TABLE

				Color with	
Compound	Fluorescence	R_f	TCNE	Picric acid	Trinitrofluorenone
Pyrene	Blue	0.63	Brown-violet	Orange	Orange
3-Methylpyrene	Yellow-blue	0.69	Brown-violet	Red	Brown-red
3,5-Dimethylpyrene	Yellow	0.74	Red-brown	Orange	Brown
3,8-Dimethylpyrene	Green-yellow	0.78	Red-brown	Orange	Brown
3-Nitropyrene	Orange	0.38	Gold	Yellow	Orange
3-Bromopyrene	Blue	0.68	Green	Red-orange	Red-orange
3,8-Dibromopyrene	Blue	0.69	Green	Orange	Orange
3-Acetylpyrene	Bright yellow	0.37	Green	Yellow	Orange
3-Hydroxymethylpyrene	Green	0.05	Brown	Red-orange	Brown
3-Carboxypyrene	Yellow	0.01	Light green	Yellow	—
3-Formylpyrene	Gold	0.37	Yellow	Orange	Orange
3-Methyl-5-formylpyrene	Orange	0.46	Light green	Orange	Brown-orange
Anthracene	Violet	0.70	—	Orange	Brown-red
9,10-Dibromoanthracene	Yellow	0.77	Green	Orange	Orange
1.2-Benzanthracene[a]	Yellow	0.60	Blue	Orange	Red-orange
1:2,5:6-Dibenzanthracene[a]	Violet	0.47	Green	Light orange	Orange
Chrysene[a]	Dark blue	0.63	Light violet	Light orange	Orange
Fluoranthene	Blue	0.79	Violet	Yellow	Yellow
20-Methylcholanthrene[a]	Yellow	0.82	Gray-green	Brown	Gray-green
10-Ethylbenzpyrene[a]	Yellow	0.66	Brown	Brown	Gray
10-Acetylbenzpyrene[a]	Gold	0.18	Gray-brown	Light orange	Tan
5-Acetylbenzpyrene[a]	Blue	0.09	Light brown	Orange	Brown-gray
Phenanthrene	Violet	0.63	Violet	Yellow	Yellow
9-Bromophenanthrene	—	0.78	Violet	Yellow	Yellow
Naphthalene	Blue	0.89	Red-violet	Yellow	Yellow
1-Nitronaphthalene	—	0.50	Orange	Yellow	Yellow
2-Methylnaphthalene	Blue	0.92	Blue-gray	Yellow	Yellow
Di-m-xylylene[b]	—	0.66	Red	—	—
Di-(2-methyl-m-xylylene)[b]	—	0.66	Gold	—	—
Acepleiadiene[b]	Black-red	0.69	Gold	Dark gray	Brown
Acepleiadylene[b]	Orange-red	0.59	Brown	Red-brown	Red-brown
Tetrahydroacepleiadane[b]	Blue	0.06	Purple	Yellow	Yellow
Perinaphthanone[a]	Light blue-violet	0.51	Salmon	Yellow	Yellow
Benzpyrene[a]	Blue	0.60	Violet-pink	Brown	Gray-brown
Fluorene[a]	Light violet	0.65	Light brown	Yellow	Yellow
1-Phenyl-1-(α-naphthyl)-propene-1[a]	Blue	0.74	Purple	Yellow	Yellow

[a] Gift of Dr. S. C. Pakrashi of this Laboratory. [b] Gift of Dr. Leslie Humber of this Laboratory.

trinitrofluorenone. It is possible to detect the position of nonfluorescent compounds, such as the xylylenes and the substituted naphthalenes, by the TCNE spots. The method is sensitive to 1 gamma of pyrene, and 10 gamma of naphthalene; the equilibrium constants for the complex formation in methylene chloride solution for these two compounds[6] are 29.5 and 11.7.

A slight drawback to the method is the impermanence of the color, which fades in some cases in the course of 3 min. but generally is visible for over 1 hr. The rate of fading appears to depend on the stability and amount of the complex present.

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1-Phenyl-2,2-dimethylbutane

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When Francis[1] published his review on the properties of the alkylbenzenes in 1948, fifteen of the seventeen possible monoalkylbenzenes of the formula $C_{12}H_{18}$ had been described. One of the two remaining unknown isomers, 1-phenyl-3,3-dimethylbutane, has since been prepared.[2] The other, 1-phenyl-2,2-dimethylbutane (VI), was reportedly obtained by Tafel and Jurgens[3] from the electrolytic reduction of "methylbenzylacetoacetic ester." Later Tafel and Andre[4] decided that their hydrocarbon was probably 1-phenyl-3-methylpentane rather than VI. Francis[1] stated that VI "must be considered unknown." This paper reports the synthesis of VI by the following reaction sequence.

Prout *et al.*[5] have reported carrying out the first two steps above, leading to the acid (III). The latter was smoothly reduced to the alcohol (IV) by means

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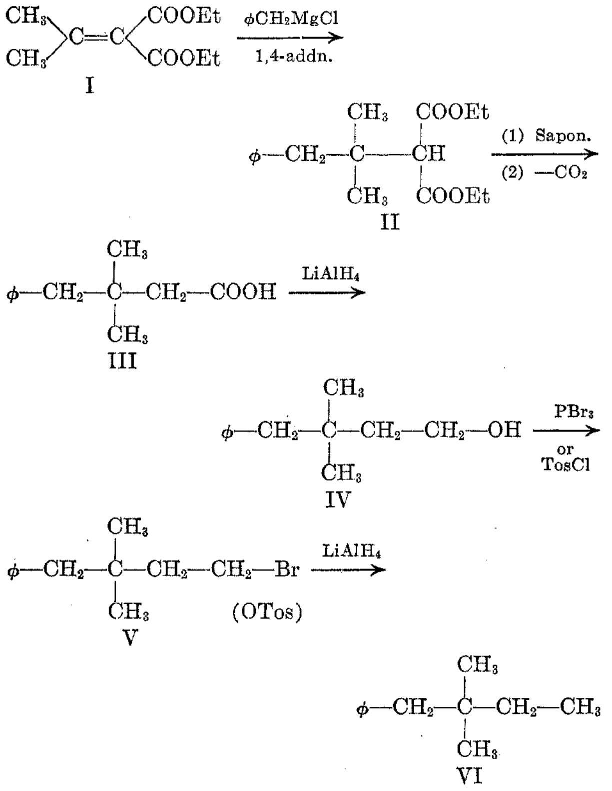
(1) A. W. Francis, *Chem. Revs.*, **42**, 107 (1948).

(2) E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **72**, 222 (1950).

(3) J. Tafel and W. Jurgens, *Ber.*, **42**, 2556 (1909).

(4) J. Tafel and F. Andre, *Ber.*, **45**, 437 (1912).

(5) F. S. Prout, E. P.-Y. Huang, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954).



of lithium aluminum hydride.[6] The reduction resulted in the disappearance of the characteristic infrared absorption bands of the acid at 3.7μ, 5.8μ and 10.5–11.5μ and the appearance of hydroxyl absorption bands at 3.4μ and 9.3–9.9μ. This alcohol proved to be singularly nonreactive. It reacted only slowly with freshly cut sodium. Although it formed a small amount of the tosylate[7] on one occasion, in numerous other attempts this derivative did not form. The 3,5-dinitrobenzoate ester resulted only when the alcohol and acid chloride were heated together. An attempt to prepare the corresponding chloride using thionyl chloride and pyridine as described by Whitmore and Bernstein[8] for a similar alcohol resulted in recovery of the unchanged alcohol. When the alcohol was heated overnight at 75° with phosphorus tribromide following the procedure of Pines *et al.*,[9] only traces of the expected bromide were formed. However, when the temperature of the latter reaction mixture was maintained above 125° for several hours, the expected bromide (V) was obtained in reasonable yields. The infrared spectrum of the bromide no longer possessed the sharp hydroxyl absorption at 3.4μ nor the broad band at 9.3–9.9μ. Inasmuch as the reaction conditions were rather severe, the possibility existed that some bromide other than V might have formed. That the expected bromide was formed was demonstrated by converting a sample of the bromide to the Grignard reagent, oxidizing the latter to the bromomagnesium alkoxide, hydrolyzing the latter, and recovering the alcohol.[8] This latter sample of alcohol formed a 3,5-dinitrobenzoate identical with the one prepared from the alcohol (IV). When bromide (V) was refluxed with lithium aluminum hydride in tetrahydrofuran solvent, hydrocarbon (VI) was formed. The infrared absorption spectrum of the hydrocarbon obtained by reduction of the tosyl ester was identical with that of the hydrocarbon obtained by reduction of the bromide. Samples of VI obtained *via* both the bromide and tosyl ester yielded the same acetamino derivative.

The physical properties of 1-phenyl-2,2-dimethylbutane (b.p. 212.4° (737 mm.), n_D^{20} 1.4935, d_4^{20} 0.8704) observed here compare favorably with the physical constants listed by Francis[1] for the other $C_{12}H_{18}$ alkylbenzenes with similar branching. The above refractive index and density are higher than the n_D^{19} 1.4882 and d_4^{19} 0.860 reported by Tafel and Jurgens[3] for presumably the same hydrocarbon and recalculated by Francis as n_D^{20} 1.4878 and d_4^{20} 0.8592.

EXPERIMENTAL[10]

Ethyl isopropylidene malonate (I) was prepared in about 50% yield from acetone and malonic ester by the procedure of Cope and Hancock,[11] b.p. 110–111° (9 mm.), n_D^{20} 1.4490 to 1.4503.

Ethyl 4-phenyl-3,3-dimethyl-2-carbethoxybutanoate (II). To the Grignard reagent prepared from 26.75 g. (1.1 moles) of magnesium and 139.1 g. (1.1 moles) of benzyl chloride in 400 ml. of anhydrous ether was added over a period of 4 hr., a solution of 200 g. (1.0 mole) of ester I in 200 ml. of anhydrous ether. After standing overnight the reaction mixture was hydrolyzed by pouring onto chipped ice, acidified (Congo paper) with dilute sulfuric acid and stirred vigorously and the oil layer cleared. The oil was separated, the water extracted with ether, and the combined extracts were washed, dried, and the ether was distilled. Fractionation through a 1-ft. Fenske-type column packed with $^3/_{32}$ in. glass helices yielded the following: *Fractions 1–3,* 14.8, b.p. up to 103° (1 to 2 mm.); *Fractions 4–6,* 24 g., b.p. 104–107° (1 mm.), which solidified as it distilled (probably bibenzyl); *Fractions 7–8,* 18.4 g., 119 to 148° (1 mm.), n_D^{20} 1.4952–1.4935, ester II contaminated with a little bibenzyl; *Fractions 9–12,* 106.5 g., b.p. 148–153° (1 mm.), n_D^{20} 1.4908–1.4912, n_D^{25} 1.4887–1.4892; *Fractions 13–14,* 17.7 g., b.p. 148° falling to 131° (1 mm.), n_D^{25} 1.4880–1.4862. Fractions 7 through 14 weighed a total of 142.6 g., or a 49% yield of crude product. Fractions 9–12 are essentially pure ester II, which is reported[5] to have b.p. 185–186° (8 mm.), n_D^{25} 1.4890.

4-Phenyl-3,3-dimethylbutanoic acid (III). Saponification was achieved by refluxing ester II (206 g., 0.704 mole) for 3.5 hr. with 120 g. potassium hydroxide in 400 ml. ethylene glycol. The cold reaction mixture was poured into 1 l. of

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[6] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

[7] M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2108 (1950).

[8] F. C. Whitmore and H. Bernstein, *J. Am. Chem. Soc.*, **60**, 2626 (1938).

[9] H. Pines, W. D. Huntsman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **75**, 2311 (1953).

[10] All melting points and boiling points are uncorrected unless otherwise indicated. Analyses by Micro-Tech Laboratories, Skokie, Ill.

[11] A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **60**, 2644 (1938).

water, filtered (Celite) and neutral oils were removed by extraction with ether. After acidification, acidic materials were extracted into ether and the ether was stripped at the water pump. Decarboxylation of the malonic acid was brought about by heating under an air-cooled condenser to an internal temperature of 230°. A short-path distillation of the above oil, by placing a distilling head directly on a distilling flask, yielded the following at 2 mm.: *Fractions 1–2*, 12.3 g., b.p. up to 152°; *Fractions 3–4*, 78.2 g., b.p. 152–153°, n_D^{20} 1.5142–1.5143; *Fractions 5–6*, 11.5 g., b.p. 154–163°, n_D^{20} 1.5142–1.5140. Fractions 3 through 6 weighed 89.7 g., a yield of 66%. Other preparations gave yields of 49 and 72%. In a final preparation, the yield was low and the residue unusually large. This residue, about 75 g., possibly an ester of ethylene glycol, was saponified by refluxing with excess aqueous potassium hydroxide and worked up as described above. Distillation gave an additional 58 g. of acid, an amount sufficient to raise the yield to 89%.

Acid (III) has a reported[5] b.p. 181–182° (18 mm.), n_D^{25} 1.5140.

4-Phenyl-3,3-dimethyl-1-butanol (IV). In a 1-l. three necked flask equipped with a stirrer, condenser, dropping funnel, and necessary drying tubes there were placed 16.35 g. lithium aluminum hydride[6] (about a 20% excess) and 300 ml. anhydrous ether. To this was added 91.7 g. (0.478 mole) of acid (III) in 100 ml. absolute ether during 2 hr. The reaction mixture was refluxed for an additional 1.5 hr. and permitted to stand overnight. Decomposition of the complex was accomplished by the slow dropwise addition of (a) 10 ml. ethyl acetate and then (b) water (care!). When the hydrolysis was complete, the mixture was acidified. The ether layer was separated, washed with sodium carbonate solution, and dried over anhydrous potassium carbonate. The solvent was stripped at the water pump and the last traces of water were azeotroped off with benzene. Distillation through a 2 × 20 cm. column packed with $^3/_{16}$ in. glass helices gave the following fractions at approximately 1-mm. pressure: *Fraction 1*, 0.4 g., b.p. up to 103°; *Fraction 2*, 9.7 g., b.p. 103–108.5°, n_D^{25} 1.5150; *Fractions 3–6*, 55.4 g., b.p. 107–108°, n_D^{20} 1.5168, n_D^{25} 1.5150; *Fraction 7*, 2.7 g., b.p. 106–96°, n_D^{25} 1.5140. *Fraction 4*, selected as the analytical sample, had d_4^{20} 0.9713. d_4^{25} 0.9680. Fractions 2 through 7 weighed 67.8 g., a yield of 79.7%. The alcohol possesses the odor of roses. It reacts slowly with sodium.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.70; H, 10.24.

The *3,5-dinitrobenzoate*, prepared by heating the acid chloride and alcohol together directly and recrystallized from ethanol (charcoal), melted at 75.5–76.5 corr. The mixture m.p. with 3,5-dinitrobenzoyl chlcride was 55°.

Anal. Calcd. for $C_{19}H_{20}N_2O_6$: N, 7.52. Found: N, 7.59.

4-Bromo-1-phenyl-2,2-dimethylbutane (V). The above described alcohol (48.8 g., 0.274 mole) was placed in a 500-ml. three necked flask equipped with stirrer, thermometer, condenser and dropping funnel and supported in a Glas-Col mantle. The alcohol was heated to about 65° and redistilled phosphorus tribromide (74.3 g., 0.274 mole) was added rapidly dropwise. The temperature rose to and was maintained at 95° for 4 hr. by the application of external heat. The mixture was then heated at 120° for two additional hours, during which time it became orange colored. Excess phosphorus tribromide was hydrolyzed by pouring onto ice, and the product separated. The aqueous layer was extracted with benzene. Acidic materials were washed from the combined product and benzene phases with water, sodium carbonate solution, and salt water. After brief drying over anhydrous sodium sulfate, the benzene was stripped at the water aspirator and the product fractionated through the previously described column at about 1-mm. pressure. After a small forerun, there was collected a total of 57.1 g. (86.5% yield) of bromide, b.p. 103–106° (1–2 mm.), n_D^{25} 1.5275–1.5302. Purification of a part of the bromide was achieved by repeated shaking with fresh portions of cold concentrated sulfuric until the acid no longer became colored. After washing and drying, the purified bromide distilled constantly at 95–96° (*ca.* 1 mm.), n_D^{25} 1.5327, d_4^{20} 1.2110, d_4^{25} 1.2065.

Anal. Calcd. for $C_{12}H_{17}Br$: C, 59.76; H, 7.10; Br, 33.14. Found: C, 59.84; H, 7.21; Br, 33.06.

Conversion of V to IV. The Grignard reagent was made in the usual fashion in an 8-in. test tube from 2 g. of the bromide and 0.5 g. magnesium turnings. The test tube was cooled in an ice-salt bath and air (dried by a calcium chloride–sodium hydroxide–soda lime tube), was sucked through the ether solution and the latter permitted to stand overnight. After working up the reaction mixture in the usual way, the ether was evaporated to leave a thick oil. The latter formed a 3,5-dinitrobenzoate which melted at 75.5–76.5° after two recrystallizations (ethanol). The mixture m.p. with the previously prepared 3,5-dinitrobenzoate was 75.5–76.7°.

1-Phenyl-2,2-dimethylbutane (VI). (a) *From the bromide.* A suspension of 5 g. (0.13 mole) of lithium aluminum hydride in 50 ml. of dry purified tetrahydrofuran was prepared in a 500-ml. three necked flask equipped with a stirrer, condenser, thermometer, dropping funnel, and drying tubes. To this a solution of 50 g. (0.207 mole) of bromide (V) in 50-ml. tetrahydrofuran was added dropwise and the whole heated at 75° for 7 hr. Next morning the excess lithium aluminum hydride was destroyed by the dropwise addition of 15 ml. of ethyl acetate, followed by the dropwise addition of water. Finally excess water was added and the solution acidified (hydrochloric acid). The organic layer was separated and the water layer extracted with benzene. The combined organic layers were washed successively with water, 5% sodium carbonate solution and water, and then dried briefly with calcium chloride. The solvents were stripped at the water pump and the product was fractionated at 10 mm. A total of 22.2 g. (0.137 mole) of VI, b.p. 84–87°, n_D^{25} 1.4915 to 1.4935 was collected.

(b) *Via the tosylate.* To a solution of 29.7 g. (0.167 mole) of alcohol (IV) in 50-ml. dry pyridine was added, over a period of 1 hr. and with frequent cooling, a solution of 31.8 g. (0.167 mole) of tosyl chloride in dry pyridine. After standing overnight the reaction mixture was poured onto a mixture of ice and excess dilute sulfuric acid. The emulsion was extracted successively with benzene and the benzene layer dried over anhydrous sodium sulfate. The benzene was stripped at the water aspirator, and the residual oil evacuated at 1–2 mm. pressure at room temperature. This oil, possessing the odor of the initial alcohol, was added to a suspension of 6.7 g. of lithium aluminum hydride in 125 ml. anhydrous ether[12] and refluxed for 4 hr. The next morning excess lithium aluminum hydride was destroyed by the addition of ethyl acetate, and water and excess acid were added. The organic phase was separated and the water extracted with ether. After the ethereal solution was washed (sodium carbonate solution) and dried, the ether was removed and the residual oil fractionated through the 2 × 20 cm. column. The following fractions were collected at 10 mm.: *Fraction 1*, 0.6 g., b.p. 81–83°, n_D^{25} 1.4884; *Fraction 2*, 7.6 g., 83–84°, n_D^{25} 1.4912; *Fraction 3*, 0.4 g., 83° and less, n_D^{25} 1.4917. The *residue*, based on odor and refractive index, appeared to be largely unchanged alcohol (IV).

The purification of VI was carried out in the manner described by Berliner[2] for a similar hydrocarbon. A total of 53 g. of hydrocarbon was washed successively with four 25-ml. portions of ice-cold concentrated sulfuric acid, with water, and with sodium carbonate solution and was dried over anhydrous calcium chloride. A small amount of added benzene was distilled to remove any traces of water. The hydrocarbon was then distilled from 1 g. sodium metal through the 2 × 20 cm. Fenske-type column, giving the following at

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(12) H. Rapoport and R. M. Bonner, *J. Am. Chem. Soc.*, **73**, 2872 (1951).

10 mm.: *Fraction 1*, 7.2 g., b.p. 85-86°, n_D^{20} 1.4933, n_D^{25} 1.4912; *Fractions 2–4*, 23.3 g., b.p. 85.3–86°, n_D^{20} 1.4935, n_D^{25} 1.4912; *Fraction 5*, 8.6 g., n_D^{20} 1.4938, n_D^{25} 1.4916; *Fraction 6*, 6.1 g., n_D^{20} 1.4940, n_D^{25} 1.4920. *Fraction 3*, taken as the pure hydrocarbon, had micro b.p. 213.5° (745 mm.) corr. and d_4^{20} 0.8694, d_4^{25} 0.8658.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.01; H, 11.38.

The diacetamino derivative (from ethanol) had a m.p. 231.5–232.5° corr.

Anal. Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75; N, 10.14. Found: C, 69.44; H, 8.83; N, 10.42.

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