Alkylations of Benzhydryl-Type Alkanes and Alkenes by Means of Alkali Amides and Metals in Liquid Ammonia to Form $(C_6H_5)_2CRR'$[1]

WILLIAM S. MURPHY AND CHARLES R. HAUSER

Department of Chemistry, Duke University, Durham, North Carolina

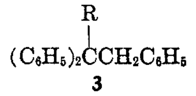
Received November 2, 1965

1,1,2-Triphenylethane was converted by potassium amide, and 1,1,2-triphenylethene by sodium, in liquid ammonia to a common, red carbanion that underwent alkylation with alkyl and aralkyl halides and twofold alkylation with 1,4-dibromobutane to form corresponding derivatives in satisfactory yields. Similarly, 1,1-diphenylbutane and 1,1-diphenylbutene were converted to a common, red carbanion that underwent such alkylations. Also, 1,1,3-triphenylpropene was benzylated by means of sodium. These methods appear to be quite general.

Wooster and Ryan[2] have observed that treatment of 1,1-diphenylalkanes with potassium amide or sodium amide, and of 1,1-diphenylalkenes with potassium or sodium, in liquid ammonia produces red carbanions, certain of which may be isolated as alkyl derivatives. Thus **1** and **2** were converted to a common carbanion that underwent alkylation with benzyl chloride to form the same product, presumably **3** ($R = CH_2C_6H_5$). However, few details and no yields were given.

$(C_6H_5)_2CHCH_2C_6H_5$ $(C_6H_5)_2C{=}CHC_6H_5$

1 **2**

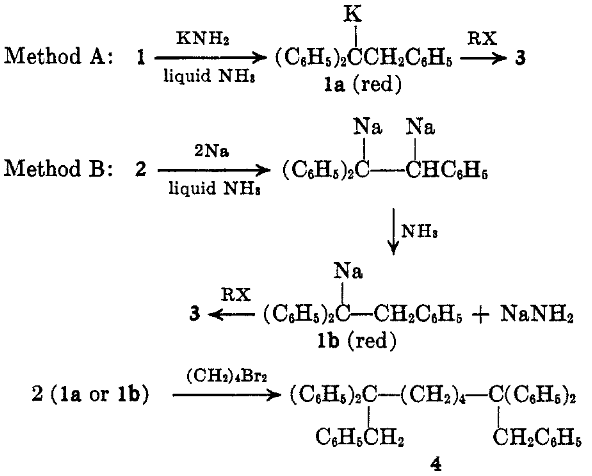


$$(C_6H_5)_2\overset{R}{\overset{|}{C}}CH_2C_6H_5$$

3

We have now developed and extended these two types of reactions to afford useful methods for the synthesis of various alkyl derivatives. Preliminary experiments indicated that potassium amide, but not sodium amide, is satisfactory with saturated hydrocarbon **1** (method A), and that both potassium and sodium are suitable with olefin **2** (method B). At least when sodium is employed, however, the halide should be added immediately after the intermediate, red monocarbanion is prepared from **2** (through rapid ammonolysis of an intermediate 1,2 dicarbanion),[3] since the monocarbanion soon undergoes partial, further ammonolysis to produce hydrocarbon **1**.[4] Thus, **1** was alkylated by means of potassium amide, and **2** by means of sodium, to form several alkyl derivatives **3** and bis derivatives **4** (Scheme I). The results are summarized in Table I.

SCHEME I



$$\text{Method A:}\quad 1 \xrightarrow[\text{liquid } NH_3]{KNH_2} (C_6H_5)_2\overset{K}{\overset{|}{C}}CH_2C_6H_5 \xrightarrow{RX} 3$$

$$\text{1a (red)}$$

$$\text{Method B:}\quad 2 \xrightarrow[\text{liquid } NH_3]{2Na} (C_6H_5)_2\overset{Na}{\overset{|}{C}}-\overset{Na}{\overset{|}{C}}HC_6H_5 \xrightarrow{NH_3}$$

$$3 \xleftarrow{RX} (C_6H_5)_2\overset{Na}{\overset{|}{C}}-CH_2C_6H_5 + NaNH_2$$

$$\text{1b (red)}$$

$$2\,(\text{1a or 1b}) \xrightarrow{(CH_2)_4Br_2} (C_6H_5)_2\underset{C_6H_5CH_2}{\underset{|}{C}}-(CH_2)_4-\underset{CH_2C_6H_5}{\underset{|}{C}}(C_6H_5)_2$$

$$4$$

In method A in which 1 mole equiv of potassium amide was employed, less than 1 mole equiv of an alkyl or aralkyl halide was required to discharge the red color of intermediate potassio salt **1a**; this indicated that not all of **1** was converted to **1a** by the amide and that this amide present in equilibrium reacted with the halide.[4] To minimize formation of side reaction products from the amide, only sufficient halide was added to discharge the red color (see Table I). Although the crude product contained some unchanged hydrocarbon **1** and by-products, essentially pure alkyl derivatives **3** were generally obtained after one or two recrystallizations.

In method B in which 2 g-atoms of sodium were used, more than 1 mole equiv of an alkyl or aralkyl halide was required to discharge the red color of intermediate sodio salt **1b**; this is not surprising since the reagent contained 1 mole equiv each of **1b** and sodium amide, both of which can react with the halide. It was found expedient to use only 1 equiv of benzyl chloride, since this halide was converted by sodium amide to stilbene (see eq 1,[5] shown below), which was somewhat difficult to remove from the desired alkylation product **3** ($R = CH_2C_6H_5$). Actually, the crude product obtained under these conditions consisted of 71% of **3**, only 4% stilbene, and 25% of starting compound **1** (by vpc); from this mixture **3** was isolated in good yield (see Table I). Evidently the halide reacted preferentially with sodio salt **1b** rather than with sodium amide.[6] More than 1 equiv of the other halides studied were used (see Table I), and no difficulty was encountered in removing by-products from alkylation products **3** (see Table 1).

$$2C_6H_5CH_2Cl \xrightarrow[\text{liquid } NH_3]{2NaNH_2} C_6H_5CH{=}CHC_6H_5 \qquad (1)$$

In both methods A and B, β phenylethylation of the carbanion was accompanied by appreciable β elimina-

---

[1] Supported by the National Science Foundation.

[2] C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **54**, 2419 (1932).

[3] The initially formed reaction mixture, which is black, may contain not only the 1,2 carbanion (see Scheme I) but also the corresponding ion radical in equilibrium with the dicarbanion and olefin; see, *e.g.*, N. L. Bauld, M. S. Brown, *J. Am. Chem. Soc.*, **87**, 4390 (1965); N. L. Bauld, D. Banks, *ibid.*, **87**, 128 (1965); J. F. Garst, E. R. Zabolotny, and R. S. Cole, *ibid.*, **86**, 2257 (1964); E. R. Zabolotny, J. F. Garst, *ibid.*, **86**, 1645 (1964).

[4] The details of these experiments will be published later in connection with a current study of the influence of the metallic cation on such acid-base reactions.

[5] See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

[6] When 2 equiv of benzyl chloride was employed, the crude product consisted of 74% of **3**, 18% of stilbene, and 8% of **1** (by vpc), but essentially pure **3** was isolated in only 31% yield after several recrystallizations.

TABLE I

ALKYLATIONS OF HYDROCARBONS 1 AND 2 BY METHODS A AND B (SCHEME I)

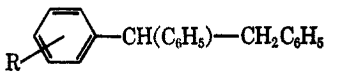
Alkyl or other halide	Mole % of halide Method A[a]	Mole % of halide Method B	Product No.	Product R	Recrystn solvent	Mp, °C	Yield, % Method A from halide	Yield, % Method A from 1	Yield, % Method B from halide	Yield, % Method B from 2
Benzyl chloride	89	100	**3**	$C_6H_5CH_2$[b]	95% ethanol	125–127[c]	84	75	65	65
α-Phenylethyl chloride	75	130[a]	**3**	$C_6H_5CH(CH_3)$[b]	Ethyl acetate	162–165	95	71	52	68
n-Butyl bromide	88	200	**3**	*n*-C_4H_9[b]	Methanol	65–67	73	64	41	82
β-Phenylethyl bromide	80	200	**3**	$C_6H_5CH_2CH_2$[b]	Ethyl acetate	170–172[d]	68	54	33	65
1,4-Dibromobutane	86	200	**4**		Chloroform, ethyl acetate	194–197	82	72	33	65

[a] Amount required to discharge red color of reaction mixture. [b] Pure by vpc. [c] Lit.[2] mp 127°. [d] Mp 170.5–173° when prepared by method B; lit.[11] mp 172°.

tion of the halide which, presumably was effected mainly by the alkali amide, eq 2.

$$C_6H_5CH_2CH_2Br \xrightarrow[\text{liquid } NH_3]{NaNH_2 \text{ or } KNH_2} C_6H_5CH{=}CH_2 \qquad (2)$$

That methods A and B produced the same alkyl derivatives was established by the mixture melting point method and by comparison of infrared spectra. That the product from benzylation by the two methods was **3** (R = $CH_2C_6H_5$), not the possible *o* or *p* derivative **5** or the mono- or dibenzyl derivative **6** or **7** (R = $CH_2C_6H_5$), was supported by its nmr spectrum, which consisted of a singlet (τ 5.35) and a multiplet (τ 1.3–2.5) in the calculated ratio of 1:5. Structure **5–7** should have a more complex spectrum.



5

$$(C_6H_5)_2CH{-}CH(R)C_6H_5$$

6

$$(C_6H_5)_2C(R){-}CH(R)C_6H_5$$

7

Table I shows that the yields of alkyl derivatives **3** and **4** based on the halide in method A and on the hydrocarbon in method B were good to excellent (65–95%). While the yields were generally lower when based on the hydrocarbon in method A and on the halide in method B, they were still fair to good (33–75%).

The starting hydrocarbons in methods A and B were both readily prepared. Saturated compound **1** was obtained in excellent yield by benzylation of diphenyl methane through sodium diphenylmethide, eq 3,[7] and olefin **2** in good yield by the reaction of benzophenone with benzylmagnesium chloride.[8]

$$(C_6H_5)_2CH_2 \xrightarrow[\text{liquid } NH_3]{NaNH_2} (C_6H_5)_2CHNa \xrightarrow{C_6H_5CH_2Cl} \mathbf{1} \qquad (3)$$

Incidentally, method A represents a further alkylation of **1**, the over-all yields of **3** from diphenylmethane being only slightly lower than those recorded in Table I.

Next, saturated hydrocarbon **8** and olefin **9** were alkylated by methods A and B, respectively, to form alkyl derivatives **10**.

$$(C_6H_5)_2CHCH_2CH_2CH_3 \qquad (C_6H_5)_2C{=}CHCH_2CH_3$$

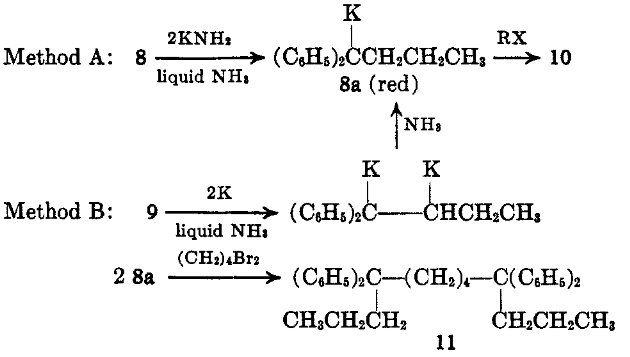
8 **9**

$$(C_6H_5)_2\overset{R}{\overset{|}{C}}CH_2CH_2CH_3$$

10

In method A, 2 mole equiv of potassium amide was used to increase the concentration of the carbanion, since a preliminary experiment with a homolog of **8**, 1,1-diphenylpentane, employing 1 mole equiv of the alkali amide afforded the benzylation product in only 49% yield (by vpc). In method B, potassium was generally used, though sodium afforded a slightly better yield in the one case that it was employed. Alkylations to form **10** and twofold alkylation to afford **11** are shown in Scheme II. The results are summarized in Table II.

SCHEME II



$$\text{Method A:}\quad \mathbf{8} \xrightarrow[\text{liquid } NH_3]{2KNH_2} \underset{\mathbf{8a}\ (\text{red})}{(C_6H_5)_2\overset{K}{\overset{|}{C}}CH_2CH_2CH_3} \xrightarrow{RX} \mathbf{10}$$

$$\uparrow NH_3$$

$$\text{Method B:}\quad \mathbf{9} \xrightarrow[\text{liquid } NH_3]{2K} (C_6H_5)_2\overset{K}{\overset{|}{C}}{-}\overset{K}{\overset{|}{C}}HCH_2CH_3$$

$$2\ \mathbf{8a} \xrightarrow{(CH_2)_4Br_2} (C_6H_5)_2\underset{CH_3CH_2CH_2}{\underset{|}{C}}{-}(CH_2)_4{-}\underset{CH_2CH_2CH_3}{\underset{|}{C}}(C_6H_5)_2$$

11

Since an extra equivalent of potassium amide was used in method A and 1 equiv of this base was formed in method B (not shown in Scheme II), the alkylations by both methods were accompanied by the formation of stilbene from benzyl chloride and of styrene from β-phenylethyl bromide (see Experimental Section). Although no attempt was made to remove the stilbene in method A, this by-product was removed by distillation in method B (see Table II).

The structures of alkyl derivatives **10** and **11** were supported by their nmr spectra (Table IV). These spectra showed no chemical shifts for vinylic hydrogens indicating that the products were saturated and were uncontaminated with the starting olefin **9**.

Table II shows that the yields of **10** and **11** were 45–66% based on saturated hydrocarbon **8**, and 35–53% based on olefin **9**. Since the yields from olefin **9** and somewhat lower than those obtained from olefin **2** (See Table I), they could probably be improved. Hydrocarbon **8** was readily prepared in excellent yield by alkylation of diphenylmethane by means of sodium amide (see eq 3), and olefin **9** in good yield by reaction of *n*-butyrophenone with phenylmagnesium bromide, followed by dehydration (see Experimental Section).

---

[7] C. R. Hauser and P. J. Hamrick, Jr., *J. Am. Chem. Soc.*, **79**, 3142 (1957).

[8] H. Adkins and W. Zartman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 606.

TABLE II

ALKYLATIONS OF HYDROCARBONS 8 AND 9 BY METHODS A AND B (SCHEME II)

	Mole % of halide		Product					Yield,[b] %	
Alkyl or other halide	Method A[a]	Method B	No.	R	Recrystn solvent	Mp, °C	Bp (mm), °C	Method A	Method B
Benzyl chloride	160	200	**10**	$C_6H_5CH_2$[c]	Methanol	108–111	...	66[d]	53
n-Butyl bromide	160	200	**10**	*n*-C_4H_9[c]	...	...	130 (1.5)	55	49
β-Phenylethyl bromide	200	200	**10**	$C_6H_5CH_2CH_2$[c]	95% ethanol	92–95	190 (2)	45	39
1,4-Dibromobutane	200	200	**11**	...	Methanol	146–149	...	62	35 (41[e])

[a] Amount required to discharge red color of reaction mixture. [b] Based on hydrocarbon. [c] Pure by vpc. [d] By vpc; not isolated. [e] Yield of **11** when sodium was used instead of potassium.

TABLE III

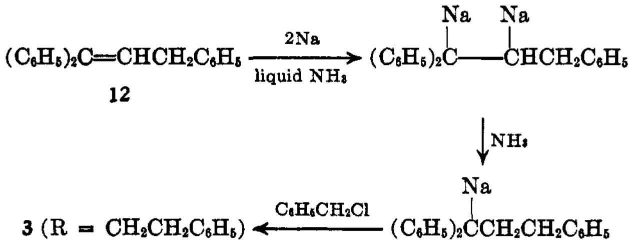
ANALYSES FOR NEW PRODUCTS

Product			Empirical	Calcd, %		Found, %	
No.	R	Name	formula	C	H	C	H
3	*n*-C_4H_9	1,2,2-Triphenylhexane	$C_{24}H_{26}$	91.67	8.27	91.70	8.44
3	$C_6H_5CH(CH_3)$	1,2,2,3-Tetraphenylbutane	$C_{28}H_{26}$	92.77	7.23	93.06	7.19
4		1,2,2,7,7,8-Hexaphenyloctane	$C_{44}H_{42}$	92.58	7.42	92.79	7.49
10	*n*-C_4H_9	4,4-Diphenyloctane	$C_{20}H_{26}$	90.16	9.84	90.31	9.70
10	$C_6H_5CH_2$	1,2,2-Triphenylpentane	$C_{23}H_{24}$	91.95	8.05	92.16	7.93
10	$C_6H_5CH_2CH_2$	1,3,3-Triphenylhexane	$C_{24}H_{26}$	91.67	8.28	91.54	8.33
11		4,4,9,9-Tetraphenyldodecane	$C_{36}H_{24}$	91.08	8.92	90.86	8.78

It should be pointed out that, although the alkylation products listed in Tables I and II melted over 2 or 3°, they were indicated to be pure by vpc, nmr, and/or analyses (see Table III). The yields in Tables I and II were based on these essentially pure compounds.

Finally, method B was extended to olefin **12** with which sodium was employed The intermediate sodio salt was alkylated with benzyl chloride to afford **3** (R = $CH_2CH_2C_6H_5$) in 39% yield (Scheme III).

SCHEME III



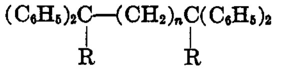
$$(C_6H_5)_2C{=}CHCH_2C_6H_5 \xrightarrow[\text{liquid NH}_3]{2\text{Na}} (C_6H_5)_2\overset{\text{Na}}{\overset{|}{C}}{-}\overset{\text{Na}}{\overset{|}{C}}HCH_2C_6H_5 \xrightarrow{\text{NH}_3} (C_6H_5)_2\overset{\text{Na}}{\overset{|}{C}}CH_2CH_2C_6H_5 \xrightarrow{C_6H_5CH_2Cl} \mathbf{3}\ (R = CH_2CH_2C_6H_5)$$

12

It may be concluded from these results that method A and/or B may be satisfactory for the synthesis of various hydrocarbons of types **13** and **14** in which R and R′ in **13** are the same or different alkyl or aralkyl groups and *n* in **14** is 1–4; bis derivatives **14** in which R is hydrogen have been prepared by twofold alkylations of sodium diphenylmethide with the appropriate methylene halides.[9] Also, R or R′ might contain a functional substituent such as β-diethylamino or β-hydroxyl, since R groups containing these substituents have previously been introduced into diphenylmethane through alkylations of alkali diphenylmethide with β-diethylaminoethyl chloride and ethylene oxide, respectively.[10]

$$(C_6H_5)_2CRR'$$

13



$$(C_6H_5)_2\underset{\underset{R}{|}}{C}{-}(CH_2)_n\underset{\underset{R}{|}}{C}(C_6H_5)_2$$

14

The present methods appear more convenient than an earlier one[11] in which a methyl ether such as **15** was cleaved by sodium in ethyl ether during 8 weeks; the resulting sodio intermediate **1b** was alkylated with β-phenylethyl chloride to form **3** (R = $CH_2CH_2C_6H_5$), eq 4, but the yield was not reported.[11]

$$\underset{\mathbf{15}}{(C_6H_5)_2C(OCH_3)CH_2C_6H_5} \xrightarrow[\text{ether}]{\text{Na}} \mathbf{1b} \xrightarrow{\text{RX}} \mathbf{3} \qquad (4)$$

Experimental Section[12]

Alkylations of Hydrocarbon 1 and Olefin 2 to Form Derivatives 3 and 4.—In Table I are summarized the yields and other data for alkylations of saturated hydrocarbon **1**[7] and **2**[8] by methods A and B, respectively (see Scheme I). The general procedures are given below.

Method A.—To a stirred solution of 0.0275 mole of potassium amide in 300 ml of commercial, anhydrous liquid ammonia[13] was added 6.4 g (0.025 mole) of 1,1,2-triphenylethane (**1**) in 100 ml of dry ether to produce immediately the red potassio salt **1a**. More ether was added when necessary to ensure complete solubility. After 10–15 min, solution of 0.0275 mole of an appropriate halide in 60 ml of dry ether was added dropwise over 5–10 min from a graduated dropping funnel until the red color was discharged;[14] then addition was stopped, and the amount of the remaining halide solution was measured (see Table I). The resulting suspension was placed on the steam bath and stirred until the liquid ammonia had evaporated. Ether and water were added to the resulting ethereal suspension, and the mixture was shaken. The two layers were separated. The ethereal layer (with which was combined an ethereal extract of the aqueous layer) was dried over anhydrous magnesium sulfate, and the solvent was removed. The residue was recrystallized from an appropriate solvent to afford the alkyl derivatives **3** (see Table I). The residue from the reaction with β-phenylethyl bromide, which contained polystyrene, was triturated with cold ligroin (bp 30–

---

[9] C. R. Hauser, C. F. Hauser, and P. J. Hamrick, Jr., *J. Org. Chem.*, **24**, 397 (1959).

[10] C. R. Hauser, M. T. Tetenbaum, and R. S. Yost, *ibid.*, **23**, 916 (1958).

[11] W. Schlenk and E. Bergmann, *Ann.*, **479**, 78 (1930).

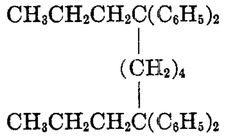
[12] Melting points (Uni-Melt capillary melting point apparatus) and boiling points are uncorrected. An F and M Model 500 programmed temperature gas chromatograph equipped with a Disc chart integrator with a 2-ft column of 10% Silicone Gum Rubber SE 30 (Wilkins Instrument and Research, Inc.) on 60–80 mesh Chromosorb W, was used. The carrier gas was helium. All nmr spectra were investigated (carbon tetrachloride solvent) on a Varian A-60 high resolution spectrometer.

[13] In all experiments the liquid ammonia was further dried by the addition of small pieces of alkali metal until the blue color persisted.

[14] In the reaction with benzyl chloride, a slight, transient purple flash associated with the formation of stilbene was observed but this could be readily distinguished from the red color of the carbanion.

TABLE IV

NMR SPECTRA OF PRODUCTS LISTED IN TABLE II

Compd	Type of hydrogen	Shifts, τ	Relative areas Found	Relative areas Calcd
$C_6H_5CH_2C(C_6H_5)_2CH_2CH_2CH_3$	Aromatic	2.50–3.70[a]	14.8	15
	Benzylic	6.67[b]	1.8	2
	Methyl, methylenes	7.85–9.20[a]	7.6	7
$CH_3(CH_2)_3C(C_6H_5)_2CH_2CH_2CH_3$	Aromatic	2.60–3.10[a]	9.6	10
	Methyl, methylenes	7.65–9.50[a]	16.3	16
$C_6H^cCH_2CH_2C(C_6H_5)_2CH_2CH_2CH_3$	Aromatic	2.50–3.20[a]	14.8	15
	Methyl, methylenes	7.40–9.20[a]	11.2	11
 $CH_3CH_2CH_2C(C_6H_5)_2-(CH_2)_4-C(C_6H_5)_2CH_2CH_2CH_3$	Aromatic	2.93[b]	19.6	20
	Methyl, methylenes	7.81–9.20[a]	22.4	22

[a] Multiplet. [b] Singlet.

60°) and the mixture was filtered. The solid on the funnel was recrystallized to give the alkyl derivative **3**.

In the reaction with 1,4-dibromobutane, the ethereal suspension obtained on evaporating the liquid ammonia was reduced in volume and filtered. The solid was recrystallized.

Method B.—To a stirred mixture of 6.4 g (0.025 mole) of 1,1,2-triphenylethene (**2**) in 50 ml of dry ether and 300 ml of anhydrous liquid ammonia[13] was added 1.26 g (0.055 g-atom) of sodium in small pieces. If the reaction became too vigorous stirring was stopped. The mixture was initially black, then transiently purple, and finally deep red. As soon as these changes in color had occurred, which generally required about 10 min, a solution of 1–2 mole equiv (0.025–0.055 mole) of the appropriate halide[15] in 60 ml of ether was added with stirring (see Table I). The reaction mixtures were worked up essentially as described above under method A.

1,1-Diphenylbutane (8) and 1,1-Diphenylpentane.—1,1-Diphenylbutane was prepared by alkylation of diphenylmethane with *n*-propyl bromide by means of sodium amide in liquid ammonia, essentially as described previously for related alkylations.[7] The product **8** obtained in 87% yield (pure by vpc), boiled at 154–156° (10 mm) [lit.[16] bp 145° (16 mm)]. Its nmr spectrum showed a singlet (τ 2.9, aromatic), a triplet (τ 6.19, J = 7.5 cps, benzhydrylic), and a complex multiplet (τ 7.70–9.35, aliphatic) in the calculated ratio 10:1:7.

Similarly, 1,1-diphenylpentane, which was obtained in 92% yield (pure by vpc), boiled at 138–139° (1.5 mm), $n^{26}D$ 1.5501 [lit.[17] bp 80–81° (0.005 mm), $n^{20}D$ 1.5510]. Its nmr spectrum showed a multiplet (τ 8.50–7.0, aromatic), a triplet (τ 6.13, J = 7.5 cps, benzhydrylic), and a complex multiplet (τ 3.67–1.43, aliphatic) in the calculated ratio 10:1:9.

1,1-Diphenyl-1-butene (9).—This olefin was prepared from 74 g (0.5 mole) of butyrophenone and phenylmagnesium bromide (obtained from 1.1 moles each of bromobenzene and magnesium) in 200 ml of ether essentially as described for olefin **2**.[8] The intermediate carbinol was refluxed 1 hr with 200 ml of 20% sulfuric acid to give 57 g (54%) of olefin **9** (pure by vpc), bp 268–269° (750 mm) [lit.[18] bp 108–110° (0.4 mm)]. Its nmr spectrum showed a multiplet (τ 2.50–3.25), a triplet (τ 4.00, J = 7.5 cps), a quintuplet (τ 7.95, J = 7.0 cps), and a triplet (τ 9.1, J = 7.5 cps) in the calculated ratio 10:1:2:3.

Alkylations of Hydrocarbon 8 and Olefin 9 to Form 10 and 11.—In Table II are summarized the yields and other data for alkylations of **8** and **9** by methods A and B, respectively (see Scheme II), while Table IV outlines the nmr spectra of these products. The general procedures are indicated below.

Method A.—To a stirred solution of 0.055 mole of potassium amide in 300 ml of anhydrous liquid ammonia[13] was added 5.2 g (0.025 mole) of 1,1-diphenylbutane (**8**) in 60 ml of dry ether to produce immediately the red potassio salt **8a**. After 10–15 min, a solution of 0.05 mole of an appropriate halide in 60 ml of dry ether was added dropwise until the red color was discharged[15] (see Table II), and the liquid ammonia was then evaporated. The resulting ethereal suspension was shaken with water (and more ether), and the alkylation product was isolated from the ethereal layer (see method A under hydrocarbon **1**). The product from *n*-butyl bromide was distilled and that from β-phenylethyl bromide was distilled and then recrystallized. The product from 1,4-dibromobutane was purified by recrystallization.

Method B.—To a stirred mixture of 5.2 g (0.025 mole) of 1,1-diphenylene (**9**) in 300 ml of anhydrous liquid ammonia[13] was added 2.3 g (0.055 g-atom) of potassium in small pieces. A red color formed immediately. No transient purple color was observed. When addition was complete, the solution was stirred 5 min. A solution of 0.05 mole of an appropriate halide in 60 ml of dry ether was then added[15] and the liquid ammonia was removed. The resulting ethereal suspension was shaken with water (and more ether), and the alkylation product was isolated from the ethereal layer (see method B under olefin **2**). The product from benzylation was initially purified by subliming off the stilbene[15] and then recrystallizing the residue; that from β-phenyl ethyl bromide was triturated with cold ligroin (bp 30–60°), filtered, and recrystallized. Purification of the product from 1,4-dibromobutane required only recrystallization.

Benzylation of Olefin 12 to Form 3 (R = $CH_2CH_2C_6H_5$).—To a stirred solution of 0.055 g-atom of sodium in 300 ml of anhydrous liquid ammonia was added 6.5 g (0.025 mole) of 1,1,3-triphenylpropene (**12**)[19] in 60 ml of dry ether to produce immediately a deep red color. After 10 min, 6.35 g (0.05 mole) of benzyl chloride in 60 ml of dry ether was added dropwise (5 min),[15] and the reaction mixture was worked up as described above for olefin **2** under method B. The residue was washed with cold ether and recrystallized from ethyl acetate to give 3.5 g (39%) of 1,2,2,4-tetraphenylbutane, mp 170–172°, which was undepressed on admixture with a sample of **3** (R = $CH_2C_6H_5$) prepared by β-phenylethylation of hydrocarbon **1** or olefin **2** (see Table I). The infrared spectra of the samples were identical.

---

(15) In the reaction with benzyl chloride, purple coloration occurred (indicating stilbene formation) such that the red of the carbanion could not be distinguished readily.

(16) V. N. Ipatieff, H. Pines, and R. E. Schaad, *J. Am. Chem. Soc.*, **66**, 816 (1944).

(17) H. Gilman and B. J. Gaj, *ibid.*, **82**, 6326 (1960).

(18) A. W. Schmidt and C. Hartmann, *Ber.*, **74B**, 1325–32 (1942).

(19) C. F. Koelsch and P. R. Johnson, *J. Org. Chem.*, **6**, 534 (1941).