

Syntheses of Dimethyldibenzyls

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The symmetrical 2,2'-, 3,3'-, and 4,4'-dimethyldibenzyl were obtained respectively by the Wurtz reaction of the corresponding methylbenzyl chlorides prepared from *o*-, *m*-toluidine and *p*-cymene through several steps. The unsymmetrical 2,3'-, 2,4'-, and 3,4'-dimethyldibenzyl were obtained respectively by the Wolf-Kishner reduction of the corresponding semicarbazones derived from ketones which were prepared from the appropriate tolunitrile and tolyl magnesium bromide. The gas chromatographic separation of a mixture of the six isomers was successfully made with a 90m. butanediol succinate polyester-coated capillary column at 170°.

INTRODUCTION

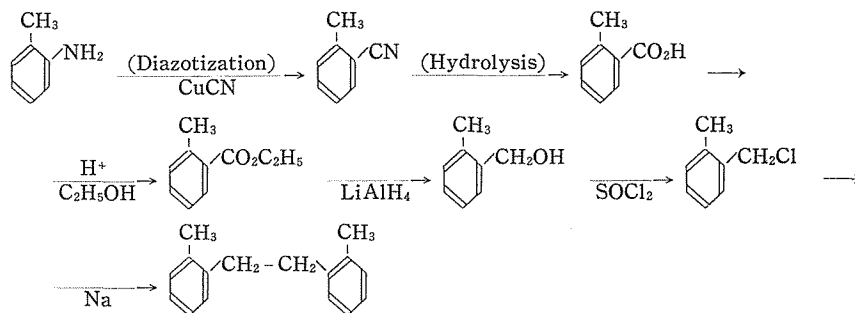
The Friedel-Crafts reaction of 1,2-dichloroethane with toluene studied by several investigators¹⁻⁴⁾ gave a mixture of six isomers of dimethyldibenzyls which would be raw materials for the production of aromatic dibasic acids. No details, however, were available for the relationship between the reaction conditions and the isomers distribution, because the separation or analytical determination of these isomers was very difficult.

For the purpose of clarifying the above relationship by establishing the effective analytical method, the present authors have for the first time carried out the syntheses of the six pure isomers which are required for the standard samples on the gas chromatographic analysis of their mixtures.

RESULTS

Several well-known reactions which include neither isomerization of the products, nor formation of unseparable by-products, were used for the syntheses of the pure isomers.

Syntheses of the symmetrical isomers. For example, the synthetic route to 2,2'-isomer is shown as follows.

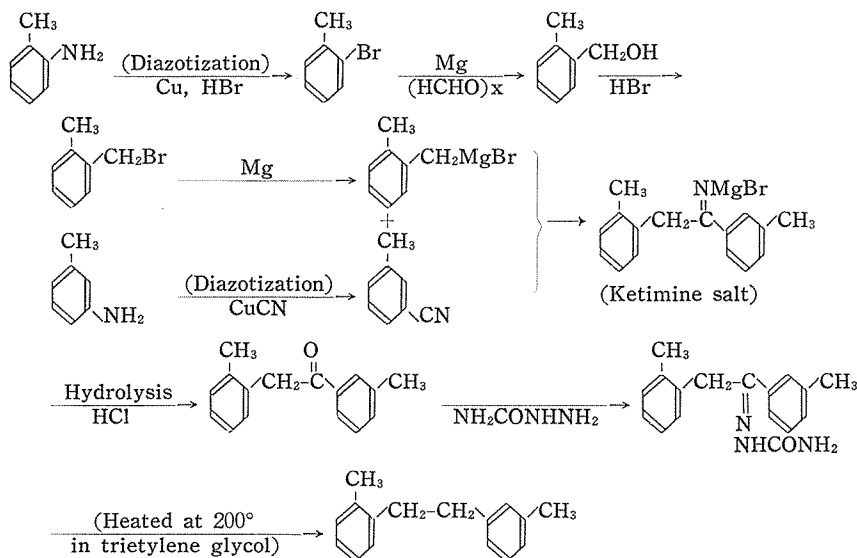


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In the case of 4,4'-isomer, the starting material was *p*-cymene and it yielded *p*-toluic acid by oxidation with nitric acid. The three symmetrical dimethyldibenzyls were obtained in a pure state by the Wurtz reaction of the corresponding methylbenzyl chlorides with metallic sodium, as has been reported by Farthing⁹.

Syntheses of the unsymmetrical isomers. For example, the synthetic route to 2,3'-isomer is shown as follows.



Though the intermediate ketimine salts were resistant to usual hydrolysis⁶⁾ with aqueous ammonium chloride, further addition of dil. hydrochloric acid effected completely the hydrolysis. The resulting ketones were contaminated with a small amount of the symmetrical dimethyldibenzyls which were formed from two molecules of the methylbenzyl chlorides by the action of magnesium. These impurities were easily removed off by recrystallization of the semicarbazones derived from the ketones. According to the Huang-Minlon procedure⁷⁾, the semicarbazones were decomposed by alkali in triethyleneglycol to give the three unsymmetrical dimeth-

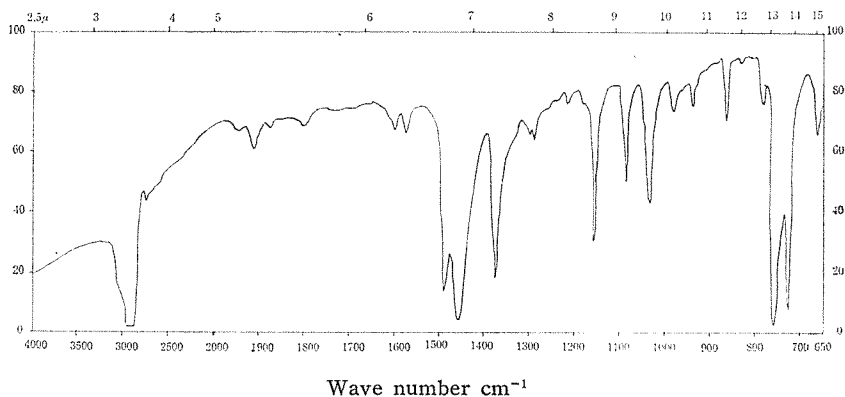


Fig. 1. Absorption spectrum of 2,2'-dimethyldibenzyl**.

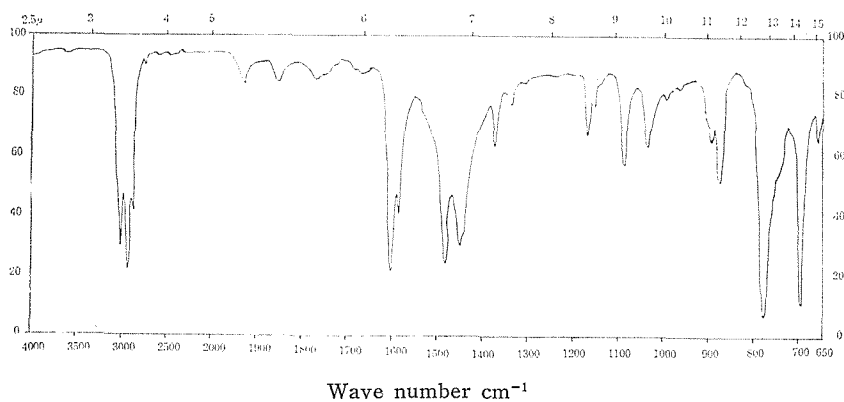


Fig. 2. Absorption spectrum of 3,3'-dimethyldibenzyl.

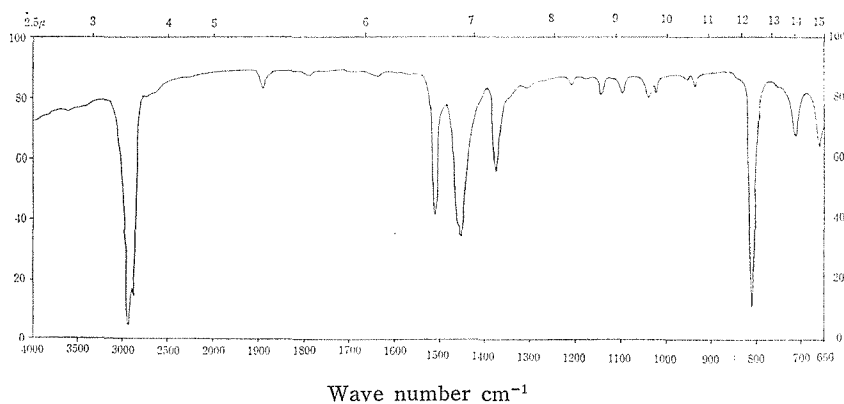


Fig. 3. Absorption spectrum of 4,4'-dimethyldibenzyl**.

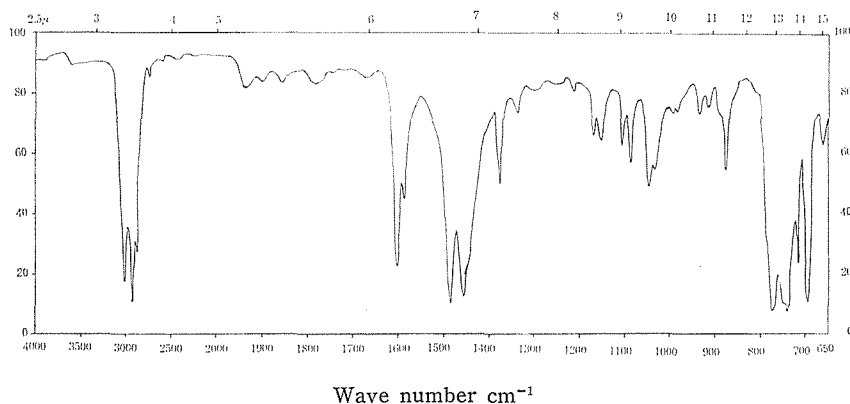


Fig. 4. Absorption spectrum of 2,3'-dimethyldibenzyl.

yldibenzyls in a pure state. Isolation of their pure specimens are not yet found in the literature, though the Friedel-Crafts reaction of 1,2-dichloroethane with toluene gave a mixture containing them¹⁻⁴.

The purity of the six isomers thus obtained was determined by gas chroma-

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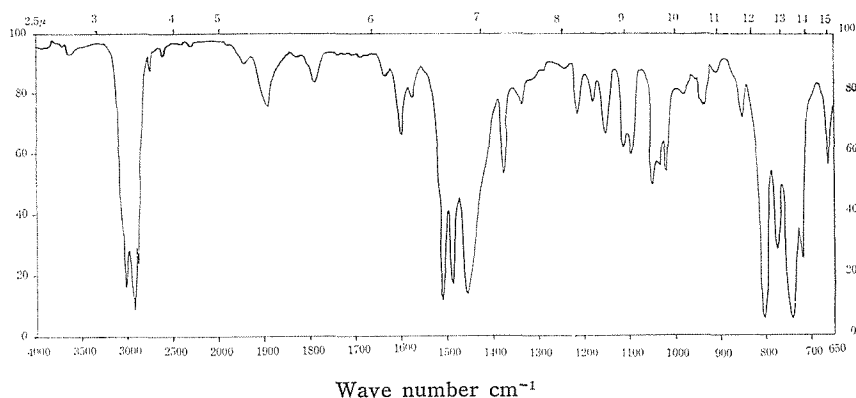


Fig. 5. Absorption spectrum of 2,4'-dimethyldibenzyl.

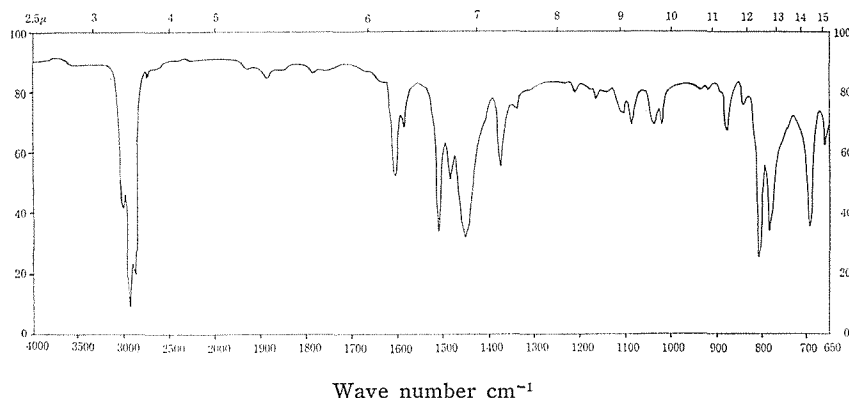


Fig. 6. Absorption spectrum of 3,4'-dimethyldibenzyl**.

** Conventional methods of mulling the sample in Nujol were used.

tographic analysis to be better than 98%.

Infrared spectra of the symmetrical isomers (Figs. 1-3) showed characteristic strong bands (CH out-of-plane deformation vibrations) of *o*-, *m*-, and *p*-disubstituted aromatics⁸⁾ at 752cm⁻¹, 778 and 695cm⁻¹, and 810cm⁻¹, respectively. As was expected, those of the unsymmetrical isomers (Figs. 4-6) showed strong bands due to two kinds of the corresponding disubstituted aromatics at 773, 742 and 698cm⁻¹, 808 and 743cm⁻¹, and 805, 785 and 695cm⁻¹, respectively.

Gas chromatographic separation of a mixture of the six isomers. Attempts with several kinds of packed columns to separate the isomers under various conditions, were all unsuccessful. Apparently the too high boiling point (about 300°) of the samples limited the selection of the columns.

Recently a highly efficient gaschromatograph with the Golay-type capillary column has been used for a mixture of isomers of disubstituted aromatics and others, of which separations are very difficult with packed columns.

The examinations on several kinds of capillary columns have resulted in finding that 90m. butanediol succinate polyester-coated capillary column effects the satisfactory separation of a mixture of six dimethyldibenzyls as shown in Fig. 7.

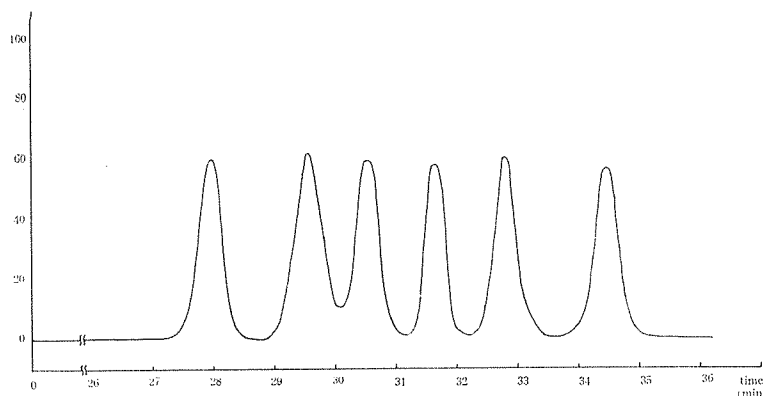


Fig. 7. Chromatogram of dimethyldibenzyl isomers.

EXPERIMENTAL

Materials. *o*-, *m*-Toluidine, and *p*-cymene were commercial materials of highest available purity. The purity of toluidines was checked by gas chromatographic analysis with 45m. polypropylene glycol-coated capillary column at 125° to be better than 99%.

o-, and *m*-Tolunitrile were prepared by the Sandmeyer reaction of the diazotized toluidines with cuprous cyanide, as has been described in "Organic Syntheses"⁹

	Toluidine g.	Tolunitrile g.(%)	b.p.	n_D
<i>o</i> -	71	29(37) ref. ⁹⁻¹⁰	94~96° (20 mm) 94~96° (20 mm)	1.5328(13°) 1.5272(23°)
<i>m</i> -	104	40(35) ref. ¹¹	97~98° (19 mm) 84.5° (10 mm)	1.5302(13°)

p-Toluic acid was prepared by the oxidation of *p*-cymene with nitric acid, as has been described in "Organic Syntheses"¹². From 17.5 g. of *p*-cymene there was obtained 12g. (68%) of the acid, m.p. 179~181° (ref.¹² 176~177°).

o-, and *m*-Toluic acid were prepared by the hydrolysis of the tolunitriles with sulfuric acid, as has been described in "Organic Syntheses"¹³.

	Tolunitrile g.	Toluic acid g.(%)	m.p.
<i>o</i> -	53	55(89)	105~106° (ref. ¹³ 102~103°)
<i>m</i> -	70	57(70)	111~112° (ref. ¹⁴ 110.5°)

Toluic acid ethyl esters were prepared by refluxing the toluic acids with excess ethanol in the presence of a small amount of conc. sulfuric acid for six hours.

	Toluic acid g.	The ester g.(%)	b.p.	n_D
<i>p</i> -	36	20(46) ref. ¹⁵	113~115° (18 mm) 66.5° (0.1 mm)	1.5062(24.5°) 1.5056(25°)
<i>o</i> -	55	27(41) ref. ¹⁶	107~110° (18 mm) 102~102.5° (13 mm)	1.5021(27°) 1.507(21.6°)
<i>m</i> -	57	45(65) ref. ^{11,16}	117~118° (19 mm) 103~105° (10 mm)	1.5040(27°) 1.505(21.6°)

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Methylbenzyl alcohols were prepared by the reduction of the toluic acid ethyl esters with lithium aluminum hydride as has been described in "Organic Reactions"¹⁷⁾.

	The ester g.	Methylbenzyl alcohol g.(%)	m.p.	b.p.	n_D
<i>p</i> -	20	7.5(50)	57~58°	(ref. ¹⁸⁾ 60°	
<i>o</i> -	27	9.5(45)	35~37°	(ref. ¹⁶⁾ 36°	
<i>m</i> -	40	12.0(40)		115~116° (23mm)	1.5290(25°)
			ref. ¹⁸⁾	223°	

Methylbenzyl chlorides were prepared by refluxing the methylbenzyl alcohols with an equimolar quantity of thionyl chloride in the presence of a few drops of pyridine.

	The alcohol g.	Methylbenzyl chloride g.(%)	b.p.	n_D
<i>p</i> -	14.0	12.0(75)	87° (20 mm)	1.5291(25°)
		ref. ¹⁹⁾	90° (20 mm)	
<i>o</i> -	9.1	5.7(55)	85~87° (19 mm)	1.5380(25°)
		ref. ²⁰⁾	197~199°	
<i>m</i> -	11.0	7.0(52)	91~92° (22 mm)	1.5330(25°)
		ref. ²¹⁾	85~88° (16 mm)	1.5345(20°)

4,4'-Dimethyldibenzyl. Refluxing 11.5 g. of *p*-methyl-benzylchloride and 4 g. of sodium in *p*-xylene for two hours with stirring gave 5.0 g. (58%) of 4,4'-dimethyldibenzyl which was recrystallized from ethanol, m.p. 83~84° (ref.⁵⁾ 82°).

Anal. Calcd. for C₁₆H₁₈: C, 91.38; H, 8.63. Found: C, 91.07; H, 8.70.

2,2'-Dimethyldibenzyl. From 5.7g. of *o*-methylbenzyl chloride there was obtained 1.0g. (23%) of 2,2'-dimethyldibenzyl, m.p. 64~66° (ref.²²⁾ 66.5°).

Anal. Calcd. for C₁₆H₁₈: C, 91.37; H, 8.63. Found: C, 91.40; H, 8.51.

3,3'-Dimethyldibenzyl. From 7.0g. of *m*-methylbenzyl chloride there was obtained 2.1g. (40%) of 3,3'-dimethyldibenzyl, b.p. 143~144.5° (3.5mm), n_D^{22} 1.5560 (ref.²³⁾ b.p. 163° (10mm)).

Anal. Calcd. for C₁₆H₁₈: C, 91.37; H, 8.63. Found: C, 91.27; H, 8.76.

***p*-, and *o*-Bromotoluene** were prepared by the Gattermann reaction of the diazotized toluidines with hydrogen bromide in the presence of copper powder, as has been described in "Organic Syntheses"²⁴⁾.

	Toluidine g.	Bromotoluene g.(%)	m.p.	b.p.	n_D
<i>p</i> -	81	86(66)	26°	71° (18 mm)	
		ref. ²⁵⁾	28.5°	185.2°	
<i>o</i> -	81	59(46)		73° (20 mm)	1.5568(19°)
		ref. ^{26, 27)}		181°	1.5608(*)

* Description of the temperature is not found in the literature.

***p*-Methylbenzyl alcohol.** As has been shown by Newman²⁸⁾, the Grignard reagent, prepared from 80g. of *p*-bromotoluene and 13.3 g. of magnesium turning in 200ml. of ether, was allowed to react with 20 g. of dry paraformaldehyde for one day. After decomposing the reaction mixture with aqueous ammonium chloride,

there was obtained 20 g. (35 %) of *p*-methylbenzyl alcohol, m.p. 57.5~58.0° (ref.¹⁸⁾ 60°).

***o*-Methylbenzyl alcohol.** From 130g. of *o*-bromotoluene there was obtained 38g. (41%) of *o*-methylbenzyl alcohol, m.p. 35~37° (ref.²⁹⁾ 36°).

***p*-, and *m*-Methylbenzyl bromide** were prepared by refluxing of the methylbenzyl alcohols with excess hydrobromic acid in the presenece of conc. sulfuric acid.

	The alcohol g.	Methylbenzyl bromide g.(%)	m.p.	b.p.	<i>n</i> _D
<i>p</i> -	51	42(54) ref. ^{30,31)}	34~35° 35.5°	98~101° (18 mm) 109° (15 mm)	
<i>o</i> -	38	34(59) ref. ³¹⁾		102° (17 mm) 108° (16 mm)	1.5748(20°)

α -Oxo-2,4'-dimethyldibenzyl. In 500 ml. three-necked flask equipped with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser attached with calcium chloride tube, were placed 2.5g. of magnesium turnings and 150ml. of ether. After the Grignard reagent had been prepared by dropping 15g. of *p*-methylbenzyl bromide dissolved in 100 ml. of ether, 10 g. of *o*-tolunitrile dissolved in 100 ml. of ether was added with stirring. Stirring and refluxing were continued for ten hours. Then the reaction mixture was decomposed with ammonium chloride solution; 100ml. of dil. hydrochloric acid (10%) was added, and the mixture was stirred for half an hour to hydrolyze the ketimine salt completely. The ether layer dried over anhydrous sodium sulfate, yielded 8.0g. (44%) of crude α -oxo-2,4'-dimethyldibenzyl, b.p. 140 ~ 147° (3mm), which gave a 2,4-dinitrophenylhydrazone melting at 155~157°.

Anal. Calcd. for C₂₂H₂₀O₄N₄: C, 65.33; H, 4.99; N, 13.86. Found: C, 64.91; H, 4.99; N, 13.53.

α -Oxo-2,3'-dimethyldibenzyl. From 10g. of *m*-tolunitrile and 15g. of *o*-methylbenzyl bromide there was obtained 8.9g. (40%) of crude α -oxo-2,3'-dimethyldibenzyl, b.p. 140~147° (3mm), which gave a 2,4-dinitrophenylhydrazone melting at 173~176°.

Anal. Calcd. for C₂₂H₂₀O₄N₄: C, 65.33; H, 4.99; N, 13.86. Found: C, 64.91; H, 4.99; N, 13.53.

α -Oxo-3,4'-dimethyldibenzyl. From 10g. of *m*-tolunitrile and 15 g. of *p*-methylbenzyl bromide there was obtained 9.2g. (51%) of α -oxo-3,4'-dimethyldibenzyl, b.p. 115~128° (0.2mm), which gave a 2,4-dinitrophenylhydrazone melting at 192~193°.

Anal. Calcd. for C₂₂H₂₀O₄N₄: C, 65.33; H, 4.99; N, 13.86. Found: C, 65.47; H, 4.97; N, 13.60.

2,4-Dimethyldibenzyl. Refluxing 6.8g. of crude α -oxo-2,4'-dimethyldibenzyl with 7 g. of semicarbazide hydrochloride. 11 g. of sodium acetate and 70 ml. of ethanol gave 3.7 g. (43 %) of the semicarbazone which was recrystallized from benzene, m.p. 156~158°.

Anal. Calcd. for C₁₇H₁₆ON₃: C, 72.57; H, 6.81; N, 14.94. Found: C, 72.80; H, 6.71; N, 14.81.

In 20ml. of triethylene glycol, 2 g. of this semicarbazone was refluxed with a small amount of sodium hydroxide for two hours. Then the product was extracted

with ether. The ether extract was washed several times with water to remove triethylene glycol. The dried ether extract gave 1.3g. (87%) of 2,4'-dimethyldibenzyl.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.35; H, 8.89.

2,3'-Dimethyldibenzyl. From 6g. of crude α -oxo-2,3'-dimethyldibenzyl there was obtained 5.7g. (76%) of its semicarbazone, m.p. 166~168°.

Anal. Calcd. for $C_{17}H_{19}ON_3$: C, 72.57; H, 6.81; N, 14.94. Found, C, 72.48; H, 6.50; N, 15.41.

From 3g. of the semicarbazone, there was obtained 1.6g. (71%) of 2,3'-dimethyldibenzyl, b.p. 148~149° (4 mm), n_D^{25} 1.5645.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.09; H, 8.91.

3,4'-Dimethyldibenzyl. From crude 7.2g. of α -oxo-3,4'-dimethyldibenzyl there was obtained 6.2g. (68%) of its semicarbazone, m.p. 157~158°.

Anal. Calcd. for $C_{17}H_{19}ON_3$: C, 72.57; H, 6.81; N, 14.94. Found: C, 72.48; H, 6.69; N, 14.86.

From 3g. of the semicarbazone, there was obtained 1.8 g. (80 %) of 3,4'-dimethyldibenzyl.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.45, H, 8.76.

Gas chromatographic separation. Hitachi Model F 6 gas chromatograph equipped with Golay-type capillary columns and hydrogen flame ionization detector was used. Separations were made in a 90 m. column coated with butanediol succinate polyester. The column was operated at 170° with N_2 gas pressure of 1.5 kg./cm², and N_2 flow rate at 7.7 ml. per minute. The separation of a mixture of the six dimethyldibenzyls is shown in Fig. 7. Characteristic retention times of the six isomers are summarized in Table 1.

Table 1. Retention time of dimethyldibenzyls.

Dimethyldibenzyl	Retention time, (min.)
3,3'-	29.35
3,4'-	31.20
2,3'-	32.15
4,4'-	33.32
2,4'-	34.50
2,2'-	36.20

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