was refluxed for 2 hr. The manganese dioxide precipitate was removed by filtration from the boiling solution. Acidification of the hot filtrate with 10% sulfuric acid resulted in the crystallization of 2-methoxy-3,5-dibromobenzoic acid, mp 193–194° (lit.[7] 193–194°). These crystals were filtered off as soon as they formed. Upon concentration of the solution a second product, 2-hydroxybenzoic acid, with mp 157–159° (confirmed by an undepressed mixture melting point with authentic material) precipitated.

3-(2-Acetoxyphenyl)coumarin.—One-half gram of III and 0.3 g of anhydrous sodium acetate were refluxed with 10 ml of acetic anhydride for 2 hr. Upon addition of 30 ml of ice–water the acetate crystallized. The material was filtered off and yielded colorless needles upon recrystallization from ethanol, yield 0.25 g, mp 139–140° (lit.[3] mp 137–138°).

Anal. Calcd for $C_{17}H_{12}O_4$: C, 72.9; H, 4.32. Found: C, 73.0; H, 4.47.

Light-Induced Synthesis of 3-(2-Hydroxyphenyl)coumarins.—A stirred $1 \times 10^{-4}\ M$ solution at 47 ± 0.05° was irradiated for 2–4 hr with a 75-w G.E. tungsten lamp (FG 1096 AX) placed into a water-cooled quartz immersion well (Hanovia Lamp Division, 19434, C.F. Quartz, Engelhardt Industries). At timed intervals a sample was taken and its absorption spectrum was scanned in the 220- to 400-mμ range. The final curve was superimposable with the ultraviolet spectrum of a $1 \times 10^{-4}\ M$ solution of authentic III.

Base-Catalyzed Cyclization of 3-(2-Hydroxybenzylidene)-2(3H)-coumaranones.—Two-tenths of a gram of II was heated to 80° in 2 ml of triethylamine (or pyridine). Within a few minutes the color of the solution turned from deep red to yellow. After 1 hr the solvent was evaporated and the residue was recrystallized from ethanol. The δ-lactones III were isolated in almost quantitative yields, and their identity was established by undepressed mixture melting points and by comparison of their infrared spectra with those of authentic material.

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Sterically Hindered Group IVa Organometallics. VI.[1] Preparation and Some Properties of Neophyltins and Related Compounds

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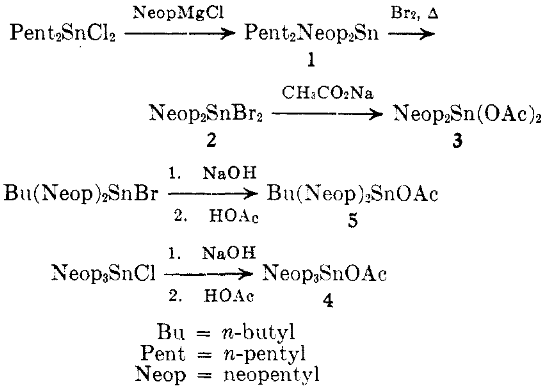
Received May 12, 1966

In the course of our investigations into sterically hindered group IV-A organometallics, we prepared several previously unreported organotin compounds containing the 2,2-dimethyl-2-phenylethyl (neophyl), the 2-phenylpropyl, the 3-phenylpropyl, and the 2,2,4-trimethylpentyl groups. In addition several more as yet unreported neopentyltins were prepared.[3] The typical reactions associated with this bulky group were again observed. The formation of the tetrasubstituted compounds proceeded rather sluggishly only with groups having a "neo" structure, though it occurred faster with these substituted "neo" structures than with the parent neopentyl group. On the other hand, no significant decrease in the tendency of the formation of tetrakis(2-phenylpropyl)tin and tetrakis(3-phenylpropyl)tin was observed. These findings seem to permit the conclusion to be drawn that the formation of symmetrically tetrasubstituted organotins is most difficult if an aliphatic neopentyl type group is involved. That not only size and thus steric effects play a role was demonstrated by the fact that tetraneophyltin was formed in a higher yield than was the case with any of the other "neo" structures. Only one bulky group either at the β or γ position of the alkyl chain does not effectively interfere with the formation of the corresponding tetrasubstituted organotin compound. Also, only those tetrasubstituted organotins which have a "neo" structure react sluggishly with bromine and do not undergo the Kozechkov reaction. Among the organotins containing a "neo" group the tetraneophyltin was more reactive than its aliphatic analogs, again pointing to the fact that steric hindrance is not solely responsible for the chemical behavior of this type of compound. Noteworthy also is the failure to obtain tris(2,2,4-trimethylpentyl)tin bromide by treating tetrakis(2,2,4-trimethylpentyl)tin with bromine. Instead of undergoing the expected Sn–C bond cleavage reaction considerable amounts of HBr were generated. When preparing this manuscript an article by Reichle appeared in which several neophyltins were reported.[4] Specifically compounds **7**, **12**, and **18** (see Table I) were described also by this author. There are, however, two noteworthy differences in the results: one, while we found 12 to be formed in a 27% yield, Reichle reported a yield of 8.8%; two, we definitely characterized compound 14 as bis(trineophyltin) oxide by virtue of a C–H analysis and lack of an OH absorption peak in the 3600–3000-cm area of the infrared spectrum.

The position of the neopentyl group in the cleavage series of Bullard[5] was found to be below the *n*-pentyl group. Di-*n*-pentyldineopentyltin was cleaved by bromine to yield dineopentyltin bromide. In Scheme I are listed the reactions involving organotin substituted by the neopentyl group.

SCHEME I



$$\mathrm{Pent_2SnCl_2} \xrightarrow{\mathrm{NeopMgCl}} \underset{\mathbf{1}}{\mathrm{Pent_2Neop_2Sn}} \xrightarrow{\mathrm{Br_2},\ \Delta}$$

$$\underset{\mathbf{2}}{\mathrm{Neop_2SnBr_2}} \xrightarrow{\mathrm{CH_3CO_2Na}} \underset{\mathbf{3}}{\mathrm{Neop_2Sn(OAc)_2}}$$

$$\mathrm{Bu(Neop)_2SnBr} \xrightarrow[\text{2. HOAc}]{\text{1. NaOH}} \underset{\mathbf{5}}{\mathrm{Bu(Neop)_2SnOAc}}$$

$$\mathrm{Neop_3SnCl} \xrightarrow[\text{2. HOAc}]{\text{1. NaOH}} \underset{\mathbf{4}}{\mathrm{Neop_3SnOAc}}$$

Bu = *n*-butyl
Pent = *n*-pentyl
Neop = neopentyl

In Scheme II the reactions involving the neophyl and the 3-phenylpropyl groups are summarized. Table I contains a summary of all new compounds prepared together with their analyses and some pertinent physical constants.

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[1] Part V of this series: H. Zimmer and O. A. Homberg, *J. Org. Chem.*, **30**, 947 (1966).

[2] Part of Ph.D. Thesis, University of Cincinnati, 1965.

[3] H. Zimmer, I. Hechenbleikner, O. A. Homberg, and M. Danzik, *J. Org. Chem.*, **29**, 2632 (1964).

[4] W. T. Reichle, *Inorg. Chem.*, **5**, 87 (1966).

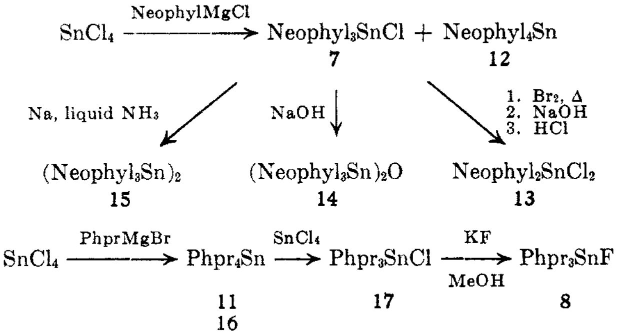
[5] R. H. Bullard, *J. Am. Chem. Soc.*, **51**, 3065 (1929).

TABLE I

No.	Compd[a]	Mp, °C	Bp, °C (mm)	d_t	$n^{25}D$	Formula	Mol wt	Calcd, % C	Calcd, % H	Calcd, % Halogen	Found, % C	Found, % H	Found, % Halogen
1	Pent$_2$Neop$_2$Sn	...	135 (1.6)	1.0118 (27)	1.4742	$C_{20}H_{44}Sn$	403.25	59.58	11.00	...	59.45	10.74	...
10	Oct$_4$Sn	...	183 (1.0)	0.9792 (27)	1.4798	$C_{32}H_{68}Sn$	571.56	67.24	11.99	...	66.65	11.61	...
12	Neophyl$_4$Sn[b]	96–97	...	...	...	$C_{40}H_{52}Sn$	651.52	73.74	8.04	...	73.64	7.95	...
16	2-Phpr$_4$Sn	...	290 (3)	...	...	$C_{36}H_{44}Sn$	595.41	72.61	7.45	...	72.43	7.31	...
11	3-Phpr$_4$Sn												
4	Neop$_3$SnOAc	...	104 (0.1)	...	1.4747	$C_{17}H_{36}O_2Sn$	391.16	52.20	9.28	...	52.59	9.63	...
5	BuNeop$_2$SnOAc	44.5–45.5	...	...	...	$C_{16}H_{34}O_2Sn$	377.13	50.95	9.09	...	50.94	8.96	...
7	Neophyl$_3$SnCl[c]	116.5–117.5	...	...	...	$C_{30}H_{39}ClSn$	553.77	65.06	7.10	6.40	64.65	7.14	6.42
18	Neophyl$_3$SnF[d]	98.5–99.5	...	...	...	$C_{30}H_{39}FSn$	537.31	67.01	7.32	3.54	66.90	7.14	3.39
8	3-Phpr$_3$SnF	209–211[e]	...	...	...	$C_{27}H_{33}FSn$	495.23	65.46	6.75	3.84	65.47	6.60	3.67
17	3-Phpr$_3$SnCl	61–61.5	...	...	...	$C_{27}H_{33}ClSn$	511.37	63.37	6.50	...	63.12	6.46	...
3	Neop$_2$Sn(OAc)$_2$	66–67	...	...	...	$C_{14}H_{28}O_4Sn$	379.06	44.36	7.44	...	44.34	7.67	...
13	Neophyl$_2$SnCl$_2$	50.5–51.5	...	...	...	$C_{20}H_{26}Cl_2Sn$	456.02	52.68	5.75	15.55	52.63	5.35	15.53
14	(Neophyl$_3$Sn)$_2$O	143–144	...	...	...	$C_{60}H_{78}OSn$	1052.62	68.46	7.47	...	68.80	7.56	...
15	(Neophyl$_3$Sn)$_2$	153.5–154	...	...	...	$C_{60}H_{78}Sn$	1036.62	69.52	7.58	...	69.21	7.64	...
9a	OctCl	...	68 (40)	...	1.4284	$C_8H_{17}Cl$	148.68	64.62	11.53	23.85	64.80	11.37	23.95
9b	OctBr	...	84.5 (40)	...	1.4510	$C_8H_{17}Br$	193.14	49.76	8.88	41.38	49.88	8.42	41.53

[a] Bu = *n*-butyl; Neop = neopentyl; Pent = *n*-pentyl; 2-Phpr = 2-phenylpropyl; Oct = 2,2,4-trimethylpentyl; 3-Phpr = 3-phenylpropyl; Neophyl = 2,2-dimethyl-2-phenylethyl. [b] Lit.[4] mp 90–91.5°. [c] Lit.[4] mp 117.5–118.5°. [d] Lit.[4] mp 98–100°. [e] Sintering starts at ~185°.

SCHEME II



Neophyl = 2,2-dimethyl-2-phenylethyl
Phpr = 3-phenylpropyl (**8**, **11**), 2-phenylpropyl (**16**)

TABLE II

PMR SPECTRA OF NEOPENTYLTINS

Compd	Group	δ	$J^{119}{}_{SnH}/J^{117}{}_{SnH}$	$J^{13}{}_{CH}$
Neop$_4$Sn	CH_3	−62.2	107.9/105.8	124.4
	CH_2	−71.8	49.2/46.2	...
(Neop$_3$Sn)$_2$[a]	CH_3	−62.2	115.0/112.5	123.6
	CH_2	−81.0	40.4[b]	
(Neop$_3$Sn)$_2$O	CH_3	−62.4	70.9/67.9	124.8
	CH_2	−71.6	56.0/52.4	...
Neop$_3$SnOOCCH$_3$	CH_3 (Neop)	−63.3	69.7/65.8	124.5
	CH_2	−87.8	*c*	...
	CH_3 (acetate)	−113.4	*c*	...
Neop$_3$SnCl	CH_3	−66.0	*d*	*d*
	CH_2	−86.8	*d*	
Neop$_2$SnCl$_2$	CH_3	−68.0	69.4[e]	124.5
	CH_2	−116.2	55.1[b]	

[a] The $J_{^{119,117}SnSnCH_2}$ of (Neop$_3$Sn)$_2$ observed as 14.2. [b] Half of satellite peaks obscured by main peak. [c] Satellite peak obscured by main peak. [d] Satellite peak immersed in background noise. [e] Satellite peak not resolved.

TABLE III[a]

PMR SPECTRA OF NEOPHYLTINS

Compd	Group	δ	$J^{119}{}_{SnH}/J^{117}{}_{SnH}$	$J^{13}{}_{CH}$
Neophyl$_4$Sn (in CCl$_4$)	CH_3	−66.3	91.2/85.7	128.4
	CH_2	−43.6	81.6/77.1	...
	C_6H_5	−437.9	...	...
Neophyl$_4$Sn (in CDCl$_3$)	CH_3	−68.4	101.1/98.1	124.2
	CH_2	−47.5	98.6[e]	...
	C_6H_5	−427.0	...	...
(Neophyl$_3$Sn)$_2$	CH_3	−76.2	75.5/78.5	125.3
	CH_2	−63.5	52.0[e]	...
	C_6H_5	−430.9		...
(Neophyl$_3$Sn)$_2$O	CH_3	−77.2	87.1[e]	125.3
	CH_2	−63.9	53.2/51.5	...
	C_6H_5	−431.6	...	...
Neophyl$_3$SnCl	CH_3	−71.6	74.6/73.1	125.5
	CH_2	−68.2	48.9/46.9	...
	C_6H_5	−430.1	...	...
Neophyl$_2$SnCl$_2$	CH_3	−82.1	96.4[e]	125.5
	CH_2	−110.0	57.3[b]	...
	C_6H_5	−435.3		...

[a] See corresponding footnotes in Table II.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra were recorded at 42° on a Varian A-60 spectrometer. Peak positions were determined by bracketing peaks with audio side bands generated by a Hewlett-Packard 521 D electronic counter. Proton resonance peaks were compared to an internal tetramethylsilane reference. The neopentyltin compounds were run in carbon tetrachloride solution, while the neophyltins, except as noted, were investigated in deuteriochloroform solution.

The compounds yielded the expected A_9B_2X and $A_2B_2CM_6N_2X$ patterns for the neopentyl and neophyl compounds, respectively. The peak areas were in the ratio of 9:2 for the neopentyl compounds and 5:6:2 for the neophyl compounds, the various phenyl protons (A, B, and C) not being resolved.

Tabulated in Tables II and III are the observed chemical shifts and spin–spin coupling constants, both reported in cycles per second, of the various protons in the molecules studied. The most striking result of the study is the large methyl proton to tin coupling as compared to the methylene proton to tin coupling. Previous investigations have shown that large long-range coupling between a proton and tin through three bonds;[6] however, in this instance the methyl protons are separated from the tin by four bonds.

It is also of interest to note that increasing substitution in tetraneopentyltin has little effect on the chemical shift of the methyl protons, whereas the methylene proton resonance migrates to a lower field with increasing substitution. In the neophyltins the various protons all appear to shift to lower fields with increasing electronegative substitution. The methylene proton

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(6) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961).

resonance, however, ranges over a far greater region than the others. In tetraneophyltin the methylene proton resonance is observed at a higher field than that of the methyl protons, the reverse of that observed in the neopentyltins. However, with progressive substitution of the neophyl groups the $\delta_{CH_2CH_3}$ becomes smaller, and in the dineophyltin dichloride spectrum the methylene proton resonance appears at a lower field strength than that of the methyl protons.

The $J_{^{13}CH_3}$ values are of the expected order of magnitude and appear to be little affected by substitution.

Experimental Section

All melting points are uncorrected. Analyses were done by A. Bernhardt, Microanalytical Laboratories, Mülheim (Ruhr), Germany.

Di-*n*-pentyldineopentyltin (**1**).—A Grignard solution prepared from 53.3 g (0.5 mole) of neopentyl chloride and 12.1 g (0.5 g-atom) of magnesium in 100 ml of ether was treated with 66.4 g (0.2 mole) of di-*n*-pentyltin dichloride in the previously described manner[3] to give 62.8 g (78%) of **1**.

Dineopentyltin Dibromide (**2**).—A mixture of 30.1 g (0.075 mole) of **1** and 24.0 g (0.15 mole) of bromine in 100 ml of refluxing carbon tetrachloride gave 28.4 g (90%) of **2**, bp 86.7° (0.1 mm), $n^{25}D$ 1.5292 [lit.[3] bp 87° (0.1 mm), $n^{25}D$ 1.5290].

Dineopentyltin Diacetate (**3**).—A solution of 10.5 g (0.025 mole) of **2** in 25 ml of ether was shaken twice with 20 ml of 10% sodium hydroxide solution. The resulting ethereal solution was then treated with 6 ml (0.1 mole) of acetic acid and washed well with water. After drying over calcium sulfate the solvent was removed under reduced pressure and the residue was crystallized from ethanol to yield 8.0 g (84%) of **3**.

Trineopentyltin Acetate (**4**).—A solution of 25.0 g (0.068 mole) of trineopentyltin chloride[3] in 25 ml of benzene and a solution of 21.0 g (0.15 mole) of sodium acetate trihydrate in 25 ml of water were mixed and heated under reflux for 1 hr. After cooling to room temperature the organic layer was separated, washed once with water, and dried over calcium sulfate. The benzene was removed under reduced pressure and the residue was distilled to yield 12.5 g (47%) of **4**.

***n*-Butyldineopentyltin Acetate** (**5**).—A solution of 14.5 g (0.039 mole) of dibutyldineopentyltin[3] in 50 ml of ether was was treated at −10° with 6.2 g (0.039 mole) of bromine. The resulting solution was warmed slowly to room temperature and treated with 15 ml of 10% sodium hydroxide solution and 4.6 g (0.08 mole) of acetic acid as described above to give 6.8 g (46%) of **5**.

1-Chloro-2,2,4-trimethylpentane (**9a**).—Over a 2-hr period a mixture of 505 g (2.5 moles) of tributylphosphine and 226 g (2.0 moles) of 2,2,4-trimethylpentanol-1 was treated with 176 g (2.5 moles) of chlorine, at such a rate that the temperature did not rise above 50°. The reaction mixture was then stripped to 190° (10 mm), and the distillate was washed well with water, dried over calcium chloride, and distilled to yield 213 g (72%) of **9a**.

2-Bromo-2,2,4-trimethylpentane (**9b**).—Tributylphosphine, 2,2,4-trimethylpentanol-1 and bromine were treated as described above for the chloride to give an 80% yield of **9b**.

Tetrakis(2,2,4-trimethylpentyl)tin (**10**).—A Grignard solution was prepared from 149 g (1.0 mole) of **9a** and 24.3 g (1.0 g-atom) of magnesium in 600 ml of ether and treated with 65.3 g (0.25 mole) of stannic chloride in 600 ml of benzene. After work-up of the reaction mixture in the usual manner and removal of the solvent, the residue (86 g) was found to contain approximately 6% distannane. The residue was taken up in ether, treated with 1.0 g of bromine to decompose the ditin, and then subjected to a slow stream of anhydrous ammonia until the amine complex no longer precipitated. The resulting suspension was filtered, the solvent was removed under reduced pressure, and the residue was distilled to yield 33.0 g (23%) of **10**.

Trineophyltin Chloride (**7**).—A Grignard solution, prepared from 84.3 g (0.5 mole) of neophyl chloride[7] and 12.1 g (0.5 g-atom) of magnesium in 100 ml of ether, was treated with 26.1 g (0.1 mole) of stannic chloride in 100 ml of benzene. The reaction mixture was decomposed in the usual manner and the solvent was removed under reduced pressure to yield 59 g of residue. Several recrystallizations of the residue gave 26.5 g (48%) of **7**.

Tri(neophyl)tin Fluoride (**18**).—To a refluxing solution of 5 g (0.009 mole) of $[C_6H_5C(CH_3)_2CH_2]_3SnCl$ in 150 ml of methanol was added a solution of 1.3 g (0.014 mole) of $KF \cdot 2H_2O$ in 50 ml of methanol. After 30 min of additional reflux, the product was obtained by removal of methanol and washing with water. It was recrystallized from methanol to give 4.2 g (86.6%) of **18**, mp 98.5–99.5°.

Tetraneophyltin (**12**).—The ligroin filtrates from the preparation of **7** were evaporated to dryness, taken up in ether, treated with anhydrous ammonia until the precipitation of the amine complex was complete, and filtered, and the ether was removed under reduced pressure. The residue was crystallized from methanol to yield 17.0 g (27%) of **12**.

Dineophyltin Dichloride (**13**).—A mixture of 11.1 g (0.02 mole) of **12** and 3.5 g (0.022 mole) of bromine in 50 ml of carbontetrachloride was heated under reflux for 4.5 hr, cooled, diluted with 150 ml of ether, and treated successively with dilute sodium bisulfite solution, two 10-ml portions of 10% sodium hydroxide solution, two 50-ml portions of distilled water, two 10-ml portion of 10% hydrochloric acid, and again with 50 ml of water. After drying the resulting solution with calcium chloride, the solvent was removed and the residue was recrystallized several times from ligroin to give 6.5 g (71%) of **13**.

Bis(trineophyltin) Oxide (**14**).—An ethereal solution of 5.5 g (0.01 mole) of trineophyltin chloride was treated with 10% sodium hydroxide solution and worked up in the usual manner to yield 4.0 g (76%) of **14**. The infrared spectrum of this compound did not exhibit a peak in the OH region, thus excluding it to be trineophyltin hydroxide.

Hexaneophylditin (**15**).—A suspension of 2.75 g (0.005 mole) of trineophyltin chloride in 25 ml of liquid ammonia was treated with 0.25 g (0.011 mole) of sodium in four small portions. After evaporation of the ammonia the residue was washed with water and the organic portion was crystallized from ligroin to yield 1.5 g (57%) of **15**.

Tetrakis(2-phenylpropyl)tin (**16**).—A Grignard solution was prepared from 12.1 g (0.5 g-atom) of magnesium and 100 g (0.5 mole) of β-bromoisopropylbenzene[8] in 100 ml of ether and treated with a solution of 26.1 g (0.1 mole) of stannic chloride in 100 ml of benzene in the usual manner to give 42.5 g (71%) of **16**.

Tetrakis(3-phenylpropyl)tin (**11**).—To a mixture of 12.1 g (0.5 g-atom) of magnesium turnings and 100 ml of dry ether was added, over a 2-hr period, 99.55 g (0.5 mole) of 3-bromopropyl benzene. After 1 hr of reflux the reaction mixture was slightly cooled and to it was added dropwise, during 90 min, a solution of 26.1 g (0.1 mole) of $SnCl_4$ in 100 ml of benzene. After 1 hr of reflux, the reaction mixture was cooled in an ice bath and added carefully, with stirring, to an ice–dilute hydrochloric acid mixture. The organic layer was separated, dried over $CaCl_2$, and filtered, and the oil obtained after removal of solvent was briefly heated at 150° (1.5 mm) to give 56.2 g (94.3%) of **11**, bp >250° (1.5 mm). Since it gave a negative halogen test and would not crystallize, it was used without further purification for the following reaction.

Tris(3-phenylpropyl)tin Chloride (**17**).—A mixture of 56.2 g (0.0944 mole) of **11**, and 8.22 g (0.0315 mole) of $SnCl_4$ was heated to 95° for 45 min.and then to 200–205° for 2 hr. On cooling the reaction mixture was heated briefly under vacuum at 100°, when a few milliliters of volatile by-products distilled. The residue solidified on cooling and gave 61 g of crude **17** which on recrystallization from petroleum ether (bp 90–120°) gave 36 g (55.8%) of pure **17**, mp 61–61.5°.

Tris(3-phenylpropyl)tin Fluoride (**8**).—To a refluxing solution of 3.0 g (0.006 mole) of $C_6H_5(CH_2)_3SnCl$ in 50 ml of methanol was added slowly a solution of 0.8 g (0.008 mole) of $KF \cdot 2H_2O$ in 50 ml of methanol. The reaction mixture was refluxed for 30 min, methanol was removed under reduced pressure, and, when nearly dry, the residue was washed with distilled water. The product was crystallized from methanol to yield 2.5 g (84%) of **8**.

During crystallizations the solid tends to precipitate as a sticky, plastic mass if allowed to cool slowly. Crystallizations were therefore performed with rapid ice cooling of a hot methanol solution of product. The product becomes plastic even on drying

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(7) N. Rabjohn, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 702.

(8) R. Adams and J. D. Garber, *J. Am. Chem. Soc.*, **71**, 522 (1949).

at 56° under vacuum; therefore, drying at room temperature is recommended.

Acknowledgment.—The authors wish to thank Dr. Fred Kaplan for his helpful discussions and aid in interpreting the pmr spectra and to Mr. Francis E. Stary who ran the pmr spectra. Mr. Leslie Lytle's assistance with some of the syntheses is appreciated.

A New Method of Introducing the Neopentyl Group[1]

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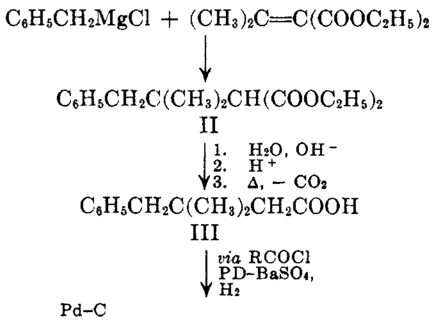
Received March 22, 1966

Because of interest in the behavior of compounds containing neopentyl groups,[3] methods of synthesis for such compounds other than the known ones[4] were in demand. In this paper, a new method by which one can construct the neopentyl group is illustrated by the synthesis of neopentylbenzene (I). Although this method of synthesis is not recommended over some known[4] methods for neopentylbenzene itself, it may be of value in other cases involving neopentyl-like structures not so readily made by the previously published methods[4] or where C^{14} or D are needed.



$$C_6H_5CH_2MgCl + (CH_3)_2C{=}C(COOC_2H_5)_2$$

$$\downarrow$$

$$C_6H_5CH_2C(CH_3)_2CH(COOC_2H_5)_2 \quad \text{II}$$

$$\downarrow \; 1.\ H_2O,\ OH^-;\ 2.\ H^+;\ 3.\ \Delta,\ -CO_2$$

$$C_6H_5CH_2C(CH_3)_2CH_2COOH \quad \text{III}$$

$$\downarrow \; \textit{via}\ RCOCl;\ \text{PD-}BaSO_4,\ H_2$$

$$\text{I} \xleftarrow[-CO]{Pd\text{-}C} C_6H_5CH_2C(CH_3)_2CH_2CHO$$

There is a feature of interest regarding the reaction of benzylmagnesium chloride with diethyl isopropylidenemalonate. The reaction takes place to give II exclusively, as shown by vpc analysis of the distilled product, and no ring-substitution products as are often found in reactions of benzyl-type Grignard reagents.

Originally, decarboxylation of III to I was intended. However, when attempted decarboxylation failed (copper or copper chromite in quinoline), the alternate route *via* the Rosenmund reduction and decarbonylation[5] was followed. Although not generally practiced, this route may be generally preferable when decarboxylation of an acid occurs in poor yield or when the temperature needed for decarboxylation is too high for the molecule in question. Often, the temperature needed for decarbonylation may be lower than that needed for decarboxylation.

Experimental Section[6]

Diethyl (α,α-Dimethylphenethyl)malonate (II).—In the best of a few runs, a solution of the Grignard reagent, prepared in 97% yield (by titration) by the addition of 100 g of benzyl chloride to 20.0 g of magnesium (2300 ml of ether in all) at a rate sufficient to maintain the ether at reflux, was added to a solution of 155 g of diethyl isopropylidenemalonate,[7] bp 110–112° (9 mm), in 200 ml of ether containing 12.0 g of purified cuprous chloride,[8] at such a rate as to maintain a gentle reflux for 2 hr, and was then cooled, treated with saturated ammonium chloride solution, and worked up as usual. Distillation through a 30 × 2.5 cm column packed with glass helices yielded 122 g (54%) of pure IIa: bp 163–165° (4 mm); one peak by vpc analysis on a 2 ft × 0.25 in. 10% SE-30 (silicone gum rubber) on 60–80 Chromosorb P column; infrared band at 5.85 μ; nmr (CCl_4), δ 1.08 (singlet, 6 H, CCH_3), 1.20 (triplet, 6 H, $J \cong 7$ cps, CH_3 of ethyl group), 2.83 (singlet, 2 H, CH_2), 3.20 (singlet, 1 H, CH), 4.11 (quartet, 4 H, $J \cong 7$ cps, $COOCH_2$), and 7.16 (singlet, 5 H, aromatic).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.8; H, 8.2. Found: C, 69.7; H, 8.0.

(α,α-Dimethylphenethyl)malonic Acid (IIb).—After alkaline hydrolysis and acidification, acid IIb was isolated in 93% yield as a colorless solid, mp 167–168° dec, neut equiv 119 (calcd 118).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8. Found: C, 66.0; H, 6.8.

3,3-Dimethyl-4-phenylbutanoic Acid (III).—After heating 54.0 g of IIb at 175–177° for 2 hr, the theoretical amount of carbon dioxide had been collected. Distillation afforded 41.6 g (95%) of III as a colorless, viscous liquid: bp 141–142° (2.5–3.0 mm); neut equiv 190 (calcd 192); nmr (CCl_4), δ 1.04 (CCH_3), 2.20 (CH_2COO), 2.66 (CH_2), 7.16 (aromatic), and 12.03 (COOH), all singlets of relative areas 6:2:2:5:1.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.0; H, 8.3. Found: C, 75.2; H, 8.5.

3,3-Dimethyl-4-phenylbutanal (IV).—A suspension of 0.7 g of predried 5% palladium-on-barium sulfate catalyst[9] in 100 ml of dry toluene was heated at reflux while nitrogen and then hydrogen were bubbled through for 1 hr. After cooling to 60°, 7.0 g of the distilled acid chloride, bp 113.0–113.5° (4.5–5.0 mm), infrared absorption at 5.55 μ, was added. As the temperature was raised to 95° the evolution of hydrogen chloride[10] became brisk and 90% of the theoretical amount was accounted for by titration in 2.5 hr. After cooling under nitrogen the catalyst was filtered and the toluene was removed under reduced

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[2] P. E. O. International Peace Scholarship holder, 1961–1963.

[3] See, for example, M. S. Newman, J. R. LeBlanc, H. A. Karnes, and G. Axelrad, *J. Am. Chem. Soc.*, **86**, 868 (1964).

[4] See for example, A. Bygden, *Ber.*, **45**, 3479 (1912); E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **71**, 1195 (1949); C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zahman, *Ber.*, **92**, 10 (1959); A. Friedman, W. Gugig, L. Mehr, and E. I. Becker, *J. Org. Chem.*, **24**, 516 (1959); J. H. Brewster, J. Patterson, and D. A. Fidler, *J. Am. Chem. Soc.*, **76**, 6368 (1954), and references cited therein.

[5] M. S. Newman and H. V. Zahm, *ibid.*, **65**, 1097 (1943).

[6] Nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane (TMS) as internal standard; δ values are given in parts per million downfield from the TMS resonance (0 ppm). Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The phrase, "worked up in the usual manner," refers to the following procedure. The organic layer of the reaction products in ether–benzene was washed successively with dilute hydrochloric acid, sodium bicarbonate solution, unless an organic acid was the product, and saturated sodium chloride solution, and was then filtered through an anhydrous magnesium sulfate bed. The solvent was usually removed in a rotary evaporator.

[7] Prepared in 53% yield as described by A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **60**, 2645 (1938).

[8] This reagent contained 12.0 g of colorless cuprous chloride prepared by treating crude solid cuprous chloride (Baker Analyzed) in a mortar with 10% of its weight of moist hydroxylamine hydrochloride until fumes of nitrous oxide were no longer apparent. The paste was transferred to a filter under nitrogen and the solid was washed with a small amount of distilled water which had been boiled and allowed to cool under nitrogen, then with absolute alcohol and ether, similarly treated. The colorless cuprous chloride was stored in a vacuum desiccator until used. We thank Dr. K. Greenlee for telling us of this method of treatment.

[9] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 627.

[10] The absence of carbon monoxide in gas samples at different times showed that no carbon monoxide was being formed. Analysis was by gas chromatography as described by G. Kyryacos and C. E. Boord, *Anal. Chem.*, **29**, 787 (1957).