give 17 g. (0.50 mole, 45%) of VII, m.p. 48–50°. The infrared absorption spectrum is given in Fig. 2, curve A.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.7; H, 6.4. Found: C, 79.7; H, 6.4.

Hydrolysis of 1.0 g. of VII with 5 ml. of concentrated hydrochloric acid and 25 ml. of ethanol under reflux for 10 hours gave a 76% yield of mandelic acid, m.p. 117–118°, as shown by mixed m.p. with no depression.

Reaction of VII with Sodium Ethoxide.—VII (10.0 g., 0.0295 mole) was treated for 1 hour under reflux with a solution of sodium ethoxide prepared from 2.3 g. (0.10 g. atom) of sodium and 100 ml. of anhydrous ethanol. The reaction mixture was poured onto a mixture of 500 ml. of ice and water and 50 ml. of acetic acid. Extraction with ether, and extraction of the ether solution with 10% sodium hydroxide followed by acidification of the aqueous solution with concentrated hydrochloric acid and filtration gave 0.51 g. (0.0016 mole, 5%) of mandelic acid benzhydryl ether, m.p. and mixed m.p. with an authentic sample prepared below, 158–160°.

The ether extract remaining above was evaporated on a steam-bath under vacuum and 35 ml. of ethanol added. When the solution was allowed to stand in a refrigerator, tetraphenylethane (0.02 g., m.p. 208–210°) first crystallized, followed by 3.5 g. of material, m.p. 95–103°, which when recrystallized from ethanol amounted to 3.1 g., m.p. 108–112°. This was further purified by chromatography on activated alumina with benzene and chloroform, successively. The benzene solution, on evaporation, gave 0.17 g. of tetraphenylethane while the chloroform solution gave 2.9 g. of **ethyl α,β,β-triphenyllactate (VIII)**, m.p. 110–113° (lit.[20] 118–120°). In view of the discrepancy in melting points, the preparation of this substance by the method of Kohler, Richtmyer and Hester[20] was repeated and found to give a 32% yield, m.p. 112–113°, which gave no depression in m.p. when mixed with the sample prepared by the rearrangement of VII. The infrared spectrum is shown in Fig. 2, curve B.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.7; H, 6.4; C_2H_5O; 3.0. Found: C, 79.8; H, 6.3; C_2H_5O, 13.3.

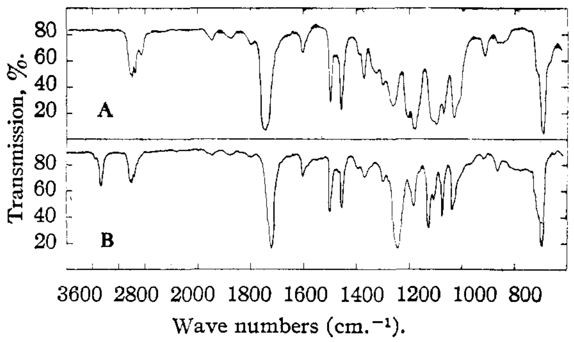

Fig. 2.—Curve A, ethyl mandelate benzhydryl ether in CCl_4; curve B, ethyl α,β,β-triphenyllactate in CCl_4.

The ethanolic filtrate from the rearrangement above was evaporated and the residue purified by chromatography on activated alumina with benzene and chloroform, successively. The benzene fractions gave unreacted VII which, after recrystallization from ethanol, amounted to 2.2 g. (0.00637 mole, 22%) and melted at 44–47°. The chloroform fractions gave 1.0 g. of additional VIII; total, 3.9 g. (0.011 mole, 39%).

Reaction of VII with Potassium Hydroxide. Mandelic Acid Benzhydryl Ether.—VII (5.0 g., 0.014 mole) was treated for 1 hour under reflux with 50 ml. of 1 *N* ethanolic potassium hydroxide. The reaction mixture was poured into 100 ml. of water, extracted with ether, the aqueous layer acidified and the mandelic acid benzhydryl ether (3.7 g., m.p. 153–155°) which precipitated collected. Recrystallization from ethanol gave 3.0 g. (0.0094 mole, 67%) of material, m.p. 161–163°.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 79.4; H, 5.8.

URBANA, ILLINOIS

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

Carboxylate Ion Displacement in Dimesitylmethyl Esters

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Dimesitylmethyl esters of acetic, benzoic and mesitoic acids, when treated with certain Grignard reagents undergo carboxylate ion displacement by the the hydrocarbon radicals of the reagents. Grignard reagents with marked reducing power replace the carboxylate ions by hydrogen, *i.e.*, they bring about hydrogenolysis, to give dimesitylmethane. The hydrocarbons produced in this way are the same as those obtained by the action of the various Grignard reagents on dimesitylmethyl chloride.

Carboxylate ion displacement in esters has been observed with various nucleophilic agents such as amines,[3] phenoxides,[4] alkoxides[5] and dilute alkalies.[6] Grignard reagents have been found to be effective with certain hindered esters[7] with 2-methyl-10-acetoxy-9-anthrone,[8] and with the acetate and benzoate of 9-(hydroxymethyl)-carbazole,[9] of triphenylcarbinol[8,10] and dimethylvinylcarbinyl acetate.[11]

The resemblance of various dimesitylmethyl derivatives to the corresponding triarylmethyl compounds[12] led to a study of the action of Grignard reagents on esters of dimesitylcarbinol. Dimesitylmethyl mesitoate (I, R = Mes) was found to undergo displacement of the mesitoxyl group to yield hydrocarbons II when treated with Grignard reagents. With reagents possessing marked reducing power hydrogenolysis occurs also, the product being dimesitylmethane (III). Isopropylmagnesium bromide gave only the methane. The formation of dimesitylmethane is comparable

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(1) Rohm and Haas Fellow, 1947–1948; Socony-Vacuum Fellow, 1948–1949.

(2) Socony-Vacuum Fellow, 1952–1953.

(3) R. Willstätter and W. Kuhn, *Ber.*, **35**, 2757 (1902); L. P. Hammett and H. L. Pfluger, THIS JOURNAL, **55**, 4079 (1933).

(4) H. King and E. V. Wright, *J. Chem. Soc.*, **155**, 1168 (1939); C. O. Guss and L. H. Jules, THIS JOURNAL, **72**, 3462 (1950).

(5) A. Magnani and S. M. McElvain, *ibid.*, **60**, 813 (1938).

(6) See J. Kenyon and R. F. Mason, *J. Chem. Soc.*, **168**, 4964 (1952).

(7) See R. T. Arnold and S. Searles, Jr., THIS JOURNAL, **71**, 1150 (1949); K. W. Wilson, J. D. Roberts and W. G. Young, *ibid.*, **71**, 2019 (1949).

(8) L. F. Fieser and H. Heymann, *ibid.*, **64**, 376 (1942).

(9) K. G. Mizuch, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 1471 (1946).

(10) C. R. Hauser, P. O. Saperstein and J. C. Shivers, THIS JOURNAL, **70**, 606 (1948).

(11) A. N. Nesmeyanov, R. K. Freidlina and A. K. Kochetknov, *Izvest. Akad. Nauk. S. S. S. R., Otdel Khim. Nauk*, 623 (1949).

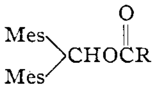
(12) R. C. Fuson and H. L. Jackson, THIS JOURNAL, **72**, 351 (1950).

TABLE I

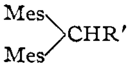
$$Mes_2CHA \xrightarrow{RMgX} Mes_2CHR,\ Mes_2CH_2$$

R	Yield of Mes_2CHR, % when A = CH_3CO_2	$C_6H_5CO_2$	$MesCO_2$	Cl	M.p., °C.	Anal. of Mes_2CHR Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Yield of Mes_2CH_2, %
Methyl	35	56	77	55	93–95	90.16	90.30	9.84	9.78	0
Benzyl	51	22	48	68	116–117	91.17	91.42	8.83	8.92	0
Allyl	35	..	..	41	101–102	90.36	90.20	9.64	9.79	0
Ethyl	20	9	10	32	85–86	89.94	89.82	10.06	9.91	Trace to 14
n-Propyl	49	..	..	35	110–112	89.73	89.52	10.27	10.20	2
n-Butyl	51	..	..	68	85–87	89.50	89.35	10.50	10.27	Trace to 9
Isobutyl	15	..	..	8	92–93	89.50	89.44	10.50	10.56	2–6
Cyclohexyl	31	..	..	46	148–149	89.66	89.89	10.34	10.11	1–4
Isopropyl	0	0	0	0	.....	...	...	...	...	21–42
s-Butyl	0	..	..	0	.....	...	...	...	...	41–46
t-Butyl	0	..	..	0	.....	...	...	...	...	13–71

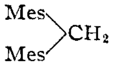
to the hydrogenolysis of dioxolones by *t*-butylmagnesium chloride.[13]


$$(Mes)_2CHOC(=O)R$$

I


$$(Mes)_2CHR'$$

II


$$(Mes)_2CH_2$$

III

The steric hindrance provided by the mesitoyl radical proved to be unnecessary; the benzoate and acetate reacted in a similar manner to yield products identical to those obtained from the mesitoate. Dimesitylmethyl chloride, by chloride ion displacement, was converted to the same hydrocarbons.

1,1-Dimesitylethane was reported by Reichert and Nieuwland to be a liquid boiling at 344–345°.[14] Later the hydrocarbon was prepared by Snyder and Roeske by hydrogenation of 1,1-dimesitylethylene and was found to melt at 94°.[15] When a sample of this solid was mixed with that prepared in the present work, no lowering of melting point was observed.

Hydrogenation of 3,3-dimesityl-1-butene yielded 1,1-dimesitylbutane; oxidation gave the known *β,β*-dimesitylpropionic acid.[12]

The yields, melting points and analytical data of the hydrocarbons are given in Table I.

Experimental

Dimesitylmethyl Acetate.—A solution of 16.5 g. of dimesitylcarbinol, 100 ml. of glacial acetic acid and 250 ml. of benzene in a 500-ml. flask, fitted with a Dean–Stark water separator,[16] was heated under reflux for 3 hours. Removal of the solvents by distillation under reduced pressure left a solid residue which, after one recrystallization from ethanol, melted at 95.5–97°; the yield was nearly quantitative. Dimesitylmethyl acetate also was prepared from dimesitylmethyl chloride and silver acetate following the procedure of Nauta and Wuis.[17]

Dimesitylmethyl Benzoate.—A mixture of 10 g. of dimesitylmethyl chloride, 10 g. of silver benzoate and 200 ml. of dry benzene was shaken for 30 minutes and filtered. The ester, left by evaporation of the solvent, was recrystallized from methanol; m.p. 151–152°, yield 64%.

Anal.[18] Calcd. for $C_{26}H_{28}O_2$: C, 83.83; H, 7.56. Found: C, 84.06; H, 7.73.

Dimesitylmethyl Mesitoate.—The procedure was similar to that employed for the benzoate. The ester separated from methanol in colorless crystals; m.p. 144–145°, yield 69%.

Anal. Calcd. for $C_{29}H_{34}O_2$: C, 84.02; H, 8.27. Found: C, 83.78; H, 8.55.

Reaction of Grignard Reagents with the Esters of Dimesitylcarbinol and with Dimesitylmethyl Chloride.—An ethereal solution of 0.01 mole of dimesitylmethyl acetate, benzoate, mesitoate or chloride was added to a Grignard reagent prepared from 0.05 mole of alkyl halide and 0.05 mole of magnesium in 75 ml. of ether. A white precipitate formed immediately. The suspension, after being stirred and heated under reflux for 1 hour, was decomposed with a mixture of ice and hydrochloric acid. The ether layer was removed, washed with 10% sodium hydroxide solution and dried. Benzoic and mesitoic acids were obtained from reactions involving the benzoate and mesitoate, respectively, when the alkaline wash solutions were acidified. The residue, left when the ether solution was concentrated, was recrystallized from ethanol to give white crystalline hydrocarbons (*vide infra*).

Identification of Products.—One product, dimesitylmethane (m.p. 131–133°), was shown to be identical with an authentic sample,[19] by a comparison of infrared spectra[20] and a mixed melting point determination.

1,1-Dimesitylethane, obtained from methylmagnesium iodide, was identical with the compound prepared by hydrogenation of *α,α*-dimesitylethylene.[15] 1,1-Dimesitylpentane was prepared from dimesitylmethyl chloride and *n*-butyllithium. The infrared spectrum of 3,3-dimesityl-1-butene, prepared from allylmagnesium bromide, contained absorption bands at 1642 and 915 cm.$^{-1}$ indicating a carbon–carbon double bond and a vinyl grouping, respectively. Hydrogenation at 3 atmospheres and room temperature for 3 hours over Raney nickel converted the hydrocarbon to 1,1-dimesitylbutane, prepared from *n*-propylmagnesium bromide. Oxidation with chromic anhydride and glacial acetic acid[19] transformed it to the known *β,β*-dimesitylpropionic acid.[12]

URBANA, ILL.

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[13] R. C. Fuson and A. I. Rachlin, THIS JOURNAL, **64**, 1567 (1942).

[14] J. S. Reichert and J. A. Nieuwland, *ibid.*, **45**, 3090 (1923).

[15] H. R. Snyder and R. W. Roeske, *ibid.*, **74**, 5820 (1952).

[16] E. W. Dean and D. D. Stark, *J. Ind. Eng. Chem.*, **12**, 486 (1920).

[17] W. T. Nauta and P. J. Wuis, *Rec. trav. chim.*, **56**, 535 (1937).

[18] The microanalysis were carried out by Miss Emily Davis, Miss Rachel Kopel, Mrs. Jean Fortney, Miss Katherine Pih and Mr. Joseph Nemeth.

[19] R. C. Fuson, P. L. Southwick and S. P. Rowland, THIS JOURNAL, **66**, 1109 (1944).

[20] The infrared analyses were carried out by Miss Helen Miklas.