

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10.3 g. (0.1 mole) of potassium nitrate. After dissolving completely, 13.4g. (0.1 mole) of 4-propylacetophenone were added to the mixture. The temperature was not allowed to rise above -5° during the addition, and the stirring was continued for 1 hr. and then the mixture was poured with stirring into a mixture of ice and water. The extraction with ether and the subsequent distillation gave 17 g. (94.4%) of 3-niro-4-propylacetophenone, b.p. 122-4°/0.05 mm., n_D^{18} 1.5400, m.p. 57-60°.

3-Amino-4-propylacetophenone (V-a). To a solution of 3-nitro-4-propylaceto-phenone (15.5 g., 0.075 mole) in ethanol, were added 52.5g. (0.23 mole) of stannous chloride in conc. hydrochloric acid (20 ml.). After stirring for 30 min., most of ethanol was distilled off and then excessive 40 % sodium hydroxide solution was slowly added. The reaction mixture was extracted with ether and the ethereal extracts, after drying over anhydrous sodium sulfate, was distilled to yield 11 g. (82.6 %) of 3-amino-4-propylacetophenone, b.p. 122-4°/0.25 mm., n_D^{13} 1.5792, m.p. 36°.

3-Amino-4-propylethylbenzene (VI-a). 3-Amino-4-propylacetophenone (3.5 g., 0.02 mole) was refluxed at 140° for 2 hrs. with 90 % hydrazine hydrate (2 g., 0.06 mole). After cooling, 27 g. (0.05 mole) of powdered potassium hydoxide were added and heating was continued at 200° until the evolution of nitrogen ceased. The reaction mixture was poured with stirring into ice-water and extracted with ether; After removal of the solvent, the distillation of the residue gave 3.23 g. (99.1 %) of 3-amino-4-propyl-ethylbenzene, b.p. 71°/4 mm., n_D^{16} 1.5379.

3-Acetamino-4-propylethylbenzene: m.p. 138° (from ethanol) Analysis Found C, 76.12, H, 9.47, N, 6.99; Calcd for $C_{13}H_{19}ON$ C, 76.05, H, 9.33, N, 6.82 %.

3-Bromo-4-propylethylbenzene (VII-a). The solution of 3-amino-4-propylethyl-benzene (12.25 g., 0.075 mole) in 80 ml. of 44 %-hydrobromic acid (0.3 mole) was cooled to −10° and diazotized with sodium nitrite (4.64 g., 0.06 mole). When the diazotization was complete, 0.5 g. of copper powder was added. The flask was attached to a reflux condenser and heated cautiously. Nitrogen was evolved vigor-ously and when the reaction subsided the mixture was distilled in steam. The distillate was made alkaline with potassium hydroxide and the lower layer of crude 3-bromo-4-propylethylbenzene was separated. After drying, it was distilled to give 7.3g. (43 %) of 3-bromo-4-propylethylbenzene, b.p.138-9°/14mm., n_D^{18} 1.5235.

Ethyl 2-propyl-5-ethylbenzoate (VIII-a). To a Grignard reagent made from 3-bromo-4-propylethylbenzene (5.22 g., 0.0023 mole) and magnesium turnings (0.6 g., 0.0025 atom) in absolute ether (20 ml.), was added a solution of ethyl chloroformate (3.15 g., 0.0025 mole) in ether (20 ml.) and the reaction mixture was allowed to stand still for *ca.* 6 hrs. When white precipitate formed, the mixture was then decomposed by pouring into ice and conc. sulfuric acid and was extracted with ether. The organic layer was distilled to afford 2.1 g. (40 %) of 2-propyl-5-ethyl-benzoic acid ethyl ester, b.p. 94-5°/4 mm., n_D^{12} 1.5020

2-Propyl-5-ethylbenzyl alcohol (IX-a). To a slurry of lithium aluminum hydride (0.36 g., 0.01 mole) in absolute ether (15 ml), was added a solution of ethyl 2-propyl-5-ethylbenzoate (2.1 g., 0.01 mole) in 20 ml. of absolute ether and the reaction mixture was stirred under gentle reflux for 1 hr. After the duration, the mixture was cooled in ice and then decomposed with 10 % hydrochloric acid solution. Extrac-

tion and distillation yielded 1.2 g. (70 %) of 2-propyl-5-ethylbenzyl alcohol, b.p. 136-9°/3mm., n_D^{20} 1.5210. The IR-spectrum was identical in every respect with that of the leaf alcohol reaction product from 3-hexen-1-ol. 3,5-Dinitrobenzoate: m. p. 78° (from methanol), not depressed on admixture with a specimen of the leaf alcohol reaction product.

4-Ethylbenzyl chloride (II-b). The Blanc chloromethylation of ethylbenzene (270 g., 2.54 mole), using conc. hydrochloric acid (1.3 l) and formalin (298 g., 3.6 moles), yielded ethylbenzyl chloride, b. p. 112-3°/28 mm., n_D^{16} 1.5350, yield 181 g. (46 %)

4-Ethylbenzaldehyde (III-b). The Sommelet aldehyde synthesis with 4-ethyl-benzylchloride (272 g., 1.75 moles), hexamethylene tetramine (244 g., 1.74 moles) in ethanol (3.4 l) gave, after working up as usual, 4-ethylbenzaldehyde. b.p. 103-5°/20 mm., n_D^{16} 1.5376. As it was indicated on v.p.c. that the product contained isomers, the purification was performed by means of recrystallization of its semicarbazone, m.p. 202-3° after two recrystallizations from ethanol. Analysis Found C, 62.57: H, 7.00: N, 21.74: Calcd for $C_{10}H_{13}ON_3$ C, 62.80: H, 6.85: N, 21.98 %. Yield of 4-ethyl-benzaldehyde regenerated from the semicarbazone, 130 g. (57.2 %)., b.p. 108-110°/23 mm.

3-Nitro-4-ethylbenzaldehyde (IV-b). The nitration of 4-ethylbenzaldehyde (44 g., 0.33 mole) was carried out in exactly the same manner as described above to give 3-nitro-4-ethylbenzaldehyde. b.p. 115-16°/3 mm., m.p. 23°, yield 55.9 g. (95 %).

3-Amino-4-ethyltoluene (VI-b). To a solution of 3-nitro-4-ethylbenzaldehyde (18 g., 0.1 mole) in 200 ml. of diethylene glycol, 30 ml. of 90 % hydrazine hydrate were added under stirring. The temperature was kept at 140° for 2 hrs. and after cooling, powdered potassium hydroxide (22 g., 0.4 mole) was added in one portion. Heating was continued at 200° under stirring until the evolution of nitrogen ceased. The resulting mixture was poured into water and extracted with ether. The ethereal solution was distilleed to give 13.5 g. (33.3 %) of 3-amino-4-ethyltoluene, b.p. 98-101°/10 mm., n_D^{12} 1.5650.

3-Acetamino-4-ethyltoluene: m.p. 142°. Analysis. Found C, 74.70: H, 8.36: N, 7.81, Calcd for $C_{11}H_{15}ON$ C, 74.54: H, 8.53; N, 7.90 %.

3-Bromo-4-ethyltoluene (VII-b). The conversion of 3-amino-4-ethyltoluene (8.12 g., 0.06 mole) into the corresponding 3-bromo-derivative was effected by means of Gattermann diazonium exchange method. 3-Bromo-4-ethyltoluene obtained in 36.8 % yield (5.4 g.) boiled at 84-90°/10 mm. and had n_D^{14} 1.5532.

Ethyl 2-ethyl-5-methylbenzoate (VIII-b). 3-Bromo-4-ethyltoluene (5.4 g., 0.027 mole) was converted *via* the Grignard reagent into ethyl 2-ethyl-5-methylbenzoate (VIII-b) in the same way as was described above, b.p. 114-17°/10 mm., n_D^{16} 1.5042, Yield 2.1 g. (40.4 %).

2-Ethyl-5-methylbenzyl alcohol (IX-b). The lithium aluminum hydride reduction of ethyl 2-ethyl-5-methylbenzoate (1 g., 0.005 mole) gave the corresponding benzyl alcohol, 2-ethyl-5-methylbenzyl alcohol, b.p. 106-8°/10 mm., n_D^{11} 1.5350, 0.45g. (56.8 %) The IR-spectrum was identical in every respect with that of the leaf alcohol reaction product from 3-penten-1-ol. 3,5-Dinitrobenzoate: m.p. 78-80° (from

methanol) Analysis Found C, 59.50 : H, 5.90 : N, 7.99 ; Calcd for $C_{17}H_{16}O_6N_2$ C, 59.30 : H, 4.68 : N, 8.14 % The melting point was not depressed on admixture with a specimen of the benzoate previously obtained from 3-penten-1-ol by the leaf alcohol reaction.

III. MECHANISM OF LEAF ALCOHOL REACTION

The structural establishment by unequivocal syntheses of the leaf alcohol reaction products in the preceding section, together with a model reaction sequencet with crotonaldehyde, enables one to propose a reasonable mechanism for aromatization reaction of olefinic alcohols by refluxing with metallic sodium.

The first step of the reaction seems to be the dehydrogenation by metallic sodium of the starting olefinic alcohols into the corresponding aldehydes. The dehydrogenation by metals of alcohols into aldehydes in general is well known as can be exemplified by the first stage of Guerbet reaction[8], in which saturated aliphatic alcohols are refluxed with alkali metals *i.e.* under the same conditions as leaf alcohol reaction is performed. Thus, 3-*cis*-hexen-1-ol is dehydrogenated by sodium into 3-*cis*-hexen-1-al which is readily rearranged by base in the reaction mixture into the more stable 2-*trans*-hexen-1-al. This is also what has been well known with unstable β,γ-unsaturated aldehydes which readily rearrange by base into the corresponding α,β-unsaturated aldehydes with the more stable *trans*-configuration[9], regardless of the original β,γ-geometry.

In the cases of homologs, isomeric β,γ-and α,β-unsaturated alcohols are equally
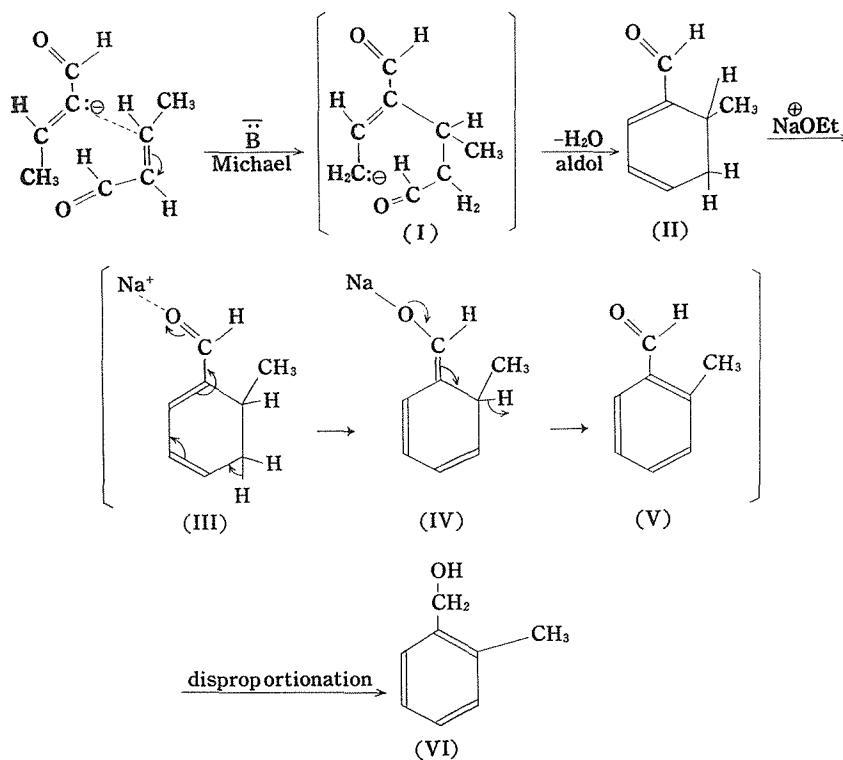
dehydrogenated to give the corresponding α,β-unsaturated aldehydes with the more stable *trans*-configuration and the latter *trans*-2-alken-1-als can be looked upon as being the operating species in the following reaction sequences. This was reasonably verified by the fact that α,β-unsaturated aldehydes, when subjected to the leaf alcohol reaction condition, afforded the same substituted benzyl alcohols as those from the corresponding β,γ-and α,β-unsaturated alcohols[2].

Judging from the carbon skeleton of the final product, it seemed very likely that this was formed by Michael- and aldol condensations of two molecules of *trans*-2-alken-1-al, followed by dehydrogenation and disproportionation, all being base-catalyzed.

A model reaction designed to follow the reaction paths was carried out with crotonaldehyde, the simplest system available for the aromatization reaction.

Crotonaldehyde, when warmed with a weak base, diethylamine, instead of sodium, gave o-dihydrotolualdehyde (II), the structure of which had previously been deduced by Bernhauer[10]. The cyclodiene aldehyde structure was here again confirmed in the light of the modern spectroscopy. The UV- and IR-spectra fully substantiated the proposed conjugated cyclodiene aldehyde structure. The formation of o-dihydrotolualdehyde (II) from crotonaldehyde shows that a base-catalyzed Michael condensation first occurred between two molecules of crotonaldehyde, one being a carbanion source, the other a Michael acceptor, and the resulting adduct dialdehyde intermediate (I) was cyclized by an intramolecular aldolization so as to form a six-membered ring. It is noticeable that the ethylenic carbanion participating in the Michael condensation retained its original *trans*-configuration to some extent[11], so that the following intramolecular cyclization could take place. In the latter stage, the aldol condensation occurred between the methylene activated by vinylogy and the carbonyl group at 6-carbon distance from the methylene, that is rationalized also by many examples in literature[12]. o-Dihydrotolualdehyde (II), when subjected to the leaf alcohol reaction condition *i.e.* refluxing with sodium ethoxide, afforded o-methylbenzyl alcohol (VI), the same as the leaf alcohhl reaction product from *trans*-crotyl alcohol[3] or crotonaldehyde*. During this process, the cyclodiene aldehyde (II) was dehydrogenated by the action of sodium cation as was depicted in the scheme (III→IV→V) into the corresponding o-tolualdehyde (V) which, in turn, was reduced to o-methylbenzyl alcohol (VI) by disproportionation.

There seems to be no doubt that the leaf alcohol reaction of homologous alkenols proceeds through the mechanism exemplified above by the stepwise model reaction with crotonaldehyde, although the probable cyclodiene intermediates were not isolated because of the strong base used in leaf alcohol reactions.

In support of the presumed reaction sequences involved, some amount of by-products such as caproic acid[3] and butyloctanol[4] has been isolated, which accounted for the fate of hydrogen-donor and acceptor at both the initial and the final stages. It is very likely that in the final aldehyde disproportionation, a crossed Cannizzaro rather than a Cannizzaro mechanism would be more favored in the

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* In an unpublished work, crotonaldehyde, when diluted with benzene and refluxed with metallic sodium in nitrogen atmosphere for 4 hrs, afforded the desired o-methyl benzyl-alcohol, which was identified with an authentic specimen from crotyl alcohol.

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environment where aliphatic aldehydes were available as hydride ion donor. This was also born out by the isolation of aliphatic acid.
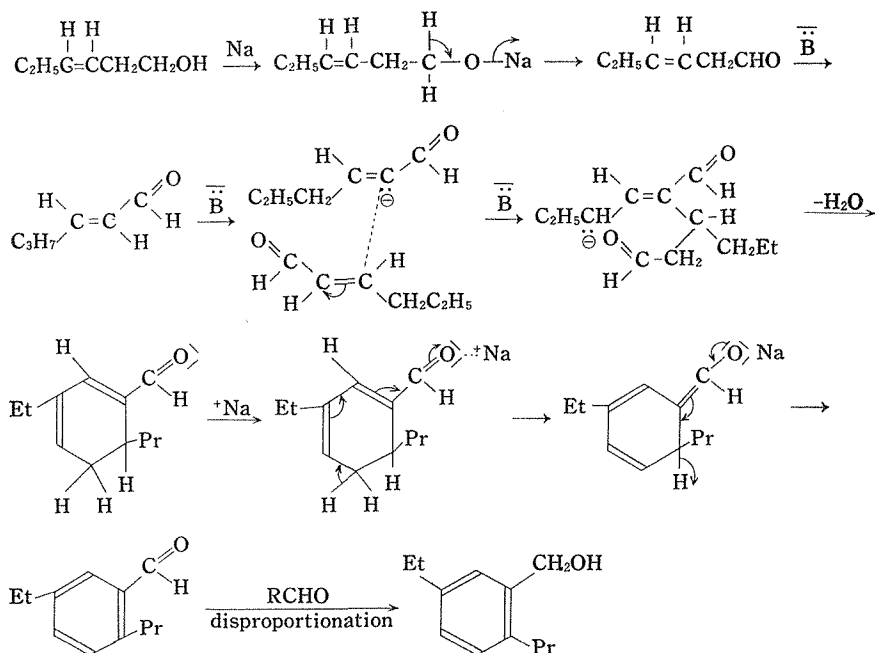
In an alternative previously presented by the same authors[3] it was assumed that the cyclodiene aldehyde might be formed by a thermal valence isomerization of a conjugated triene aldehyde which would result from an intermolecular aldol condensation of alkenals, but this cyclization of conjugated triene system should substantially necessitate a central *cis*-double bond[3]. This seems not the case with the triene aldehyde thus postulated, because the central double bond being formed by a strong base-catalyzed aldol condensation at an elevated temperature should naturally be of the more stable *trans*-configuration.

Conclusively, therefore, the reaction mechanism involving dehydrogenation, Michael condensation, aldol cyclization and dehydrogenation followed by aldehyde disproportionation is preferred to the previously proposed one.

It is of great interest that the aromatization of olefinic alcohols and aldehydes is readily effected in a rather simple process and that the leaf alcohol reaction suggests a probable biogenetic transformation *in vivo* of olefinic compounds into aromatics.

EXPERIMENTAL

o-**Dihydrotolualdehyde** (II). A mixture of crotonaldehyde (25 g., 0.3 mole) and diethylamine (1.25 ml.) was refluxed in a stream of nitrogen for 30 min. After cooling, the reaction mixture was extracted with ether. The combined ether extract, worked up as usual, gave *o*-dihydrotolualdehyde, b.p. 88-90°/25 mm., n_D^{10} 1.5310. yield 8.5g. (40%) UV. λ*max.* 252 $m\mu$, ε 7683 (in ethanol): IR. 2800-2650 cm^{-1}, 1680-1660 cm^{-1}.

Semicarbazone: m.p. 177°; Analysis Found C, 60.49: H,6.92: N, 23.25 Calcd for C_9 $H_{13}ON_3$: C, 60.31: H, 7.31: N, 23.45%, 2,4-Dinitrophenylhydrazone: m.p. 167°: Analysis Found C, 55.36: H, 4.36: N,18.16; Calcd for $C_{14}H_{14}O_4N_4$ C, 55.62: H, 4.67: N, 18.54%

o-Methylbenzyl alcohol (VI). A mixture of o-dihydrotolualdehyde (4 g., 0.33mole) and sodium ethoxide (0.4g.) in benzene was refluxed for 2 hrs. The reaction mixture was poured in water and extracted with ether. The extract, after drying and removal of the solvents, gave o-methylbenzyl alcohol, b.p. 110–112°/25 mm., n_D^{10} 1.5232, yield 0.2 g. (5%): UV. $\lambda max.$ 266 $m\mu$, ε 827 (in ethanol): The IR-spectrum was identical in every respect with that of a specimen obtained from the leaf alcohol reaction of crotyl alcohol or crotonaldehyde. 3,5-Dinitrobenzoate: m.p. 129–130°, not depressed on admixture with a specimen in stock.

IV. ATTEMPTED SEARCH FOR AROMA PRINCIPLES OF MANUFACTURED BLACK TEA

The manufacture of black tea involves the processes of wilting, mechanical rolling and so-called fermentation of the fresh tea leaves and the black tea thus manufactured, in particular, of a superior quality has a sort of flavor surmising one of lemon fruit.[1] 2-Propyl-5-ethylbenzyl alcohol, the leaf alcohol reaction product from leaf alcohol and aldehyde, was found to have a lemon-like flavor similar to that characteristic of manufactured black tea and it was suspected that this artefact might be enzymatically formed form leaf alcohol and/or leaf aldehyde naturally present in fresh tea leaves during the fermentation process in manufacturing.

An attempted search for this compound in the neutral fraction ranging over b.p. 124–150°/12 mm. (4.2 g.) of the total neutral essential oil (118.7 g) obtained by steam distillation of manufactured black tea* (684 kg.) was made, but the existence of this substituted benzyl alcohol has not so far been confirmed.

The search for this alcohol as such, or as some derivatives and for other substances responsible for black tea aroma is in current progress in the authors' laboratory and will be published elsewhere in future.

EXPERIMENTAL

Manufactured black tea 13kg was soaked in water, distilled in steam and the distillate collected (total volume 50 l) was saturated with sodium chloride. The saturated solution was divided in appropriate volumes (ca. 3.5 l) and was thoroughly extracted with ether. The combined ethereal solution which resulted from the steam distillation of 684.8 kg. of manufactured black tea yielded, after removal of the solvent, 200 g. of essential oil. This was treated with saturated sodium bicarbonate solution, 5% sodium hydroxide solution and 3% hydrochloric acid in succession to give a neutral fraction (118.7 g.). The neutral fraction was carefully fractionated through an effective column and the fraction ranging over 124–150°/

* The manufactured black tea used in this work was supplied by Makurazaki City Agricultural Union, Kagoshima Prefecture and was drawn from the bulk which was manufactured from Assam hybrid leaves (Benihomare, Benikaori and Hatsumomiji) during May through June 1964. The laboratory treatments were made from July through October in the same year.

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12 mm. was cut for further investigation.

The IR-spectrum of this fraction, however, did not show the absorption bands due to hydroxy group and the vapor phase chromatogram did not indicate the peak corresponding to that of 2-propyl-5-ethylbenzyl alcohol. The attempted derivation of any hydroxylic compounds in this fraction by treating with phthalic anhydride resulted in vain, no hydrogen-phthalate being isolated.

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