maxima: 5.87 μ (very strong), 8.80 μ (very strong) and 9.05 μ (very strong).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.66; H, 10.94.

The 2,4-dinitrophenylhydrazone gave yellow needles from ethanol, m.p. 90–91°.

Anal. Calcd. for $C_{16}H_{24}O_5N_4$: C, 54.53; H, 6.87. Found: C, 54.28; H, 7.03.

Several attempts to condense pivalaldehyde with III in tetrahydrofuran by the method employed above failed, yielding only starting materials.

Condensation of Benzaldehyde with 2,2-Dimethyl-4-hexen-3-one.—A solution of 1.0 g. (0.010 mole) of benzaldehyde and 1.2 g. (0.0095 mole) of III in 10 ml. of absolute ethanol was cooled to 0° and treated with a cooled sodium ethoxide solution prepared from 0.3 g. of sodium and 10 ml. of absolute ethanol and allowed to stand overnight. Water was added and the mixture was extracted with ether. The ethereal extracts were dried over anhydrous magnesium sulfate, concentrated and distilled giving 2,2-dimethyl-7-phenyl-4,6-heptadien-3-one (VII), b.p. 140–142° (1 mm.), yield 0.58 g. (28%).

The 2,4-dinitrophenylhydrazone was recrystallized from ethanol–ethyl acetate, m.p. 202–204°.

Authentic VII was prepared by a similar condensation between 11.9 ml. (13.2 g., 0.10 mole) of cinnamaldehyde and 12.3 ml. (9.8 g., 0.098 mole) of pinacolone in 45 ml. of absolute ethanol using a sodium ethoxide solution prepared from 2.5 g. of sodium and 30 ml. of absolute ethanol. The product, b.p. 137–141° (1.5 mm.), yield 8.0 g. (38%), was crystallized by chilling in an acetone–Dry Ice mixture. After two recrystallizations from ethanol the yellow crystals melted at 56–57°.[38]

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.23; H, 8.66.

The 2,4-dinitrophenylhydrazone gave red needles from ethanol, m.p. 203–204°, mixed m.p. with derivatives obtained previously (m.p. 202–204°), 202–204°.

Anal. Calcd. for $C_{21}H_{22}O_4N_4$: C, 63.94; H, 5.62. Found: C, 63.87; H, 5.73.

Condensation of 3-(3,4-Methylenedioxyphenyl)-2-propenal (IX) with Pinacolone.—IX was prepared by the method of Ladenburg and Scholtz[39] in 20% yield. A condensation between 4.7 g. (0.027 mole) of IX and 3.7 ml. (3.0 g., 0.030 mole) of pinacolone in 20 ml. of absolute ethanol was catalyzed by a sodium ethoxide solution prepared from 1 g. of sodium and 10 ml. of absolute ethanol as before. After 24 hours 150 ml. of water was added and the crystalline precipitate was recrystallized from ethanol giving 4,4-dimethyl-1-(3,4-methylenedioxyphenyl)-1-penten-3-one (X), m.p. 93–94°, yield 4.5 g. (73%). Pace[16] reported m.p. 98° for X prepared from a piperonal–pinacolone condensation. The ultraviolet absorption spectrum[37] of X in ethanol showed a shoulder at 221 mμ (7900) and at 241 mμ (9000) and ϵ_{max} 9500, λ_{max} 250 mμ and ϵ_{max} 18,000, λ_{max} 339 mμ.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.36; H, 6.94. Found: C, 71.68; H, 7.05.

The 2,4-dinitrophenylhydrazone gave two varieties of crystals from ethanol–ethyl acetate: fine yellow needles which became orange-red at 120° and melted at 148–155°; and thick shiny red needles, m.p. 148–153°, mixed m.p. of the two forms, 148–155°. Recrystallized from methanol the yellow needles gave orange plates, m.p. 149.5–156°.

Anal. Calcd. for $C_{20}H_{20}O_6N_4$: C, 58.24; H, 4.89. Found: C, 57.94; H, 5.13.

The red needles were recrystallized from ethanol, m.p. 149–156°.

Anal. Calcd. for $C_{20}H_{20}O_6N_4$: C, 58.24; H, 4.89. Found: C, 57.9; H, 4.85.

Both derivatives gave negative Knorr tests[40] indicating that neither possessed a pyrazoline structure. Similar phenomena were observed by Goheen[41] in the preparation of patulin phenylhydrazone.

A condensation of piperonal (4.5 g., 0.030 mole) with pinacolone (3.0 g., 0.030 mole) carried out in the same manner gave 6.6 g. (95%) of X, m.p. 92.5–93.5°, mixed m.p. with previous material (m.p. 93–94°) 92.5–94°.

The 2,4-dinitrophenylhydrazone of authentic X gave the same yellow and red crystalline mixture, m.p. 148–156°, mixed m.p. with previous material 149–156°.

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[38] 4,4-Dimethyl-1-phenyl-1-penten-3-one (colorless), the product of the condensation of benzaldehyde and pinacolone, is reported to have m.p. 43°, b.p. 144–145° (10 mm.) by G. A. Hill, C. S. Spear and J. S. Lachowicz (This Journal, **45**, 1559 (1923)).

[39] A. Ladenburg and M. Scholtz, *Ber.*, **27**, 2958 (1894).

[40] L. Knorr, *ibid.*, **26**, 100 (1893).

[41] D. W. Goheen, Dissertation, University of Washington, 1951 p. 144.

Seattle, Washington

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

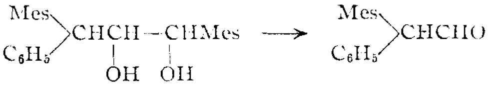
Vinyl Alcohols. XX.[1] Reaction with Lead Tetraacetate

By Reynold C. Fuson, Everett W. Maynert, Tzi-Lieh Tan, Elmer R. Trumbull[2] and F. W. Wassmundt[3]

Received December 7, 1956

Five 2,2-diarylvinyl alcohols, when treated with lead tetraacetate, have been found to yield the acetates of the corresponding diarylglycolaldehydes.

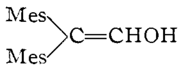
A possible route to diarylacetaldehydes or to the corresponding vinyl alcohols is the cleavage of suitably constituted glycols with lead tetraacetate or with periodic acid. The latter reagent was used successfully to make mesitylphenylacetaldehyde (II) from the glycol I.[1]



$$\mathrm{(Mes)(C_6H_5)CHCH(OH)-CH(OH)Mes} \longrightarrow \mathrm{(Mes)(C_6H_5)CHCHO}$$

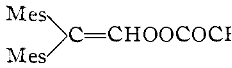
I II

Such a synthesis could not be effected, of course, if the product itself were attacked by the reagent. Experiment showed that lead tetraacetate converted 2,2-dimesitylvinyl alcohol (III) to an acetoxyl derivative which at first was assigned the vinyl peracetate structure IV.



$$\mathrm{Mes_2C{=}CHOH}$$

III



$$\mathrm{Mes_2C{=}CHOOCOCH_3}$$

IV

Evidence for this conclusion was the observation that treatment with ethylmagnesium bromide or,

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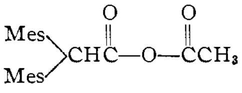
[1] For the preceding communication in this series see R. C. Fuson and T.-L. Tan, This Journal, **70**, 602 (1948).

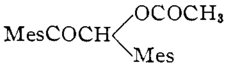
[2] Rohm and Haas Research Assistant, 1945–1946; du Pont Fellow, 1946–1947.

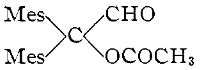
[3] Standard Oil Co. of Indiana Fellow, 1954–1955; Visking Corporation Fellow, 1955–1956.

preferably, with isobutylmagnesium chloride reconverted it to the vinyl alcohol.

The infrared spectrum of the new compound, however, was not that to be expected for the perester IV. It indicated, rather, the presence of two carbonyl groups and the absence of an olefinic bond. Structures V, VI and VII, on the other hand, would all seem to be in general agreement with the spectral data. The mixed anhydride V was ruled out, however, by the observation that the new compound reacted with ethanolic potassium hydroxide to give mesityl. Moreover, in the mesityl phenyl series, the mixed anhydride of acetic and mesitylphenylacetic acids was synthesized and found to be different from the product obtained by the lead tetraacetate oxidation of 2-mesityl-2-phenylvinyl alcohol. Comparison with an authentic specimen likewise showed the oxidation product to be different from mesitoin acetate (VI). The presence of an aldehyde C–H stretching band in the infrared absorption spectrum of the new compound supports structure VII.


V


VI


VII

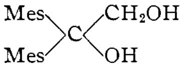
The formation of the acetoxylated compounds appears to be general for the stable 2,2-diarylvinyl alcohols. Similar derivatives have been prepared from 2-mesityl-2-phenyl-, 2-(3-bromomesityl)-2-phenyl-, 2-isoduryl-2-phenyl- and 2-mesityl-2-(*p*-tolyl)-vinyl alcohols. Indeed, the facile conversion to acetoxylated derivatives would seem to lend further support to the proposal that enolization is the rate-determining step in similar acetoxylations.[4]

The compound obtained from 2-mesityl-2-phenylvinyl alcohol was studied the most thoroughly. Its infrared spectrum, too, contained a band assignable to the aldehyde C–H stretching vibration. Oxidation with potassium permanganate provided further evidence for the α-acetoxyaldehyde structure. This reaction led to mesitylphenylglycolic acid and mesityl phenyl diketone; it was found that the diketone did not undergo the benzilic acid rearrangement under conditions of the oxidation. Confirmation of the α-acetoxydiarylacetaldehyde structure was obtained by determination of proton nuclear magnetic resonance. In a magnetic field of 7074 gauss, a peak whose area relative to the whole was 5.3 ± 0.8% was displaced −16.1 ± 1.0 milligauss from the peak of the phenyl hydrogen atoms. The former band is assignable to an aldehyde hydrogen atom.

The authors are grateful to Mr. Rollie Williams and Mr. N. F. Chamberlain of the Humble Oil and Refining Co., Baytown, Texas, for the determination and interpretation of the nuclear magnetic resonance spectrum. We also wish to thank Dr. H. S. Gutowsky for helpful advice in this connection.

Hydrolysis of 2-acetoxy-2-mesitylphenylacetaldehyde with ethanolic potassium hydroxide led to 2,4,6-trimethylbenzoin and its oxidation product, mesityl phenyl diketone. Similar rearrangements were observed with certain of the other α-acetoxyaldehydes. Apparently these compounds are hydrolyzed to the hydroxyaldehydes which then in the presence of base rearrange to the isomeric benzoins.[5]

Treatment of α-acetoxydimesitylacetaldehyde with ethylmagnesium bromide regenerated 2,2-dimesitylvinyl alcohol in 10% yield. Presumably the acetoxyl group is cleaved and the formyl group is reduced to give 1,1-dimesitylethylene glycol (VIII); dehydration of the diol would be expected to lead to the vinyl alcohol. This view is supported by the observation that isobutylmagnesium bromide, a Grignard reagent of enhanced reducing power,[6] regenerated the vinyl alcohol in better yield. Phenylmagnesium bromide, accordingly, formed no vinyl alcohol.


VIII

A striking result was obtained when 2-acetoxy-2-mesitylphenylacetaldehyde was treated with isobutylmagnesium bromide. The vinyl alcohol isolated was a *cis–trans* isomer of that employed in the preparation of the starting material. Like the "normal" vinyl alcohol, it too could be converted to the acetoxy aldehyde with lead tetraacetate. Though acetylation led to the known acetate, an isomeric acetate and an isomeric benzoate could be prepared indirectly. Saponification of the isomeric acetate regenerated the new isomeric vinyl alcohol. Curiously, treatment of the other acetoxyaldehydes with isobutylmagnesium bromide led to the original vinyl alcohols, rather than to isomers.

The infrared spectra[7] of these α-acetoxyaldehydes (Table I) show ester carbonyl absorptions displaced somewhat to higher frequencies. Similar displacements have been observed with α-acetoxyl ketones.[8] Though available data are scanty, the acetoxyl group does not appear to raise the frequency of the aldehyde carbonyl absorption observed for diarylacetaldehydes.

Experimental

2-Acetoxy-2-mesitylphenylacetaldehyde.—A solution of 5.0 g. of 2-mesityl-2-phenylvinyl alcohol in 200 ml. of glacial acetic acid was heated at 40° in a constant temperature bath while lead tetraacetate was added in small portions. A total of 10.85 g. was necessary to establish an excess of this reagent. Removal of the acetic acid by distillation under reduced pressure and crystallization of the residue from ethanol gave 4.43 g. of colorless rhombs melting at 133–134°. An additional 0.84 g. was collected from the mother liquors to give a total yield of 5.27 g. (86%).

Anal. Calcd. for $C_{19}H_{20}O_3$: mol. wt., 296; C, 77.00; H, 6.80. Found: mol. wt. (Rast), 294; C, 77.00; H, 6.94.

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[4] G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955).

[5] D. Y. Curtin and A. Bradley, THIS JOURNAL, **76**, 5777 (1954).

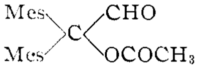
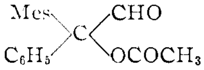
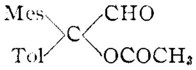
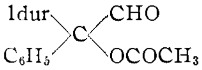
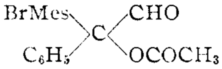
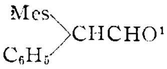
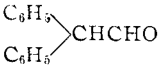
[6] M. S. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

[7] The infrared spectra were determined by Mrs. M. Louise Griffing and Mr. James J. Brader. The authors wish to thank Mr. Brader for assistance in their interpretation.

[8] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950); R. N. Jones, P. Humphries, F. Herling and K. Dobriner, *ibid.*, **74**, 2820 (1952).

TABLE I

INFRARED ABSORPTION BANDS

Compound[a]	Aldehyde C–H stretch	Ester C=O stretch	Aldehyde C=O stretch	Ester C–O– stretch
	2700	1759	1723	1229
	2695	1762	1733	1235
	2695	1759	1731	1233
	2690	1758	1729	1233
	. . [b]	1762	1733	1232
			1733	
	2690 2790		1733	

[a] All compounds were observed in dilute solutions of carbon disulfide. Bands are reported in reciprocal centimeters.
[b] The aldehyde C–H stretching band was not observed owing to the low concentration of material in the solution employed.

The acetoxyaldehyde was also prepared by treating the enolate of the vinyl alcohol, formed from the alcohol and ethylmagnesium bromide, with a suspension of lead tetraacetate in benzene. The yield by this method was 60%.

Cleavage of either 3-mesityl-3-phenyl-1,2-propanediol or 1,3-dimesityl-3-phenyl-1,2-propanediol with lead tetraacetate led to the same acetoxyaldehyde.

Other acetoxyaldehydes produced in a similar manner are listed in Table II.

TABLE II

ACETOXY ALDEHYDES

Parent vinyl alcohol	M.p. of acetoxy-acetaldehyde, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-(3-Bromomesityl)-2-phenyl	115–117	60.80	60.96	5.10	5.23
2,2-Dimesityl	159.5–160	78.07	77.91	7.74	7.87
2-Isoduryl-2-phenyl	127–128	77.39	77.96	7.14	7.45
2-Mesityl-2-*p*-tolyl	131–132	77.39	77.28	7.14	7.27

Treatment of 2-Acetoxy-2-mesitylphenylacetaldehyde with Alkali.—One gram of the acetoxyaldehyde in a 10% solution of potassium hydroxide in ethanol was heated under reflux for 3 hr. The mixture was poured into water and the resulting mixture was extracted with ether. Evaporation of the solvent and crystallization of the yellow residue (0.85 g.) from methanol yielded 0.20 g. (25%) of mesityl phenyl diketone, m.p. 133–136°. From the mother liquor was obtained 0.21 g. (25%) of 2,4,6-trimethylbenzoin which was characterized by a mixture melting point determination.

α-Acetoxydimesitylacetaldehyde and Grignard Reagents.—A solution of 0.70 g. of the aldehyde in ether was added to the reagent prepared from 0.5 g. of magnesium and 3.0 ml. of isobutyl bromide. The mixture was heated for 6 hr. and poured into water. The ether layer was washed with water, dried and evaporated in a stream of air. The solid residue was recrystallized from high-boiling petroleum ether to give 0.34 g. (59%) of product, m.p. 131–132°. A mixture melting point with 2,2-dimesitylvinyl alcohol[9] was not depressed.

Treatment with ethylmagnesium bromide led to the isolation of 2,2-dimesitylvinyl alcohol in 10% yield.

Isomeric 2-Mesityl-2-phenylvinyl Alcohol.—To the Grignard reagent prepared from 0.40 g. of magnesium and 2.5 ml. of isobutyl bromide was added 1.0 g. of 2-acetoxy-2-mesitylphenylacetaldehyde in 40 ml. of ether. A white precipitate gradually appeared. The mixture was heated under reflux with stirring for 5 hr. and was decomposed by the addition of a solution of ammonium chloride. The organic layer was washed, dried and concentrated. Trituration with low-boiling petroleum ether caused the residual oil to crystallize. Recrystallization of this material from high-boiling petroleum ether gave 0.34 g. (42%) of the isomeric vinyl alcohol as colorless prisms, m.p. 100–102°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.29; H, 7.90.

Treatment of this material with acetic anhydride in pyridine led to the 2-mesityl-2-phenylvinyl acetate described previously.[10] The same acetate could be prepared by treating the isomeric vinyl alcohol with methylmagnesium iodide and acetyl chloride.

Isomeric 2-Mesityl-2-phenylvinyl Acetate.—To the reagent prepared from 1.0 g. of magnesium and 6.0 ml. of isobutyl bromide was added 2.0 g. of 2-acetoxy-2-mesitylphenylacetaldehyde in dry ether. The mixture was heated under reflux for 4 hr. Acetyl chloride (4.0 ml.) in 20 ml. of ether was added, and the solution was heated with stirring for an additional 10 hr. After the reaction mixture was decomposed with water, the organic layer was separated, washed, dried and concentrated. The residual red oil was distilled under diminished pressure and the product was collected at 165–170° (4 mm.). This fraction was redistilled and a cut collected at 167–169° (4 mm.) was analyzed.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 80.61; H, 7.74.

A few drops of this oil in dilute alcoholic potassium hydroxide was heated at reflux overnight. Water was added and the suspension was extracted with ether. Evaporation of the ether left crystals which were recrystallized from low-boiling petroleum ether to give the isomeric 2-mesityl-2-phenylvinyl alcohol melting at 100–102°.

Isomeric 2-Mesityl-2-phenylvinyl Benzoate.—This compound was prepared in a manner analogous to that for the isomeric acetate except that 4.0 ml. of benzoyl chloride was added. The residual red oil remaining after hydrolysis and concentration of the ether layer had the odor of benzoyl chloride. The oil was allowed to stand overnight in ethanol; the volatile materials were removed under diminished pressure. The deep red glass which remained was decolorized with activated carbon and recrystallized several times from ethanol to give white needles, m.p. 116–118°. A mixture melting point with the known benzoate[10] was 95–110°.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47. Found: C, 84.34; H, 6.77.

Treatment of the Isomeric Vinyl Alcohol with Lead Tetraacetate.—A solution of 0.5 g. of the isomeric vinyl alcohol in 30 ml. of acetic acid was treated with 1.0 g. of lead tetraacetate and heated at 40–45° overnight. The mixture was poured into 150 ml. of water and the precipitate collected by filtration. Two crystallizations from high-boiling petroleum ether gave needles, m.p. 133–134°. The melting point was not affected by admixture of 2-acetoxy-2-mesitylphenylacetaldehyde.

Preparation of a Semicarbazone.—A mixture of 0.30 g. of the isomeric mesitylphenylvinyl alcohol, 0.50 g. of semicarbazide hydrochloride and 0.75 g. of sodium acetate in 20 ml. of dilute ethanol was allowed to stand in the refrigerator for 3 weeks. The crystals which had separated from solution were collected and recrystallized from methanol to give long needles, m.p. 204–205°. A mixture melting point with a sample of the semicarbazone from "normal" 2-mesityl-2-phenylvinyl alcohol[11] was not depressed.

Attempts to isomerize the isomeric vinyl alcohol with iodine, with pyridine, by conversion to its enolate with methylmagnesium iodide and by seeding with the "normal" vinyl alcohol were without success.

Neutral Permanganate Oxidation of 2-Acetoxy-2-mesitylphenylacetaldehyde.—A solution of 99 mg. of the aldehyde and 45 mg. of potassium permanganate in 4 ml. of acetone and 1 ml. of water was heated under reflux for 2 hr. The

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(9) R. C. Fuson and S. P. Rowland, This Journal, **65**, 992 (1943).

(10) R. C. Fuson, N. Rabjohn and D. J. Byers, *ibid.*, **66**, 1272 (1944).

(11) R. C. Fuson, E. W. Maynert and W. J. Shenk, Jr., *ibid.*, **67**, 1939 (1945).

manganese dioxide was removed by filtration and washed with acetone. The filtrate and washings were concentrated, made basic with sodium carbonate and extracted three times with ether. The ether extracts were washed with water, dried over magnesium sulfate and evaporated to dryness. The oily residue was taken up in a small volume of boiling methanol. Cooling to room temperature provided 8 mg. (10%) of mesityl phenyl diketone, m.p. 134–135°. A mixture melting point with an authentic sample[12] was not depressed. The methanol filtrate when cooled to 0° yielded 37 mg. (49%) of slightly colored benzoylmesitylene, m.p. 30–33° (lit. 35°).[13]

Acidification of the carbonate wash, extraction with desiccation over magnesium sulfate and evaporation of the solvent gave a residue too small to characterize by ordinary methods. The presence of the diarylglycolic acid, however, was demonstrated by a spot test: a drop of concentrated sulfuric acid caused the residue to turn reddish-purple.[14]

Basic Permanganate Oxidation of 2-Acetoxy-2-mesitylphenylacetaldehyde.—A solution of 99 mg. of the aldehyde and 35 mg. of potassium permanganate in 1 ml. of 10% aqueous sodium hydroxide and 4 ml. of pyridine was allowed to stand at room temperature for 6 hr. The manganese dioxide was removed by filtration and washed with pyridine. The filtrate and washings were concentrated to a small volume, acidified with dilute hydrochloric acid and extracted three times with ether. The extracts were washed with water, extracted twice with aqueous sodium carbonate, washed again with water and dried over magnesium sulfate. Evaporation of the solvent yielded 13 mg. (15%) of mesityl phenyl diketone, m.p. 134–135°; admixture with an authentic sample caused no depression of the melting point.

The basic extracts and the subsequent water wash were acidified with dilute hydrochloric acid, extracted three times with ether, dried over magnesium sulfate and concentrated to a small volume. A milliliter of methanol was added; the resulting solution, when taken to dryness, gave 53 mg. (52%) of the methanolate of mesitylphenylglycolic acid, m.p. 85–88°. This material melted at 87–89° after one crystallization from methanol.[15]

A solution of 84 mg. of mesityl phenyl diketone in 1 ml. of 10% aqueous sodium hydroxide and 4 ml. of pyridine was allowed to stand at room temperature for 6 hr. The solution was concentrated to a small volume, diluted with water and extracted three times with ether. The ether extracts were washed with dilute hydrochloric acid and water, dried over magnesium sulfate and evaporated to dryness. The recovered mesityl phenyl diketone, m.p. 134–135°, weighed 82 mg. (98%).

Mesityl-*p*-tolylacetic Acid.—To a solution of 50 g. of *p*-methylmandelic acid in 200 ml. of mesitylene heated to 70° was added dropwise 53 ml. of fuming stannic chloride. The mixture was heated for 8 hr. and poured into 200 ml. of water. Ether was added and the mixture washed with dilute hydrochloric acid, then extracted with 10% sodium carbonate solution. Acidification of the alkaline extract and recrystallization of the product from ethanol gave 57.4 g. (72%) of the mesityl-*p*-tolylacetic acid, a colorless solid melting at 213–215°. The acid was also prepared in 74% yield by the condensation of 5 g. of mesitylglycolic acid with 50 ml. of toluene by use of 10.2 g. of stannic chloride as catalyst.

Mesityl-*p*-tolylketene.—A solution of 8 g. of mesityl-*p*-tolylacetic acid in 150 ml. of benzene was mixed with 2.2 ml. of thionyl chloride and 0.5 ml. of pyridine and the mixture heated under reflux for 10 hr. The pyridine hydrochloride was removed by filtration and the solvent was evaporated *in vacuo*. The ketene was a yellow oil boiling at 142–145° (4 mm.), yield 6.2 g. (83%).

Mesityl-*p*-tolylvinyl Alcohol.—To the Grignard reagent prepared from 2 g. of magnesium and 9 ml. of *t*-butyl chloride was added 6.2 g. of mesityl-*p*-tolylketene in ether. The solution was heated under reflux for 3 hr. and then poured into a mixture of ice and hydrochloric acid. The ether layer was washed with water, dried and evaporated. The mesityl-*p*-tolylvinyl alcohol was recrystallized from high-boiling petroleum ether to give 2.87 g. (46%) of a colorless solid, m.p. 104–105°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 86.12; H, 8.08.

The benzoate, prepared by the use of benzoyl chloride and pyridine, was recrystallized from ethanol, m.p. 151–152°.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.51; H, 6.84.

The Mixed Anhydride of Acetic and Mesitylphenylacetic Acids.—A slow stream of ketene gas, prepared by pyrolysis of acetone, was bubbled through a solution of 5 g. of mesitylphenylacetic acid in 75 ml. of ether for 1 hr. The solution was washed with water and sodium carbonate solution, then dried. After the solvent had been removed by evaporation, the product slowly became crystalline. It crystallized from high-boiling petroleum ether in colorless rhombic crystals melting at 74–75°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.50; H, 6.91.

A portion of this anhydride was hydrolyzed by treatment with sodium hydroxide to give mesitylphenylacetic acid which was characterized by a mixture melting point determination with an authentic specimen.

Diphenylacetaldehyde was prepared according to the method of Danilov.[16]

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Addition of *t*-Butylmagnesium Chloride to 2,2-Diphenyl-1-acenaphthenone

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2,2-Diphenyl-1-acenaphthenone (I) has been found to condense with *t*-butylmagnesium chloride in the 1,6-manner to yield a dihydroaromatic derivative II. As a by-product was isolated a completely aromatized ketone, likewise containing the *t*-butyl group, which is believed to be the 8-*t*-butyl derivative XII. The action of methylmagnesium iodide on the original acenaphthenone was found to convert it to the corresponding olefin XIV. Under forcing conditions the acenaphthenone also was attacked readily in the conjugate manner by phenylmagnesium bromide to give an aromatized phenyl adduct.

2,2-Diphenyl-1-acenaphthenone (I) was selected for study because of its close similarity to β-benzopinacolone, which had been found to react in the conjugate manner with Grignard reagents.[2–4] Although the acenaphthenone had been reported to

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