Ethyl DL-β-Bromo-α-ketobutyrate (II).—α-Bromo-*n*-butyric acid was prepared in 80% yield in the manner given for α-bromoisocaproic acid.[12] Hydrolysis to α-hydroxy-*n*-butyric acid using potassium carbonate[13] and esterification with absolute alcohol and anhydrous copper sulfate[14] gave ethyl α-hydroxy-*n*-butyrate, b.p. 88–89° (51 mm.), $n^{29}\text{D}$ 1.414.[15]

To a solution of 4.63 g. (0.035 mole) of the hydroxy ester in 100 ml. of C.P. carbon tetrachloride there was added 12.59 g. (0.070 mole) of N-bromosuccinimide. The mixture was refluxed for five hours and treated as described for I to yield 4.86 g. (66%) of II, b.p. 79–81° (9 mm.), reported[4] 80–81° (12 mm.), $n^{20}\text{D}$ 1.462, d^{20}_{20} 1.455; *MR*D calcd. 39.3, found 39.5.

Ethyl DL-β-Bromophenylpyruvate (III).—Ethyl DL-α-hydroxyhydrocinnamate was prepared by the action of silver nitrite on phenylalanine[16] followed by esterification. The hydroxy ester showed b.p. 108.0–110.5° (4 mm.),[17] $n^{20}\text{D}$ 1.507, d^{20}_{20} 1.099; *MR*D calcd. 52.6, found 52.6.

A solution of 7.76 g. (0.040 mole) of the hydroxy ester in 100 ml. of C.P. carbon tetrachloride was treated with 13.68 g. (0.077 mole) of N-bromosuccinimide in the manner described above to give 7.70 g. (71%) of III, b.p. 137–139° (4 mm.), $n^{20}\text{D}$ 1.543, d^{20}_{20} 1.408; *MR*D calcd. 58.8, found 59.9.

Ethyl Phenylglyoxylate (IV).—The reaction of 10.81 g. (0.060 mole) of ethyl mandelate from the esterification of mandelic acid, with 10.68 g. (0.060 mole) of N-bromosuccinimide in 100 ml. of C.P. carbon tetrachloride refluxing for eight hours gave 8.39 g. (78.5%) of IV, b.p. 101.5–102.0° (3.5 mm.); reported[6] 118° (5 mm.), $n^{28.5}_{\text{D}}$ 1.513. The behavior of the 2,4-dinitrophenylhydrazone on heating was the same as that described by Brewer and Herbst.[18]

A portion of the keto ester was saponified according to the procedure of Baer and Kates[9] for methyl phenylglyoxylate; the crude oily phenylglyoxylic acid was not distilled but was recrystallized directly twice from carbon tetrachloride; on heating it moistened at 61° and melted at 65–66°, reported[9] m.p. 64.5–65.5°; neutral equivalent found 150.5, calcd. 150.1.

Phenacyl Bromide (V).—A solution of 9.15 g. (0.075 mole) of DL-phenylmethylcarbinol in 250 ml. of C.P. carbon tetrachloride was treated with 26.70 g. (0.150 mole) of N-bromosuccinimide. The mixture was refluxed and shortly acquired a deep red color. After 30 minutes the color changed rapidly (characteristic of the reaction of N-bromosuccinimide with secondary hydroxyl groups) to a mixture of an orange solid and pale yellow solution; much hydrogen bromide was evolved. Upon refluxing for five hours the mixture was cooled and filtered to yield 14.90 g. (*ca.* 100%) of crude succinimide, and the filtrate was dried over anhydrous sodium sulfate. Evaporation of the solvent gave a yellow-brown oil which was distilled (in one smaller scale run this oil crystallized in the refrigerator); the product was collected at 93–98° (3 mm.) and allowed to crystallize overnight in the refrigerator. The crystals were collected on a filter, washed several times with cold petroleum ether and dried on filter paper; 6.60 g. (44.2%), m.p. 45–48°[19]; a mixed melting point with a known sample of phenacyl bromide showed no depression.

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[12] N. L. Drake (Editor), *Org. Syntheses*, **21**, 74 (1941).

[13] C. A. Bischoff and P. Walden, *Ann.*, **279**, 102 (1894).

[14] Esterifications of α-hydroxy acids were carried out using the method described by E. Clemmensen and A. H. C. Heitman, *Am. Chem. J.*, **42**, 331 (1909).

[15] H. R. Henze and W. B. Leslie, *J. Org. Chem.*, **15**, 903 (1950); b.p. 74.5° (25 mm.) and $n^{20}\text{D}$ 1.4179.

[16] According to a procedure from L. E. McClure, this Laboratory, and S. Thomas, University of California at Los Angeles; see also C. G. Baker and A. Meister, THIS JOURNAL, **73**, 1336 (1951).

[17] E. H. Charlesworth, J. A. McRae and H. M. MacFarlane, *Can. J. Research*, **21B**, 37 (1943); *C. A.*, **37**, 4057 (1943); b.p. 148–150° (15 mm.).

[18] S. D. Brewer and R. M. Herbst, *J. Org. Chem.*, **6**, 867 (1941); *C. A.*, **36**, 757 (1942).

[19] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. *II*, p. 480; m.p. 45–48°.

Reaction of Isopropylmagnesium Bromide with Alkyl Aryl Ketone

BY B. F. LANDRUM AND CHAS. T. LESTER

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This communication is an extension of our studies on the reactions of seventeen alkyl *p*-alkylphenyl ketones.[1,2] We have allowed each ketone to react with the Grignard reagent, prepared from isopropylmagnesium bromide, under as nearly identical conditions as possible. The results of these reactions are recorded in Table I. As has been observed in other studies the isopropylmagnesium bromide shows a pronounced tendency to produce an enolization-type reaction with these ketones.[3]

Experimental

The Reaction Procedure.—The reactions herein reported were done as nearly exactly like those using ethylmagnesium bromide[2] as possible. This includes the preparation of the Grignard reagent, the choice of concentration of each reactant, the temperature of the reaction, the time of the reaction, the collection and analysis of gas evolved,[4] the decomposition of the complex formed, and the distillation of the liquid products. Certain variations in handling the liquid products after distillation were used.

TABLE I

ALKYL 4-R-PHENYL KETONES AND ISOPROPYLMAGNESIUM BROMIDE

4-R	E[a]	R[b]	A[c]	Liquid recovery, %[d]	Analyses of alcohols Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
	$4\text{-R-C}_6\text{H}_4\text{COCH}_3$							
H	24	2	74	97	80.49[e]	80.66[e]	9.76[e]	9.54
Me	29	7	64	80	80.90	80.76	10.11	9.96
Et	34	7	59	90	81.25	81.26	10.42	10.25
i-Prop	31	7	62	88	81.55	81.00	10.68	10.29
t-Bu	34	9	57	92	81.81	81.29	10.91	10.43
	$4\text{-R-C}_6\text{H}_4\text{COC}_2\text{H}_5$							
H	5	6	89	96	80.90[e]	80.61[e]	10.11[e]	9.88[e]
Me	7	7	86	82	81.25	81.01	10.42	10.12
Et	7	10	83	82	81.55	81.84	10.68	10.50
i-Prop	8	10	82	85	81.81	82.13	10.91	10.60
t-Bu	7	11	82	93	82.05	81.78	11.11	10.76
	$4\text{-R-C}_6\text{H}_4\text{COCH(CH}_3)_2$							
H	3	29	68	98	80.00[f]	80.26[f]	9.33[f]	9.00[f]
					81.25	80.81	10.42	10.00
Me	5	35	60	88	80.49	80.88	9.76	10.01
					81.55	81.80	10.68	11.01
Et	5	35	60	85	80.90	80.64	10.11	10.51
					81.81	82.21	10.91	11.13
i-Prop	5	37	58	85	81.25	80.96	10.42	10.72
					82.05	81.62	11.11	11.49
t-Bu	3	38	59	83	81.55	81.15	10.68	10.29
					82.26	81.68	11.29	11.08
	$4\text{-R-C}_6\text{H}_4\text{-COC(CH}_3)_3$							
H	0	97	3?	88	80.49[g]	80.18[g]	9.76[g]	9.98[g]
Me	0	98	2?	86	80.90	80.47	10.11	9.93

[a] Enolization, %. [b] Reduction, %. [c] Addition calcd. by difference, %. [d] Assuming correctness of gas analysis, this represents grams obtained/grams predicted × 100. [e] All figures in this column are analyses of tertiary alcohols. [f] The first figure in each pair refers to the analysis of the secondary alcohol; the second figure to the analysis of the tertiary alcohol. [g] All figures in this column are analyses of secondary alcohols.

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[1] M. J. Craft, B. F. Landrum, E. C. Suratt and C. T. Lester, THIS JOURNAL, **73**, 4462 (1951).

[2] B. F. Landrum and C. T. Lester, *ibid.*, **74**, 4954 (1952).

[3] V. Grignard and J. Savard, *Compt. rend.*, **179**, 1573 (1924); F. C. Whitmore and R. S. George, THIS JOURNAL, **64**, 1239 (1942).

[4] Spot checks indicate a reproducibility of ±100 ml. (±2%) in the gas analyses.

The Products from the Methyl Ketone.—The fractionation of the products was sufficient to isolate the tertiary alcohols from the other products. The analyses of the tertiary alcohols are given in the table. Weighed amounts of the lower boiling fractions in each case were treated with excess semicarbazide hydrochloride in pyridine for 48 hours. After dissolution in ether they were extracted with dilute hydrochloric acid until free of pyridine, washed with water and steam distilled to remove ether and secondary alcohol. The crude residual semicarbazones were filtered, dried and weighed. The weight of product checked within 5–10% of that predicted by the gas analysis.[5] No effort was made to isolate the secondary alcohol. In one case the lower boiling fractions were combined and the amount of ketone determined by measuring the amount of oxime produced.[6] The percentage ketone agreed within 5% of that predicted by the gas analysis.[5]

The Products from the Ethyl Ketones.—The ketones and secondary alcohols were easily separable by distillation from the tertiary alcohols. The analyses of the latter are in Table I. Qualitative tests showed the presence of both ketones and alcohols in the lower boiling fractions, but no effort at quantitative determinations was made.

The Products from the Isopropyl Ketones.—The products were distilled and divided into 3 major portions based on b.p. and refractive index. The intermediate fractions having a constant index of refraction and boiling point were taken as secondary alcohols. Their analyses are in the table. The highest boiling fractions having constant b.p. and refractive index were taken as tertiary alcohol and their analyses are also recorded. No attempt was made to establish the quantity of ketones produced.

The Products from the *t*-Butyl Ketones.—Although the gas analyses indicated a small amount of addition, only one product, having from first to last fraction an almost constant refractive index and b.p., could be found in each case. The amount of tarry residue was not noticeably greater than in the case of the other compounds. The analyses of these two secondary alcohols are recorded.

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(5) Computed on the basis that % ketone + % sec. alcohol = 100%, *e.g.*, the gas analysis indicate sthat in the case of acetophenone the lower fractions would be 92% ketone and 8% sec. alcohol.

(6) E. C. Suratt, J. R. Proffitt, Jr., and C. T. Lester, THIS JOURNAL, **72**, 1561 (1950).

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Some Long-chained Organosilicon Compounds

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As a result of the report of Kharasch and coworkers[1] of the addition of polyhalomethanes to olefins with terminal double bonds and the subsequent publications of several authors[2] of similar reactions of trichlorosilane, it was of interest to investigate the manner in which triphenylsilane, as an analog to triphenylmethane, reacts with olefins.

In the course of a current investigation of the preparation and properties of some long-chained organosilicon compounds, these compounds were synthesized employing the method used by Gadsby[3] for the synthesis of carboxyalkylsilanes. Triphenylsilane was found to add to the olefinic linkage in the presence of benzoyl peroxide to give fair yields of alkyltriphenylsilanes.

$$(C_6H_5)_3SiH + CH_2{=}CH(CH_2)_nCH_3 \xrightarrow{Bz_2O_2} (C_6H_5)_3SiCH_2(CH_2)_{n+1}CH_3$$

The authentic samples of these silanes were prepared by a more conventional method, the reaction of the corresponding organolithium compound with triphenylchlorosilane. The long-chained organolithium compounds were prepared from the corresponding bromides. The *n*-heptadecyl bromide was prepared in 84% yield by means of the silver salt reaction (Hunsdiecker reaction). It was found possible to improve the previously reported yield[4] by taking extreme care in the purification of the silver salt and by scrupulously excluding moisture from the reaction flask. This *n*-heptadecyl bromide was also used in a comparison of the yields of the corresponding organolithium and Grignard compounds. The yield of the Grignard reagent was somewhat lower than that of the corresponding organolithium compound. Since it was expected that the reactivities of the Grignard reagents would be lower than those of the organolithium compounds, only the latter were used for the reaction with triphenylchlorosilane.

Table II records the melting points observed for the *n*-alkyltriphenylsilanes as well as their mixed melting points. It is of particular interest to note that the melting points appear to increase monotonically with additional methylene groups and no al-

TABLE I

n-ALKYLTRIPHENYLSILANES

Triphenyl-silanes	Silicon, %[a] Calcd.	Silicon, %[a] Found	Yield, %[b] Method A	Yield, %[b] Method B	Organo-lithium cmpd. yield, %[c]
n-Dodecyl	6.5	6.5, 6.5	46	67	45
n-Tetradecyl	6.1	6.1, 6.1	52	50	70
n-Hexadecyl	5.8	5.6, 5.6	45	30	60
n-Heptadecyl	5.6	5.4, 5.3		43	75
n-Octadecyl	5.5	5.5, 5.6	40	70	48

[a] Silicon was determined as silica by the method of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, 72, 5767 (1950). [b] Method A represents the peroxide initiated reaction; method B, the reaction of triphenylchlorosilane with the corresponding *n*-alkyllithium compound. [c] The yield of the alkyllithium compound was determined by the "double titration" described by H. Gilman and A. H. Haubein, *ibid.*, 66, 1515 (1944).

TABLE II

MELTING POINTS OF *n*-ALKYLTRIPHENYLSILANES AND THEIR MIXTURES

Triphenylsilanes	M.p.,[a] °C.	Mixed m.p. with deriv. immediately following in table, °C.
n-Dodecyl	64–65	56–58
n-Tetradecyl	66–67	61–64
n-Hexadecyl	68.5–69	67–69.5
n-Heptadecyl	71–71.5	69.5–71.5
n-Octadecyl	72–73	
n-Dodecyl		56–59
n-Hexadecyl		61.5–69
n-Octadecyl		

[a] All melting points are uncorrected.

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(1) M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945); M. S. Kharasch, W. H. Urry and E. V. Jensen, THIS JOURNAL, **67**, 1626 (1945); M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947).

(2) C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2887 (1947); A. J. Barry, L. DePree, J. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947); L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **69**, 188 (1947); **70**, 484 (1948); R. Calas and E. Frainnet, *Bull. soc. chim. France*, 241 (1952); N. Duffant and R. Calas, *ibid.*, 241 (1952); E. Frainnet, *ibid.*, 792 (1953); R. Calas, E. Frainnet and J. Valade, *ibid.*, 792 (1953).

(3) G. N. Gadsby, *Research* (*London*), **3**, 338 (1950).

(4) J. W. H. Oldham, *J. Chem. Soc.*, 100 (1950).