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Vinyl Alcohols. III. 1,2-Diaryl-1-propen-1-ols

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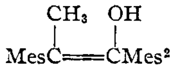
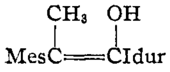
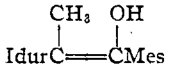
When it was discovered that the vinyl alcohol 1,2-dimesityl-1-propen-1-ol (I) was remarkably stable,[1] an exploratory research was instituted to determine the influence of the mesityl radicals. Replacement of one or the other of these by duryl or isoduryl radicals has yielded four new vinyl alcohols closely resembling the original. The method of preparation in each case was similar to that described for I.


$\mathrm{Mes}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Mes}$[2]

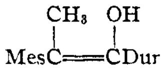
I


$\mathrm{Mes}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Idur}$

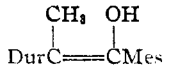
II


$\mathrm{Idur}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Mes}$

III


$\mathrm{Mes}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Dur}$

IV


$\mathrm{Dur}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Mes}$

V

The additional vinyl alcohols are: 1-isoduryl-2-mesityl-1-propen-1-ol (II), 1-mesityl-2-isoduryl-1-propen-1-ol (III), 1-duryl-2-mesityl-1-propen-1-ol (IV) and 1-mesityl-2-duryl-1-propen-1-ol (V).

The preparation of 1-(2,4,6-triethylphenyl)-2-mesityl-1-propen-1-ol and its isomer was planned but the product obtained from the reduction of α-mesitylvinyl 2,4,6-triethylphenyl ketone proved to be an intractable oil. Permanganate oxidized this oil to the original vinyl ketone. As a result of this experience the study of the triethylphenyl derivatives was discontinued.

All the enols have properties similar to those of I. They form acetates with acetic anhydride and are dehydrogenated by permanganate to give the unsaturated ketones from which they were originally derived. This same result was obtained when IV was treated with perbenzoic acid in chloroform solution. Enols II and IV were isomerized to the keto form. Sodium ethylate regenerated the enol in each case, but ethylmagnesium bromide had no effect.

The stability of the enols seems to be related to the melting point. The higher melting compounds are considerably more stable to air oxidation than are the lower melting derivatives. 1-Isoduryl-2-mesityl-1-propen-1-ol (II) crystallized from ethyl alcohol with one molecule of solvent. The subsequent loss of the alcohol gave the appearance of decomposition though the compound was stable for several weeks. Enol III turned oily in about a month while samples of IV and V had not decomposed in five months.

In one experiment in the air cleavage of V, a substance was isolated which contained three atoms of oxygen and appeared to be the enol peroxide. This result is similar to that reported for 1,2-dimesityl-1-propen-1-ol[1] and suggests that the peroxide is an intermediate in the oxidation.

Experimental

α²-Chloropentamethylbenzene.—This compound was prepared in 50% yields by the chloromethylation of isodurene according to the general method of Nauta and Dienske[3] for chloromethylation of mesitylene. If one-half the formalin is withheld initially and added after three hours the yield is increased; b. p. 113–115° (5 mm.); d^{20}_{20} 1.0545; n^{20}_{D} 1.5510.

Anal.[4] Calcd. for $C_{11}H_{15}Cl$: C, 72.30; H, 8.28. Found: C, 72.05; H, 8.18.

Isodurylacetonitrile.—This compound was obtained in 74% yield from α²-chloropentamethylbenzene by the procedure of Fuson, Corse and McKeever[1]; b. p. 134–135° (5 mm.); m. p. 74–75°.

Anal. Calcd. for $C_{12}O_{15}N$: N, 9.09. Found: N, 8.97.

1-Duryl-2-mesityl-1-propen-1-ol, 1-Isoduryl-2-mesityl-1-propen-1-ol, 1-Mesityl-2-isoduryl-1-propen-1-ol, 1-Mesityl-2-duryl-1-propen-1-ol.—These enols were prepared by a series of reactions analogous to the preparation of 1,2-dimesityl-1-propen-1-ol.[1] The pertinent data concerning these enols, their derivatives and the intermediates are summarized in Table I.

The Preparation of 2,4,6-Triethylphenylglycolic Acid.—The following procedure proved more satisfactory than that of Fuson, Emerson and Gray.[5] Ten grams of 2,4,6-triethylphenylglyoxal was heated on a steam-cone for two hours with 18 g. of potassium hydroxide in 400 cc. of water. The mixture was allowed to stand overnight. The solution was extracted with ether to remove the traces of oil present. It was then acidified with concentrated hydrochloric acid and again extracted with ether. After removal of the ether the product crystallized from ligroin to yield 8.2 g. (76% of the theoretical); m. p. 89–90° after one recrystallization.

The Preparation of 2,4,6-Triethylbenzyl Chloride.—A mixture of 90 g. of 1,3,5-triethylbenzene, 350 cc. of concentrated hydrochloric acid and 42 g. of formalin was heated at 65° with stirring for sixteen hours. During this time

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(1) Fuson, Corse and McKeever, THIS JOURNAL, **62**, 3250 (1940); Fuson, Byers and Rabjohn, *ibid.*, **63**, 2639 (1941).

(2) Mes, Dur, Idur and Tep are used to represent mesityl, duryl, isoduryl and 2,4,6-triethylphenyl, respectively.

(3) Nauta and Dienske, *Rec. trav. chim.*, **55**, 1000 (1936).

(4) The microanalyses in this paper were carried out by Mr. L. G. Fauble and Miss Mary S. Kreger.

(5) Fuson, Emerson and Gray, THIS JOURNAL, **61**, 481 (1939).

TABLE I

Compound	M. p. (cor.)	Solvent	Yield, %	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$\mathrm{MesCH_2CODur}$	118.5–119.5°	$\mathrm{C_2H_5OH}$	73	85.66	8.91	85.37	8.54
$\mathrm{MesC({=}CH_2)CODur}$	159–160	$\mathrm{C_2H_5OH}$	75	86.22	8.56	86.06	8.52
$\mathrm{MesC(CH_3){=}C(OH)Dur}$	136–136.5	$\mathrm{C_2H_5OH}$	92	85.66	9.16	85.91	9.22
$\mathrm{MesCH(CH_3)CODur}$	124.5–125	$\mathrm{C_2H_5OH}$	95	85.66	9.16	85.85	9.06
$\mathrm{MesC(CH_3){=}C(OCOCH_3)Dur}$	124.5–125	$\mathrm{C_2H_5OH}$	90	82.23	8.63	82.39	8.77
$\mathrm{MesCH_2COIdur}$	99.5–100.5	$\mathrm{C_2H_5OH}$	69	85.66	8.91	85.39	9.20
$\mathrm{MesC({=}CH_2)COIdur}$	140.5–141	$\mathrm{C_2H_5OH}$	70	86.22	8.56	86.39	8.56
$\mathrm{MesC(CH_3){=}C(OH)Idur{\cdot}C_2H_5OH}$	63–64	$\mathrm{C_2H_5OH}$	90	81.29	9.67	81.71	9.70
$\mathrm{MesC(CH_3){=}C(OH)Idur}$[a]	73–74	Pet. ether		85.66	9.16	85.41	9.15
$\mathrm{MesCH(CH_3)COIdur}$	85.5–86	$\mathrm{C_2H_5OH}$	93	85.66	9.16	85.64	9.21
$\mathrm{MesC(CH_3){=}C(OCOCH_3)Idur}$	128.5	$\mathrm{C_2H_5OH}$	88	82.23	8.63	82.01	8.56
$\mathrm{IdurCH_2COOH}$	167–168	$\mathrm{C_6H_6}$	92	74.95	8.40	75.00	8.50
$\mathrm{IdurCH_2CONH_2}$	229.5–230	$\mathrm{C_2H_5OH}$	92	75.34	8.96	75.57	8.97
$\mathrm{IdurCH_2COMes}$	98.5–100	$\mathrm{C_2H_5OH}$	75	85.66	8.91	85.90	9.02
$\mathrm{IdurC({=}CH_2)COMes}$	142–142.5	$\mathrm{C_2H_5OH}$	78	86.22	8.56	86.45	8.49
$\mathrm{IdurC(CH_3){=}C(OH)Mes}$	96–97	$\mathrm{C_2H_5OH}$	94	85.66	9.16	85.78	9.26
$\mathrm{IdurC(CH_3){=}C(OCOCH_3)Mes}$	125.5–126.5	$\mathrm{C_2H_5OH}$	90	82.23	8.63	82.46	8.72
$\mathrm{DurCH_2Cl}$[b]	67–68		72	72.30	8.28	72.02	8.26
$\mathrm{DurCH_2CN}$[c]	80–81		75	83.17	8.73	83.06	8.78
$\mathrm{DurCH_2COOH}$	204.5–205	$\mathrm{C_6H_6}$	90	74.95	8.40	75.18	8.69
$\mathrm{DurCH_2CONH_2}$	217.5–218.5	$\mathrm{C_2H_5OH}$	91	75.34	8.96	75.70	9.09
$\mathrm{DurCH_2COMes}$[d]	113–114	$\mathrm{C_2H_5OH}$	71	85.66	8.91	85.90	9.16
$\mathrm{DurC({=}CH_2)COMes}$	166.5–167.5	$\mathrm{C_2H_5OH}$	71	86.22	8.56	86.58	8.67
$\mathrm{DurC(CH_3){=}C(OH)Mes}$	144.5–145.5	$\mathrm{C_2H_5OH}$	89	85.66	9.16	85.81	9.44
$\mathrm{DurC(CH_3){=}C(OCOCH_3)Mes}$	147–148	$\mathrm{C_2H_5OH}$	90	82.23	8.63	82.35	8.68
$\mathrm{MesCH_2COTep}$[e]			82	85.66	9.38	85.90	9.49
$\mathrm{MesC({=}CH_2)COTep}$	57–57.5	$\mathrm{C_2H_5OH}$	55	86.18	9.05	85.91	8.84
$\mathrm{TepCH_2CN}$[f]	14–16		72	83.50	9.52	83.51	9.35
$\mathrm{TepCH_2CONH_2}$	182.5–183	$\mathrm{C_2H_5OH}$	85	76.64	9.65	76.82	9.61
$\mathrm{TepCH_2COMes}$[g]			67	85.66	9.38	85.24	9.47

[a] Exposure to the air gave a very small amount of a compound which appeared to be the enol peroxide. It melted at 124.5–125°. *Anal.* Calcd. for $\mathrm{C_{22}H_{28}O_3}$: C, 77.60; H, 8.28. Found: C, 77.70; H, 7.84. [b] B. p. 143–144° (18 mm.). [c] B. p. 149–153° (6–7 mm.). [d] B. p. 198–203° (2–3 mm.). [e] B. p. 215° (9 mm.); n^{20}_{D} 1.5526; d^{20}_{20} 0.9968. [f] B. p. 127° (3–4 mm.); n^{20}_{D} 1.5210. [g] B. p. 190–195° (4–5 mm.); n^{20}_{D} 1.5520.

dry hydrogen chloride was passed through the reaction mixture. The mixture was allowed to cool and the layers were then separated. The upper layer was diluted with ether, dried and distilled *in vacuo*. Though some triethylbenzene was recovered, the main fraction consisted of the monochloromethyl compound. The yield was 86 g. or 74%; b. p. 116–118° (4 mm.); 145–148° (18 mm.); n^{20}_{D} 1.5301; d^{20}_{20} 1.0011.

Anal. Calcd. for $\mathrm{C_{13}H_{19}Cl}$: C, 74.07; H, 9.09. Found: C, 73.70, 73.65; H, 9.16, 8.99.

The residue in the flask solidified on cooling. It was recrystallized from ligroin; m. p. 82°. It is very likely the dichloromethyl compound, but it was not further purified.

The Preparation of 2,4,6-Triethylphenylacetic Acid.—(a) Three grams of red phosphorus, 1.0 g. of iodine and 100 cc. of glacial acetic acid were allowed to stand at room temperature for fifteen minutes before 5 cc. of water and 10.7 g. of 2,4,6-triethylphenylglycolic acid were added. After boiling the solution under reflux for four hours the solution, while still hot, was filtered into 100 cc. of saturated sodium bisulfite solution. The solid was removed by filtration and washed thoroughly with water. A yield of 7.35 g. or 70% of the theoretical was obtained. The acid was recrystallized from low-boiling petroleum ether and melted at 96–96.5°.

Anal. Calcd. for $\mathrm{C_{14}H_{20}O_2}$: C, 76.29; H, 9.16. Found: C, 76.49; H, 9.21.

(b) Fifteen grams of 2,4,6-triethylphenylacetonitrile was allowed to reflux for seven hours with 200 cc. of diethylene glycol, 12 g. of potassium hydroxide and 5 cc. of water (oil-bath 175–180°). The refluxing was continued until no more ammonia fumes were evolved. The solution was allowed to cool, diluted with 500 cc. of water and filtered. The filtrate was acidified with concentrated hydrochloric acid to yield crude 2,4,6-triethylphenylacetic acid. This acid was dissolved in 10% sodium carbonate solution, and was then reprecipitated to yield 9 g. or 55% of the desired acid.

Summary

Four new vinyl alcohols have been described.

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