the temperature to 90–100° somewhat smaller yields (42% crude and 26% pure) of IIIa were obtained.

Lactone of 2-(α-hydroxy-α-methyl-p-fluorobenzyl)-1-naphthoic acid, VII. Reaction of 24.5 g. of II, m.p. 170–176°, with methylmagnesium bromide followed by treatment as described[4] yielded 14.2 g. (58%) of colorless VII, m.p. 105–107°, of sufficient purity for further work. An additional 6–8 g. of less pure product was obtained from the mother liquors but was not investigated further. The analytical sample, obtained after two recrystallizations from ethanol, melted at 108.0–108.5°

Anal. Calcd. for $C_{19}H_{13}FO_2$:C, 78.0; H, 4.5. Found: C, 77.7; H, 4.3.

2-(α-Methyl-p-fluorobenzyl)-1-naphthoic acid, VIII. Reduction of 13.7 g. of VII, m.p. 105–107° as described[4] yielded 12.7 g. (93%) of VIII, m.p. 174.5–175.5°. Recrystallization from benzene yielded pure VIII, m.p. 176.2–177.0°, with little loss.

Anal. Calcd. for $C_{19}H_{15}FO_2$: C, 77.6; H, 5.1. Found: C, 77.4; H, 5.1.

Reduction of crude lactone VII afforded crystalline VIII, m.p. 174.5–175.5°, in good yield also, so that it was possible to utilize noncrystalline VII directly in the preparation of VIII.

7-Fluoro-10-methyl-1,2-benzanthracene, IV. Cyclization of 13.1 g. of VIII, m.p. 174.5–175.5° with 150 ml. of concentrated sulfuric acid at 25° for 2 hr. followed by reduction of the anthrone as described[4] afforded 6.3 g. (55%) of crude IV, m.p. 100–103°. The analytical sample, obtained by further chromatography and recrystallization from benzene–Skellysolve B, formed colorless needles, m.p. 102.5–103.2°.

Anal. Calcd. for $C_{19}H_{13}F$: C, 87.7; H, 5.0; F, 7.3. Found: C, 87.4; H, 5.2; F, 7.5.

1-p-Methoxybenzyl-2-naphthoic acid, Vb. In the best of several reductions, a mixture of 5.0 g. of Ib, 75 ml. of 20% potassium hydroxide solution and 15 g. of zinc dust (activated as above) was refluxed for 30 hr. After a procedure similar to that for Va, 1.4 g. (29%) of crude Vb, m.p. 150–159°, was obtained. The analytical sample, obtained by two recrystallizations from benzene, formed colorless needles, m.p. 165.5–166.5°. The remainder was used in the next step.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 77.8; H, 5.3.

6-Methoxy-10-methyl-1,2-benzanthracene, IIIb. To a stirred solution of 50 ml. of 0.4*N* methyllithium in ether was added during 10 min. a solution of 1.5 g. of Vb (the above crude product) in 100 ml. of ether and 50 ml. of pure dry tetrahydrofurane. A purple color developed. After 1 hr. at room temperature the reaction mixture was treated as usual and the neutral oily fraction, presumably containing 1-*p*-methoxybenzyl-2-acetonaphthalene, VIb, was heated on a steam bath with 99% PPA for 20 min. Dilution with water and the usual workup, including chromatography over alumina (activated as above) afforded 0.70 g. (50%) of crude IIIb, m.p. 169–174°. Recrystallizations from benzene afforded IIIb as pale yellow needles, m.p. 174.0–174.8°, with some loss.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.2; H, 5.9; OCH_3, 11.4. Found: C, 88.5, 88.4; H, 5.9, 6.0; OCH_3, 11.2.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

Unsymmetrical Tetraalkylmethanes. IV.[1] General Method of Synthesis of Tetraalkylmethanes

NORMAN RABJOHN, L. V. PHILLIPS,[2,3] AND R. J. DEFEO[4]

Received July 6, 1959

A number of unsymmetrical tetraalkylmethanes, containing from 27 to 50 carbon atoms, have been prepared in relatively high over-all yields from unsymmetrical ketones. The latter were transformed into alkylidenecyanoacetates, which were then caused to undergo conjugate addition with Grignard reagents to give α-cyano-β,β,β-trialkylpropionates (I). These were hydrolyzed and decarboxylated to β,β,β-trialkylpropionitriles (III), which were converted through the branched ketones (IV) to the hydrocarbons (VII) which possessed the desired quaternary carbon atom structure.

The previous paper[1] in this series described a method for preparing unsymmetrical tetraalkylmethanes from β,β-disubstituted glutaric acids, which contained the desired center of asymmetry. In the present study it was found that the procedure failed when an attempt was made to apply it to the synthesis of high molecular weight hydrocarbons. Although the Guareschi reaction[5] affords good yields of α,α-dicyano-β,β-dialkylglutarimides with simple methyl and cyclic ketones, no condensation could be effected with 6-dodecanone. The amination reaction occurred exclusively and the ethyl cyanoacetate was converted to cyanoacetamide. Others[6] have reported limitations of the Guareschi condensation.

Alkylidenecyanoacetates, which can be obtained readily by Cope's procedure,[7] seemed to offer a general approach to the synthesis of molecules which possess quaternary carbon atoms. As the Michael addition of active methylene compounds to the alkylidene derivatives could lead to β,β-disubstituted glutaric acids of the type obtained

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[1] Paper III. N. Rabjohn and H. H. Farmer, *J. Org. Chem.*, **24**, 359 (1959).

[2] Abstracted in part from the Ph.D. thesis of L. V. Phillips, 1957.

[3] Supported in part by the Petroleum Research Fund of the American Chemical Society.

[4] Lubrizol Foundation Fellow, 1956–1958.

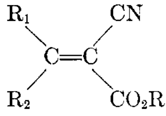
[5] I. Guareschi, *Gazz. chim. ital.*, **49**, 124 (1919).

[6] A. I. Vogel, *J. Chem. Soc.*, 1758 (1934); A. J. Birch and R. Robinson, *J. Chem. Soc.*, 488 (1942); and S. M. McElvain and D. H. Clemens, *J. Am. Chem. Soc.*, **80**, 3915 (1958).

[7] A. C. Cope, C. M. Hofmann, C. Wykoff, and E. Hardenbergh, *J. Am. Chem. Soc.*, **63**, 3452 (1941).

TABLE I

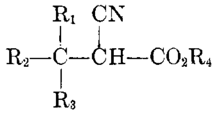
ALKYLIDENE CYANOACETATES,



							Anal.			
							Calcd.		Found	
R_1	R_2	R_3	B.P.	n_D^{25}	Yield	Formula	C	H	C	H
C_2H_5	C_3H_7	C_2H_5	100–103°/15 mm.	1.4642	59	$C_{11}H_{17}NO_2$	67.66	8.78	67.88	9.01
C_3H_7	C_4H_9	C_2H_5	158–160°/15 mm.	1.4654	74	$C_{13}H_{21}NO_2$	69.92	9.48	70.22	9.62
C_2H_5	C_7H_{15}	C_2H_5	139–142°/1 mm.	1.4651	81	$C_{15}H_{25}NO_2$	71.67	10.03	71.93	9.95
C_5H_{11}	C_6H_{13}	C_2H_5	153–156°/1 mm.	1.4652	88	$C_{17}H_{29}NO_2$	73.07	10.46	73.37	10.52
C_7H_{15}	C_8H_{17}	CH_3	208–210°/3 mm.	1.4661	68	$C_{20}H_{35}NO_2$	74.71	10.97	74.60	10.80
C_7H_{15}	$C_{10}H_{21}$	C_2H_5	199–201°/0.5 mm.	1.4660	51	$C_{23}H_{41}NO_2$	75.98	11.37	75.69	11.13
$C_{10}H_{21}$	$C_{11}H_{23}$	C_2H_5	220–222°/1.5 mm.	1.4690	69	$C_{27}H_{49}NO_2$	77.77	11.77	77.85	11.72

TABLE II

2-CYANO-3,3-DIALKYL SUBSTITUTED ESTERS,



$$R_2\text{—}\overset{R_1}{\underset{R_3}{C}}\text{—}\overset{CN}{C}H\text{—}CO_2R_4$$

								Anal.			
								Calcd.		Found	
R_1	R_2	R_3	R_4	B.P.	n_D^{25}	Yield	Formula	C	H	C	H
C_2H_5	C_3H_7	$C_{12}H_{25}$	C_2H_5	195–198°/1 mm.	1.4550	60	$C_{23}H_{43}NO_2$	75.56	11.86	75.69	12.03
C_3H_7	C_4H_9	$C_{10}H_{21}$	C_2H_5	178–180°/1 mm.	1.4552	65	$C_{23}H_{43}NO_2$	75.56	11.86	75.74	11.92
C_2H_5	C_7H_{15}	C_8H_{17}	C_2H_5	190–194°/1 mm.	1.4549	81	$C_{23}H_{43}NO_2$	75.56	11.86	75.51	11.94
CH_3	C_6H_{13}	$C_{10}H_{21}$	C_2H_5	200–204°/1 mm.	1.4529	78	$C_{23}H_{43}NO_2$	75.56	11.86	75.44	11.73
C_5H_{11}	C_6H_{13}	C_7H_{15}	C_2H_5	186–190°/1 mm.	1.4549	71	$C_{24}H_{45}NO_2$	75.93	11.95	75.78	11.74
C_7H_{15}	C_8H_{17}	$C_{10}H_{21}$	CH_3	238–240°/0.5 mm.	1.4590	60	$C_{30}H_{57}NO_2$	77.69	12.39	77.83	12.22

from the Guareschi reaction, the addition of malonic ester and cyanoacetic ester to ethyl 1-pentylheptylidenecyanoacetate was attempted. In both instances unreacted starting materials and viscous residues were obtained. Hydrolysis of the residues in alcoholic potassium hydroxide solution resulted in heavy oils which neither could be distilled nor induced to crystallize.

A conjugate addition of a Grignard reagent to an alkylidenecyanoacetate then suggested itself as a way of developing a quaternary carbon atom structure. Prout and his associates,[8] in an extension of the work of Alexander, McCollum, and Paul[9] have studied the addition of organometallic compounds to several conjugated systems which possess isopropylidene or *sec*-butylidene groups. They obtained the highest yields with cyanoacetic esters and phenyl- and benzyl-magnesium halides. *n*-Alkylmagnesium halides gave 30–50% of 1,4-addition to the ethyl alkylidenecyanoacetates and 15–20% reduction of the unsaturated ester.

Some time prior to this, Hook and Robinson[10] had investigated the addition of Grignard reagents to alkylidenecyanoacetates and found that the reduction reaction was minimized by the slow inverse addition of the Grignard reagent to an ether solution of the alkylidene compound at low temperatures (14–20°). In addition, they discovered that small amounts of cuprous iodide appeared to facilitate the 1,4-type of addition.

In the present investigation a short study was made of this addition reaction, and the results supported the work of Hook and Robinson. When ethyl 1-methylheptylidenecyanoacetate was added by the normal procedure to an ether solution of decylmagnesium bromide, a 43% yield of 1,4-addition product was obtained. In contrast, the addition of the alkylidene compound to a solution of the Grignard reagent which contained cuprous iodide gave only a 29% yield of 1,4-addition product. The inverse addition of an ether solution of decylmagnesium bromide to ethyl 1-methylheptylidenecyanoacetate, however, gave quite different results. A 47% yield of 1,4-addition product was isolated from such a reaction system on the absence of cuprous iodide, whereas a 78% yield of 1,4- addition compound was obtained when cuprous iodide was present in the ethyl 1-methylheptylidenecyanoacetate solution. In the reactions described, with the exception of the latter, a considerable quantity of reduction product, ethyl α-cyano-β-methylpelargonate, was formed. The inverse addi-

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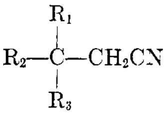
(8) F. S. Prout, *J. Am. Chem. Soc.*, **74**, 5915 (1952); F. S. Prout, E. P. Y. Huang, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954).

(9) E. R. Alexander, J. D. McCollum, and D. E. Paul, *J. Am. Chem. Soc.*, **72**, 4791 (1950).

(10) W. H. Hook and R. Robinson, *J. Chem. Soc.*, 1952 (1944).

TABLE III

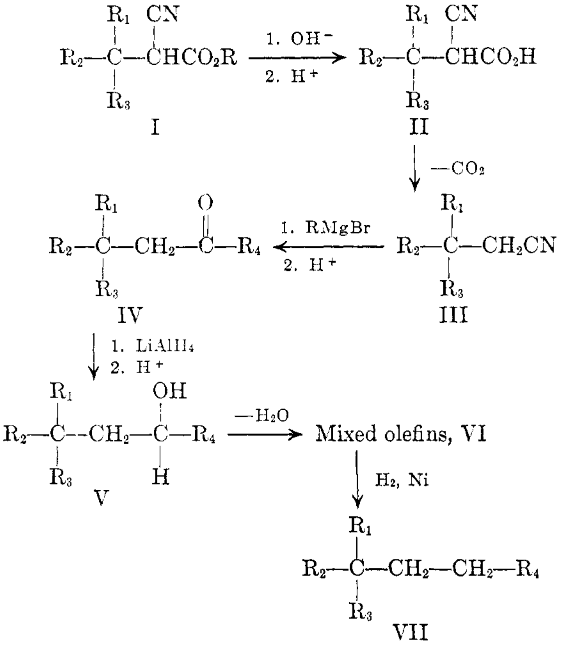
3,3-DIALKYL SUBSTITUTED NITRILES, 

$$R_2\text{—}\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}\text{—}CH_2CN$$

							Anal.			
							Calcd.		Found	
R_1	R_2	R_3	B.P.	n_D^{25}	Yield	Formula	C	H	C	H
C_2H_5	C_3H_7	$C_{12}H_{25}$	172–175°/1 mm.	1.4520	56	$C_{20}H_{39}N$	81.83	13.39	81.50	13.51
C_3H_7	C_4H_9	$C_{10}H_{21}$	168–170°/1 mm.	1.4522	69	$C_{20}H_{39}N$	81.83	13.39	81.69	13.33
C_2H_5	C_7H_{15}	C_8H_{17}	177–180°/1 mm.	1.4521	87	$C_{20}H_{39}N$	81.83	13.39	81.84	13.06
CH_3	C_6H_{13}	$C_{10}H_{21}$	181–183°/1 mm.	1.4493	86	$C_{20}H_{39}N$	81.83	13.39	82.16	13.27
C_5H_{11}	C_6H_{13}	C_7H_{15}	169–173°/1 mm.	1.4510	85	$C_{21}H_{41}N$	82.01	13.44	81.94	13.17
C_7H_{15}	C_8H_{17}	$C_{10}H_{21}$	226–228°/1 mm.	1.4570	96	$C_{28}H_{55}N$	82.88	13.66	83.12	13.66
C_7H_{15}	$C_{10}H_{21}$	$C_{12}H_{25}$	262–265°/0.5 mm.	1.4580	78	$C_{32}H_{63}N$	83.22	13.75	85.54	13.61
$C_{10}H_{21}$	$C_{11}H_{23}$	$C_{12}H_{25}$	278–281°/0.5 mm.	1.4598	36	$C_{36}H_{71}N$	83.48	13.82	83.67	13.85

tion of ether solutions of other Grignard reagents to ethyl or methyl alkylidenecyanoacetates in the presence of cuprous iodide afforded 60–81% yields of α-cyano-β,β,β-trisubstituted propionic acid esters (Table II).

The desired unsymmetrical tetraalkylmethanes (VII) were obtained from the α-cyano-β,β,β-trisubstituted propionates (I) by the following series of reactions.



The esters (I) were converted by alkaline hydrolysis to the corresponding acids with very little attack on the nitrile grouping. The cyano acids (II) were not isolated, but the crude residues from hydrolysis were transformed directly to the nitrile (III) in the presence of copper powder. The reaction was subject to an induction period and the major portion of the decarboxylation occurred over a short period of time in the temperature range of 140–160°. The nitriles, Table III, were obtained, in general, in high yields. The 3-decyl-3-undecylpentadecanonitrile resulted (36%) from thermal decarbethoxylation during attempted distillation of ethyl 2-cyano-3-decyl-3-undecylpentadecanoate.

The addition of Grignard reagents to the β,β,β-trisubstituted propionitriles gave satisfactory yields of the ketones (IV), Table IV, which were reduced then to the carbinols (V), Table V. Sodium borohydride reduction of the branched ketones, (IV), did not take place under the conditions employed. Also, catalytic reduction, even at 150° and 2500 p.s.i. in the presence of Raney nickel catalyst, was unsatisfactory because incomplete reduction made purification of the products difficult.

The dehydration of the secondary alcohols in the presence of potassium hydrogen sulfate led to mixtures of olefins (VI), Table VI. Evidence[11] has been obtained which indicates that the olefins have the expected structures, and that molecular rearrangements did not take place during the dehydration step. The mixed olefins (VI) were reduced readily to the saturated hydrocarbons (VII) with hydrogen and Raney nickel catalyst. Infrared spectra of all the compounds in the series showed the presence of the desired functional groups. Oxygen-containing and unsaturated materials could not be detected in the spectra of the tetraalkylmethanes recorded in Table VII.

EXPERIMENTAL[12]

Materials. 3-Hexanone, 2-octanone, 4-octanone, 3-decanone, and 6-dodecanone were obtained by the oxidation of the corresponding secondary alcohols by means of sodium dichromate in sulfuric acid. The carbinols had been synthesized from the appropriate Grignard reagents and aldehydes. The ketones possessed the following physical properties: 3-hexanone, b.p. 122–126°, n_D^{20} 1.4000, lit.,[13] b.p.

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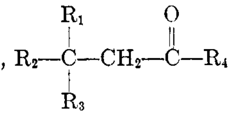
[11] Norman Rabjohn and R. J. DeFeo, unpublished results.

[12] All melting points are uncorrected. The carbon and hydrogen analyses were performed by A. Mendel of this Laboratory and the Weiler and Strauss Laboratories, Oxford, England. The authors are indebted to Professor E. E. Pickett for much of the infrared data.

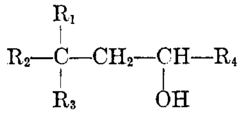
[13] J. M. Heilbron, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, 1953, p. 521.

TABLE IV

DIALKYL SUBSTITUTED KETONES, 
$R_2{-}\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R_4$

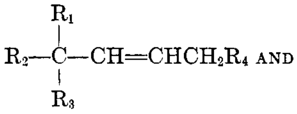
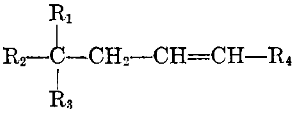
								Anal.			
								Calcd.		Found	
R_1	R_2	R_3	R_4	B.P.	n_D^{25}	Yield	Formula	C	H	C	H
C_2H_5	C_3H_7	$C_{12}H_{25}$	C_7H_{15}	215–216°/1 mm.	1.4551	43	$C_{27}H_{54}O$	82.16	13.79	82.09	13.66
C_3H_7	C_4H_9	$C_{10}H_{21}$	C_7H_{15}	223–225°/2 mm.	1.4540	86	$C_{27}H_{54}O$	82.16	13.79	82.08	13.84
C_2H_5	C_7H_{15}	C_8H_{17}	C_7H_{15}	212–214°/1 mm.	1.4548	83	$C_{27}H_{54}O$	82.16	13.79	82.07	13.83
CH_3	C_6H_{13}	$C_{10}H_{21}$	C_7H_{15}	202–206°/1 mm.	1.4531	75	$C_{27}H_{54}O$	82.16	13.79	82.08	13.87
C_5H_{11}	C_6H_{13}	C_7H_{15}	C_6H_{13}	195–197°/1 mm.	1.4531	42	$C_{27}H_{54}O$	82.16	13.79	82.12	13.94
C_7H_{15}	C_8H_{17}	$C_{10}H_{21}$	C_7H_{15}	253–256°/1 mm.	1.4582	88	$C_{35}H_{70}O$	82.92	13.92	82.87	13.83
$C_{10}H_{21}$	$C_{11}H_{23}$	$C_{12}H_{25}$	C_7H_{15}	270–273°/0.5 mm.	1.4613	57	$C_{43}H_{86}O$	83.41	14.00	83.32	13.95
C_7H_{15}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{18}H_{37}$	292–295°/0.1 mm.	1.4620	71	$C_{50}H_{100}O$	83.72	14.05	83.55	13.76

TABLE V

DIALKYL SUBSTITUTED CARBINOLS, 
$R_2{-}\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}{-}CH_2{-}\underset{\displaystyle OH}{CH}{-}R_4$

								Anal.			
								Calcd.		Found	
R_1	R_2	R_3	R_4	B.P.	n_D^{25}	Yield	Formula	C	H	C	H
C_2H_5	C_3H_7	$C_{12}H_{25}$	C_7H_{15}	207–210°/1 mm.	1.4592	93	$C_{27}H_{56}O$	81.74	14.23	81.80	13.95
C_3H_7	C_4H_9	$C_{10}H_{21}$	C_7H_{15}	221–223°/2 mm.	1.4588	95	$C_{27}H_{56}O$	81.74	14.23	81.83	14.37
C_2H_5	C_7H_{15}	C_8H_{17}	C_7H_{15}	193–195°/0.5 mm.	1.4591	97	$C_{27}H_{56}O$	81.74	14.23	81.49	13.99
CH_3	C_6H_{13}	$C_{10}H_{21}$	C_7H_{15}	200–204°/1 mm.	1.4572	96	$C_{27}H_{56}O$	81.74	14.23	81.87	14.51
C_5H_{11}	C_6H_{13}	C_7H_{15}	C_6H_{13}	199–203°/1 mm.	1.4580	97	$C_{27}H_{56}O$	81.74	14.23	81.62	14.00
C_7H_{15}	C_8H_{17}	$C_{10}H_{21}$	C_7H_{15}	256–260°/0.5 mm.	1.4610	96	$C_{35}H_{72}O$	82.60	14.26	82.30	14.27
$C_{10}H_{21}$	$C_{11}H_{23}$	$C_{12}H_{25}$	C_7H_{15}	290–293°/0.5 mm.	1.4633	77	$C_{43}H_{88}O$	83.14	14.28	82.91	14.43
C_7H_{15}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{18}H_{37}$	305–306°/0.1 mm.	1.4636	91	$C_{50}H_{102}O$	83.48	14.29	83.17	14.32

TABLE VI

ALKENES, 
$R_2{-}\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}{-}CH{=}CHCH_2R_4$
AND 
$R_2{-}\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}{-}CH_2{-}CH{=}CH{-}R_4$

								Anal.			
								Calcd.		Found	
R_1	R_2	R_3	R_4	B.P.	n_D^{25}	Yield	Formula	C	H	C	H
C_2H_5	C_3H_7	$C_{12}H_{25}$	C_6H_{13}	189–193°/1 mm.	1.4569	91	$C_{27}H_{54}$	85.63	14.37	85.68	14.34
C_3H_7	C_4H_9	$C_{10}H_{21}$	C_6H_{13}	218–220°/2 mm.	1.4562	94	$C_{27}H_{54}$	85.63	14.37	85.76	14.17
C_2H_5	C_7H_{15}	C_8H_{17}	C_6H_{13}	200–203°/2 mm.	1.4570	92	$C_{27}H_{54}$	85.63	14.37	85.96	14.18
CH_3	C_6H_{13}	$C_{10}H_{21}$	C_6H_{13}	193–196°/1 mm.	1.4549	98	$C_{27}H_{54}$	85.63	14.37	85.59	14.24
C_5H_{11}	C_6H_{13}	C_7H_{15}	C_5H_{11}	185–187°/1 mm.	1.4559	90	$C_{27}H_{54}$	85.63	14.37	85.49	14.18
C_7H_{15}	C_8H_{17}	$C_{10}H_{21}$	C_6H_{13}	243–246°/0.5 mm.	1.4599	98	$C_{35}H_{70}$	85.63	14.37	85.66	14.30
$C_{10}H_{21}$	$C_{11}H_{23}$	$C_{12}H_{25}$	C_6H_{13}	259–261°/0.5 mm.	1.4630	92	$C_{42}H_{86}$	85.63	14.37	85.63	14.15
C_7H_{15}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{17}H_{35}$	292–295°/0.1 mm.	1.4629	91	$C_{50}H_{100}$	85.63	14.37	85.89	14.30

123–123.5°, n_D^{22} 1.3990; 2-octanone, b.p. 72–74°/17 mm., n_D^{20} 1.4151, lit.,[14] b.p. 172.9°, n_D^{20} 1.4161; 4-octanone, b.p. 63–64°/14 mm., n_D^{20} 1.4138, lit.,[15] b.p. 165–168°; 3-decanone, b.p. 98–102°/17 mm., n_D^{20} 1.4240, lit.,[16] b.p. 203°, n_D^{20} 1.4251; and 6-dodecanone, b.p. 92–95°/2 mm., n_D^{25} 1.4270, m.p. 8–9°, lit.,[17] b.p. 112°/9 mm., m.p. 9°. The 8-octadecanone was prepared by the reaction of caprylyl chloride with decylcadmium; b.p. 178–180°/3 mm., m.p. 44–45° (from 2-butanone); lit.,[18] m.p. 44.8–46°. Similarly, the 11-docosanone was obtained from decylcadmium and lauroyl chloride; m.p. 59–60°, lit.,[18] m.p. 58.6–59.8°.

Ethyl 1-methylheptylidenecyanoacetate was synthesized by the condensation of ethyl cyanoacetate with 2-octanone

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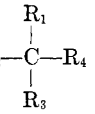
TABLE VII

TETRAALKYLMETHANES,



$$R_2\text{—}\overset{R_1}{\underset{R_3}{C}}\text{—}R_4$$

								Anal.			
								Calcd.		Found	
R_1	R_2	R_3	R_4	B.P.	n_D^{25}	Yield	Formula	C	H	C	H
C_2H_5	C_3H_7	$C_{12}H_{25}$	C_9H_{19}	195–196°/1 mm.	1.4521	84	$C_{27}H_{56}$	85.17	14.83	85.05	14.97
C_3H_7	C_4H_9	$C_{10}H_{21}$	C_9H_{19}	200–201°/1 mm.	1.4524	88	$C_{27}H_{56}$	85.17	14.83	84.96	14.69
C_2H_5	C_7H_{15}	C_8H_{17}	C_9H_{19}	189–190°/1 mm.	1.4520	93	$C_{27}H_{56}$	85.17	14.83	85.19	14.89
CH_3	C_6H_{13}	$C_{10}H_{21}$	C_9H_{19}	190–191°/1 mm.	1.4501	85	$C_{27}H_{56}$	85.17	14.83	85.37	14.52
C_5H_{11}	C_6H_{13}	C_7H_{15}	C_8H_{17}	180–182°/1 mm.	1.4508	94	$C_{27}H_{56}$	85.17	14.83	84.94	14.76
C_7H_{15}	C_8H_{17}	$C_{10}H_{21}$	C_9H_{19}	243–245°/0.5 mm.	1.4560	92	$C_{35}H_{72}$	85.28	14.72	85.42	14.69
$C_{10}H_{21}$	$C_{11}H_{23}$	$C_{12}H_{25}$	C_9H_{19}	268–270°/0.5 mm.	1.4596	82	$C_{43}H_{88}$	85.34	14.66	85.47	14.54
C_7H_{15}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{20}H_{41}$	298–300°/0.05 mm.	1.4610	68	$C_{50}H_{102}$	85.38	14.62	85.37	14.39

according to the method of Cope, Hofmann, Wykoff, and Hardenbergh,[7] b.p. 134–137°/3 mm., n_D^{25} 1.4649; lit.,[7] b.p. 124–125°/2 mm., n_D^{25} 1.4656. The alkylidene esters listed in Table I were prepared also by this general method.

Ethyl 2-cyano-3-hexyl-3-methyltridecanoate. Method A. A Grignard reagent was prepared from 5.74 g. (0.24 g. atom) of magnesium and 52.7 g. (0.24 mol.) of decyl bromide in 100 ml. of ether. The mixture was allowed to stir for 30 min. after addition of the decyl bromide had been completed. This Grignard reagent was added dropwise to a mixture of 35 g. (0.16 mol.) of ethyl 1-methylheptylidenecyanoacetate and 0.8 g. (5 g./mol. of alkylidene) of cuprous iodide in 93 ml. (590 ml./mol.) of ether. The reaction mixture became blue-black. After the addition had been completed, the reaction mixture was refluxed with stirring for 1 hr. and stood at room temperature for 20 hr. The mixture was poured onto 47 ml. of concentrated hydrochloric acid and 100 g. of ice with rapid stirring. The resulting mixture was shaken thoroughly in a separatory funnel, and after the aqueous layer had been removed, was extracted with several small portions of ether. The ether solutions were combined, washed with water, 10% sodium bicarbonate, and water, and dried over anhydrous sodium sulfate. After the ether had been removed by distillation, the residue was distilled to give 45.2 g. (78.5%) of ethyl 2-cyano-3-*n*-hexyl-3-methyltridecanoate; b.p. 195–202°/1 mm.; 5.66 g. of eicosane and 1.76 g. of material which boiled at 120–126°/1 mm.

Method B. The Grignard reagent was prepared as above, and the cuprous iodide was added to the Grignard reagent. To this solution was added the alkylidene compound in ether solution. All other conditions were the same as above. There were obtained 16.64 g. (29%) of ethyl 2-cyano-3-*n*-hexyl-3-methyltridecanoate, 5.23 g. eicosane, and 17.6 g. of a lower boiling material; b.p. 122–130°/1 mm.

Method C. The reaction was carried out under the same conditions as Method A without the use of cuprous iodide. There resulted 26.9 g. (46.9%) of ethyl 2-cyano-3-*n*-hexyl-3-methyltridecanoate, 6.68 g. of eicosane, and 9.38 g. of material; b.p. 115–130°/1 mm.

Method D. The conditions of Method B were employed without the use of cuprous iodide to give 24.77 g. (43%) of ethyl 2-cyano-3-*n*-hexyl-3-methyltridecanoate, 5.89 g. of eicosane and 14.85 g. of a material; b.p. 115–130°/1 mm.

The remainder of the alkylidene compound was converted to ethyl 2-cyano-3-hexyl-3-methyltridecanoate by Method A; b.p. 200–204°/1 mm., n_D^{25} 1.4529.

Anal. Calcd. for $C_{23}H_{43}NO_2$: C, 75.56; H, 11.86. Found: C, 75.44; H, 11.73.

The material which boiled at 115–130°/1 mm. was redistilled and the fraction which was collected at 118°/1 mm., n_D^{25} 1.4380, was submitted for analysis.

Anal. Calcd. for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29. Found: C, 69.26; H, 10.72.

An infrared spectrum of this substance showed the presence of the ester and nitrile groups, and the intensity for the double bond absorption was reduced considerably compared to that shown by the spectrum of ethyl 1-methylheptylidenecyanoacetate. The material apparently was a mixture which contained a large portion of ethyl 2-cyano-4-methyldecanoate and some of the corresponding alkylidene compound. Hook and Robinson[10] and Prout[8] have observed similar reduction products.

3-Hexyl-3-methyltridecanenitrile. The following procedure is representative of the method employed for the conversion of the 2-cyano-3,3-dialkyl substituted esters (I) to the dialkyl substituted nitriles. A mixture of 150 g. (2.4 mol.) of 85% potassium hydroxide in 660 ml. of water, 179.9 g. (0.49 mol.) of ethyl 2-cyano-3-hexyl-3-methyltridecanoate and 128 ml. of ethanol was heated at reflux for 6 hr. The alcohol was removed by distillation, 800 ml. of 20% sulfuric acid was added to the residue, and the mixture was refluxed 4 hr. After it had cooled, the organic layer was removed and the aqueous solution was extracted with several small portions of ether. The organic layer and the ether extracts were combined and the ether was evaporated.

The residue was mixed with 0.8 g. (0.005 part by weight) of copper powder and heated slowly with mechanical stirring. Decarboxylation occured at 150–160°. After the vigorous evolution of carbon dioxide had ceased, the reaction mixture was heated to 180° for a short period. The residue was distilled to give 124 g. (86%) of 3-hexyl-3-methyltridecanenitrile; b.p. 181–183°/1 mm., n_D^{25} 1.4493.

10-Ethyl-10-heptyl-8-octadecanone. The ketones listed in Table IV were synthesized in the following representative manner. A Grignard reagent was prepared from 18.7 g. (0.78 g. atom) of magnesium and 138 g. (0.77 mol.) of *n*-heptyl bromide in 400 ml. of anhydrous ether. It was stirred mechanically while 150 g. (0.51 mol.) of 3-ethyl-3-heptylundecanenitrile was added dropwise. After the addition had been completed, the reaction mixture was heated at reflux for 11 hr. It was allowed to cool and was poured onto a mixture of 180 ml. of concentrated hydrochloric acid and 280 g. of ice. The ether layer was separated, the solvent was evaporated, and a solution of 65 ml. of concentrated hydrochloric acid and 450 ml. of water was added. The mixture was heated and stirred for 1 hr., allowed to cool, and extracted with ether. The extracts were washed with water, 10% sodium bicarbonate solution, again with water and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue was distilled to give 167 g. (83%) of 10-ethyl-10-heptyl-8-octadecanone; b.p. 212–214°/1 mm., n_D^{25} 1.4548.

9-Pentyl-9-hexyl-7-hexadecanol. The carbinols listed in Table V were obtained by means of the following typical lithium aluminum hydride reduction. A solution of 14 g. (0.34 mol.) of lithium aluminum hydride in 640 ml. of anhydrous ether was stirred mechanically while 126 g. (0.32 mol.) of 9-pentyl-9-hexyl-7-hexadecanone in 160 ml. of anhydrous ether was added at a rate sufficient to cause gentle refluxing. After the addition had been completed, the mixture was stirred at room temperature for 1 hr. and heated under reflux for an additional 5 hr. Then a 50% by volume solution of ethyl acetate in ether was added slowly until refluxing ceased. This was followed by the addition of 500 ml. of 10% sulfuric acid. The ether layer was removed, washed with water, 10% sodium bicarbonate, again with water, and was dried over anhydrous sodium sulfate. After removing the ether, the residue was distilled to give 124 g. (98%) of the carbinol; b.p. 199–203°/1 mm., n_D^{25} 1.4580.

Attempted reduction of 9-pentyl-9-hexyl-7-hexadecanone with sodium borohydride. The method of Chaikin and Brown[19] was followed. To a solution of 50 g. (0.13 mol.) of 9-pentyl-9-hexyl-7-hexadecanone in 50 ml. of methanol was added 2.4 g. (0.07 mol.) of sodium borohydride in 20 ml. of methanol. No reaction appeared to occur even when the mixture was heated to boiling for some time. It was heated then with 100 ml. of 10% sodium hydroxide solution for 1 hr. The organic layer was removed, taken up in 100 ml. of ether, washed with water and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue was distilled to give 48 g. of unchanged ketone.

10-Propyl-10-butyl-7(8)-eicosene. This procedure is typical of those used to obtain the mixtures of olefins given in Table VI. A mixture of 111 g. (0.3 mol.) of 10-propyl-10-butyl-8-eicosanol and 20 g. of anhydrous potassium bisulfate was heated under reduced pressure at 150–160° for 24 hr. It was allowed to cool, the liquid was decanted, and the potassium bisulfate was extracted with several small portions of ether. The oil and extracts were combined and the ether was evaporated. The residue was distilled to give 101 g. (94%) of material which boiled between 218 and 220°/2 mm., n_D^{25} 1.4562.

10-Butyl-10-propyleicosane. The tetraalkylmethanes in Table VII were obtained by the hydrogenation of the mixtures of olefins reported in Table VI. The preparation of 10-butyl-10-propyleicosane is representative. A mixture of 51 g. of 10-butyl-10-propyl-7(8)-eicosene, 75 ml. of methylcyclohexane, and 10 g. of Raney nickel catalyst was heated, and rocked at 180° and 3200 p.s.i. of hydrogen for 7 hr. The reaction mixture was allowed to cool, was filtered and the solvent was removed by distillation. The residual oil was washed with three 100-ml. portions of cold, concentrated sulfuric acid, then with saturated sodium chloride solution, 10% sodium bicarbonate solution, and water. It was distilled to give 45 g. (88%) of a colorless liquid; b.p. 200–201°/1 mm., n_D^{25} 1.4524.

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[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Synthesis of Hydrocarbon Derivatives by the Wittig Reaction II. Diarylbutadienes and Quinquephenyls[1]

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The reaction of triphenylcinnamylphosphonium chloride and *p*-xylylenebis(triphenylphosphonium chloride) with aromatic aldehydes and cinnamaldehydes has given diarylbutadienes and 1,4-bis(4-arylbutadienyl)benzenes in yields of 60–100%. 1,4-Diphenylbutadiene, 1-(*p*-tolyl)-4-phenylbutadiene, and 1,4-bis(*p*-tolyl)butadiene were converted by the method described by Lohaus into *p*-terphenyl, 4-methylterphenyl, and 4,4″-dimethylterphenyl, respectively. This technique was extended to 1,4-bis(4-phenylbutadienyl)benzene, 1,4-bis[4-(*p*-tolyl)butadienyl]benzene, and 1,4-bis(3-methyl-4-phenylbutadienyl)benzene. *p*-Quinquephenyl, 4,4⁗-dimethylquinquephenyl, and 2′,3‴-dimethylquinquephenyl were obtained, respectively, in good yields. This represents the best route to this aromatic hydrocarbon system reported and the latter two methyl derivatives are the first derivatives to appear in the literature. This route is considered to be unambiguous.

Diarylbutadienes and 1,4-bis(arylbutadienyl)benzenes, $\mathrm{ArCH{=}CH{-}CH{=}CH{-}C_6H_4{-}CH{=}CH{-}CH{=}CH{-}Ar}$, have proved relatively difficult to synthesize in good yield, particularly with functional groups on the aryl rings. The dehydrogenation of 1,4-diphenylbutene-2 with *n*-butyllithium[2] gave 1,4-diphenylbutadiene in 12% yield. The Meerwein reaction between, for example, benzenediazonium chloride and cinnamylidene acetic acid,[3] has also been employed in the synthesis of diarylbutadienes. Probably the most widely used reaction has been the Perkin or Kuhn condensation of a β-arylacrolein with an arylacetic acid in the presence of lead oxide.[4,5] This is the basis of the *Organic Syntheses* preparation of diphenylbutadiene in 25% yield.[4a] A variation of this latter method is the condensation of two molecules of an aromatic aldehyde with succinic acid in the presence of lead oxide.[5] 1,4-Bis(4-phenylbutadienyl)benzene has been prepared in low over-all yield by similar techniques.[4b]

The synthesis of 1,4-diarylbutadienes and of 1,4-bis(arylbutadienyl)benzenes may be carried out conveniently in two steps, and in high over-all yields using the Wittig synthesis in an extension of

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