ion canonical structure, II_c, to the over-all resonance hybrid of the transition state.

$$R-H \cdot CCl_3 \longleftrightarrow R \cdot H-CCl_3 \longleftrightarrow R^+ H \cdot CCl_3$$
 $II_a \qquad II_b \qquad II_c$

The results already obtained suggest that studies involving hydrogen abstraction from other substituted rigid systems may prove capable of assessing the mode

of transmission of electronic effects in radical reactions. Work has already begun on the 1-substituted bicyclo-[2.2.2]octane system. 35

Acknowledgments. We wish to thank Professor J. C. Decius for many helpful discussions on the manipulation of the Kirkwood-Westheimer equations.

(35) G. J. Gleicher, et al., work in progress.

Displacement on Halogen vs. Carbon and on Halogen vs. Hydrogen of Certain Polyhalides by Diphenylmethide Ion in Liquid Ammonia

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Abstract: Sodium and potassium diphenylmethide (I'), prepared from diphenylmethane (I) and the corresponding alkali amide in liquid ammonia, underwent displacement on halogen with ethylene bromide and iodide to form the dimer, 1,1,2,2-tetraphenylethane (III), and presumably ethylene; in contrast, I' underwent displacement on carbon (SN2) with ethylene chloride to give the twofold alkylation product. Similarly, potassio salt I' underwent displacement on halogen with 2,3-dibromo-2,3-dimethylbutane, 1,1,2,2-tetrabromoethane, and hexachloroethane to form dimer III and an olefinic product. The olefinic products from the tetrabromo- and hexachloroethanes were dibromoethylene and tetrachloroethylene, respectively; potassio salt I' also underwent displacement on halogen with these olefinic halides to afford apparently acetylene. Potassio salt I' underwent displacement on hydrogen with 1,1-dichloroethane to regenerate I, and displacement on halogen with 1,1,1-trichloroethane and benzotrichloride to form a mixture of I and III; in these cases the halide was converted to an aldimine. Potassio salt I' underwent displacement on halogen with N-bromosuccinimide to give dimer III and succinimide.

The diphenylmethide ion I', which is readily pre-pared from sodium amide or potassium amide in liquid ammonia (eq 1), has previously been shown to undergo displacement on carbon with alkyl halides¹ and certain dihalides,2 displacement on halogen with carbon tetrachloride and bromotrichloromethane,3 and displacement on hydrogen with chloroform.3 In order to ascertain the influence of the structure of the halide on the course of reaction, a study of the reactions of various other halides with anion I' was made.

$$(C_6H_5)_2CH_2 \xrightarrow{MNH_2 (liq NH_2)} (C_6H_5)_2CHM$$
 (1)

I

I'

Results with Vicinal Dihalides. Sodium diphenylmethide (I', M = Na) has been shown² to undergo twofold alkylation with ethylene chloride to form hydrocarbon II in excellent yield (eq 2, M = Na).

$$2I' \xrightarrow{\text{ClCH}_2\text{CH}_2\text{Cl}} (C_6\text{H}_5)_2\text{CHCH}_2\text{CH}_2\text{CH}(C_6\text{H}_5)_2 \qquad (2)$$
II

We have found that potassium diphenylmethide (I', M = K) similarly reacts with ethylene chloride to afford hydrocarbon II, but, more significantly, that both sodium and potassium diphenylmethides react with ethylene bromide or iodide under similar conditions to produce little if any of hydrocarbon II. Instead, the dimeric product, 1,1,2,2-tetraphenylethane (III), was isolated in yields of 60-67%. Presumably ethylene was also produced (eq 3).

2I'
$$\xrightarrow{\text{BrCH}_2\text{CH}_2\text{Br}}$$
 (C₆H₅)₂CHCH(C₆H₅)₂ + CH₂=CH₂ (3)

This complete change in the course of the reaction brought about merely by changing the halogen from chlorine to bromine or iodine is rather remarkable, and represents one of the first such changes reported. The mechanism of the twofold alkylation (eq 2) presumably involves displacement on carbon (SN2), and that of the dimerization (eq 3) displacement on halogen accompanied by β elimination of halide ion, followed by alkylation of unchanged diphenylmethide ion by the resulting benzhydryl bromide or iodide (eq 4).4

$$(C_6H_5)_2\overline{C}H_2 \xrightarrow{\Gamma} Br \xrightarrow{\Gamma} (C_6H_5)_2CHBr \xrightarrow{\Gamma'} III$$
(4)

⁽¹⁾ C. R. Hauser and P. J. Hamrick, J. Am. Chem. Soc., 79, 3142 (1957).
(2) C. R. Hauser, C. F. Hauser, and P. J. Hamrick, J. Org. Chem., 24,

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⁽³⁾ C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, ibid., 26, 2627 (1961).

⁽⁴⁾ The intermediate benzhydryl halide has been isolated in the related coupling of diphenylmethide ion with carbon tetrachloride: W. G. Kofron and C. R. Hauser, ibid., 28, 577 (1963).

Such a change in the course of the reaction is so far limited to vicinal dihalides, since methylene iodide, like methylene chloride reported previously,² was found to effect twofold alkylation of potassium diphenylmethide to form IV, and 1,3-dibromopropane has also been shown² to effect twofold alkylation of I' to give hydrocarbon V.

$$(C_6H_5)_2CHCH_2CH(C_6H_5)_2 \qquad \qquad (C_6H_5)_2CHCH_2CH_2CH_2CH(C_6H_5)_2 \\ IV \qquad \qquad V$$

Similarly, potassium diphenylmethide underwent coupling with several other vicinal polyhalides to form the dimeric hydrocarbon III. The yields (based on starting di henylmethide) and the amount of each halide required to discharge the orange color of I' are summarized in Table I.

Table I. Yields of Coupled Product III from Alkali Diphenylmethides and Vicinal Halides in Liquid NH₃

Halide	M (I')	Ratio I':halide	Yield,
BrCH₂CH₂Br	Na	2:1	67
BrCH₂CH₂Br	K	2:1	62
ICH₂CH₂I	K	2:1	60
$(CH_3)_2CBrCBr(CH_3)_2$	K	2:1	98
Br ₂ CHCHBr ₂	K	5:1	63
BrCH=CHBr	K	3:1	77
Cl3CCCl3	K	2:1	66 ⁸
Cl ₃ CCCl ₃	K	8:1	96
Cl ₂ C=CCl ₂	K	6:1	80

 $[^]a$ Yields of hydrocarbon III based on starting diphenylmethide. b Much (53%) of the starting halide was recovered.

Interestingly, while the dihaloalkanes, ethylene bromide, ethylene iodide, and 2,3-dibromo-2,3-dimethylbutane, neutralized 2 molecular equiv of diphenylmethide ion I', tetrabromoethane neutralized 5 equiv of I'; that is, the orange color of I' was discharged when approximately 0.2 equiv of the tetrahalide had been added (see Experimental Section). Moreover, dibromoethylene, presumably an intermediate from the tetrabromide, itself neutralized 3 equiv of I'. The final product in these reactions, the acetylide ion VI, was detected in one experiment after reaction with bromobutane, as the alkylation product, 1-hexyne, isolated as the mercuric salt (eq 5).

$$\begin{array}{c} Br_{2}CHCHBr_{2} \xrightarrow{2I'} BrCH = CHBr \xrightarrow{2I'} HC \equiv CH \xrightarrow{I'} \\ HC \equiv C^{-} \xrightarrow{C_{4}H_{9}Br} HC \equiv CC_{4}H_{9} \quad (5) \end{array}$$

Hexachloroethane similarly underwent stepwise reaction with at least 8 molar equiv of potassium diphenylmethide to produce dimeric hydrocarbon III. The reaction was shown to take place in several steps by the isolation of tetrachloroethylene as well as III from the reaction of hexachloroethane and I', and by the formation of dimer III from the reaction of I' with tetrachloroethylene (eq 6). The final product from the

$$Cl_3CCCl_3 \xrightarrow{I'} Cl_2C = CCl_2 \xrightarrow{I'} ClC = CCl \xrightarrow{I'} HC = CH \quad (6)$$

hexachloroethane is presumed to be an anion of acetylene. Thus, a cuprous salt was formed when a stream of nitrogen was passed through the reaction mixture, after neutralization, and into an ammoniacal cuprous solution.⁵

It can be seen from Table I that 2,3-dibromo-2,3-dimethylbutane gives the highest conversion of carbanion I' to dimer III. Thus, in contrast to displacement on carbon (SN2 reaction), which was not observed with tertiary butyl chloride and I' in liquid ammonia,¹ displacement on halogen actually proceeds better with the ditertiary halide than with ethylene bromide. Similarly, the vinylic halides, dibromoethylene and tetrachloroethylene, react readily with I' by the displacement on halogen reaction.

Results with 1,1-Dihalides and 1,1,1-Trihalides. Previously, the diphenylmethide ion I' has been shown to undergo displacement on carbon with methylene chloride,² but displacement on hydrogen with chloroform.³ We have now found that I' undergoes displacement on hydrogen with 1,1-dichloroethane (eq 7); that is, this

ride,² but displacement on hydrogen with chloroform.³
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CH₃CHCl₂
$$\xrightarrow{I'}$$
 I + CH₃CCl₂ $\xrightarrow{-Cl^-}$

CH₃CCl $\xrightarrow{NH_3}$ CH₃CHClNH₂ (7)

I + CH₃CH=NH

halide reacts like chloroform rather than methylene chloride. This result is interesting since although the

halide reacts like chloroform rather than methylene chloride. This result is interesting since, although the added methyl group should decrease the acidity of the 1 proton of dichloroethane relative to methylene chloride, the added steric effect of the methyl group apparently hinders displacement on carbon so that displacement on hydrogen takes place. Presumably the anion formed by removal of the proton reacts similarly to the trichloromethyl anion from chloroform, losing chloride ion to form a chlorocarbene which adds ammonia, followed by β elimination of hydrogen chloride to afford acetaldimine (see eq 7). A derivative of this product was isolated.

Previously, anion I' has been shown to undergo displacement on halogen with carbon tetrachloride. We have now found that I' reacts similarly with 1,1,1-trichloroethane and benzotrichloride (VII, $R = CH_3$ and C_6H_5 , respectively); the products were dimer III and the corresponding aldimine, derivatives of which were isolated (eq 8). Presumably a chlorocarbene was an intermediate in the formation of the aldimine from the dichlorocarbene (see eq 7).

$$\begin{array}{cccc}
RCCl_3 & \xrightarrow{I'} R\overline{C}Cl_2 & + & (C_6H_5)_2CHCl \\
VII & & \downarrow^{I'}, NH_4 & & \downarrow^{I'} & (8) \\
I + RCH = NH & III
\end{array}$$

These results, together with earlier ones with chloroform and carbon tetrachloride, are summarized in Table II. It should be noted that the aldimine produced with the present halides corresponds to the cyanide ion which was obtained in almost quantitative yield from chloroform and carbon tetrachloride. The lower yields of the aldimines realized were due in part to their volatility and water solubility, and perhaps to their ability to undergo self-condensation reactions.

Displacement on Halogen in Synthesis. Table I shows that the best yields (96-98%) of tetraphenyl-

(5) See F. Feigl, "Spot Tests in Organic Analysis," 7th ed, Elsevier Publishing Co., New York, N. Y., 1966, p 405.

Table II. Reactions of Potassium Diphenylmethide with Terminal Polyhalides

Halide	Ratio I':halide	Hydro- carbon product	Yield,	Other product (%)
CHCl ₃ ^a	4:1	I	85	CN- (92)
CCl_4^a	5:1	III	89	CN-(85)
		I	78	•
CH ₃ CHCl ₂	2:1	I	70	$CH_3CH=NH$ (11)
CH ₃ CCl ₃	3:1	I	96	CH ₃ CH=NH (12)
		III	96	, ,
C ₆ H ₅ CCl ₃	3:1	I	93	$C_6H_5CH=NH$ (26)
• • •		III	83	. ,

^a Reference 3.

ethane (III) from the dimerization of I' were obtained with 2,3-dibromo-2,3-dimethylbutane and hexachloroethane. Although equally high yields of III are reported in Table II, they are based on the stoichiometry of eq 8, and do not represent conversion of I' to III. In these reactions, part of anion I' was consumed in an acid-base reaction to regenerate I (see eq 8).

Also, the monohalide, N-bromosuccinimide (NBS), was found to effect coupling of potassium diphenylmethide in liquid ammonia to form III in high yield (82%); succinimide was obtained in 76% yield (eq 9).

These three halides appear to be the most useful of those here reported for effecting the dimerization of carbanions. Actually, 2.3-dibromo-2.3-dimethylbutane, from which 2,3-dimethyl-2-butene is the byproduct, has previously been employed for effecting the dimerization of potassio salts VIII (R = alkyl) in ether6 and of sodio salts IXa7 and IXb8 in liquid ammonia.

$$(C_{e}H_{5})_{2}CK$$

$$R$$

$$VIII \qquad IXa, Y = o. \text{ or } p \cdot CN$$

$$b, Y = p \cdot SO_{2}N(CH_{3})_{2}$$

$$X$$

Such halides with which carbanions undergo displacement on halogen may also be useful for introducing halogen into certain molecules, as illustrated recently by iodination of lithiobenzyldimethylamine (X) and chlorination of lithiodimethylaminomethylferrocene with methylene iodide and hexachloroethane, respectively.9

Experimental Section¹⁰

Reactions of Alkali Diphenylmethides with Vicinal Dihalides. In Table I are summarized the results obtained with various halides. The details of some typical experiments are described below. Several of the reactions reported in Table I with potassium diphenylmethide were also carried out with sodium diphenylmethide, with only minor variations in the yields.

A. Reaction with Ethylene Bromide. To a stirred solution of 0.05 mol of sodium diphenylmethide in 200 ml of liquid ammonia³ was added an ethereal solution of 4.7 g (0.025 mol) of ethylene bromide. The orange color was discharged, and a white solid (III, and probably inorganic salts) separated. The ammonia was evaporated and the residue was stirred with water and ether and filtered. The solid was recrystallized from methylene chlorideethanol to give 5.6 g (67%) of 1,1,2,2-tetraphenylethane, mp and mmp 210-211°,

In another experiment, an ethereal solution of 2.35 g (0.012 mol) of ethylene bromide just discharged the orange color of 0.025 mol of potassium diphenylmethide³ in 125 ml of liquid ammonia. The tetraphenylethane, isolated as above, weighed 2.6 g (62%), mp and mmp 210-211°.

- B. Reaction with 2,3-Dibromo-2,3-dimethylbutane. To a solution of 0.025 mol of potassium diphenylmethide in 125 ml of ammonia and a little ether was added an ethereal solution of 3.05 g (0.012 mol) of 2,3-dibromo-2,3-dimethylbutane. 11 The orange color was just discharged by the halide, and a white solid separated. The mixture was stirred until the ammonia had evaporated, and the residue was stirred with ether and water and filtered. solid was recrystallized from methylene chloride-ethanol or from acetone to give 4.06 g (98%) of tetraphenylethane, mp and mmp 210-211°.
- C. Reaction with 1,2-Dibromoethylene. An ethereal solution of 6.2 g (0.033 mol) of 1,2-dibromoethylene just discharged the orange color of 0.1 mol of potassium diphenylmethide in 200 ml of liquid ammonia. To the faint pink mixture was added an ethereal solution of $5\,\mathrm{g}$ of butyl bromide. The mixture was stirred until the ammonia had evaporated, and the residue was stirred with $1\,N$ hydrochloric acid and filtered. The ethereal solution was separated, combined with 20 ml of ethanol, and distilled. The distillate boiling up to about 80° was poured into an alcoholic solution of alkaline mercuric cyanide, 12 and the precipitate was recrystallized from methanol to give 1.51 g (25%) of dihexynylmercury, mp and mmp 95.5-96°. This represents the minimum yield, and the actual yield of hexyne is probably much higher, since incorporation of the codistillation with ethanol into the published 13 synthetic procedure for 1-hexyne, followed by conversion to the mercury derivative, gave a comparable yield (27%) of the recrystallized mercuric acetylide, instead of the 70-77% reported yield of 1-hexyne.
- D. Reaction with Hexachloroethane. To a solution of 0.05 mol of potassium diphenylmethide in 200 ml of ammonia and a little ether was added an ethereal solution of 1.5 g (0.006 mol; 0.125 molar equiv) of hexachloroethane. The solution immediately turned dark brown, and the equivalence point (disappearance of orange color) could not be observed. The ammonia was evaporated and the residue was stirred with ether and water and filtered. The solid was recrystallized from acetone to give 6 g of yellowbrown crystals of tetraphenylethane, mp and mmp 210°. Several successive evaporations and recrystallizations afforded an additional 2 g of material from the mother liquors. The total yield was 8 g (96%). Decolorization of an acetone solution with Nuchar afforded colorless material.

In another experiment, the residue after evaporation of the ammonia was stirred with hydrochloric acid, and a stream of nitrogen was passed through the solution into an ammoniacal cuprous solution.⁵ A red precipitate, apparently cuprous acetylide, formed.

In another experiment, an ethereal solution of 11.83 g (0.05 mol) of hexachloroethane was added to 0.1 mol of ammoniacal potassium diphenylmethide. The dark solution was allowed to warm to room temperature as the ammonia evaporated, and the residue was stirred with hexane and water and filtered. The hexane solution was shown by gas chromatography to contain 6.33 g (53%) of hexachloroethane and 2 g (25%) of tetrachloroethylene, both identified by comparison of retention times with authentic materials. The solid was recrystallized from chloroform-ethanol to give 8.67 g (52%) of tetraphenylethane, mp and mmp 211°. A further 3.3 g of this compound was obtained from the mother liquor and the hexane solution (total, 66%).

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⁽¹⁰⁾ Melting points were determined on a Thomas-Hoover melting point apparatus, using a calibrated thermometer,

⁽¹¹⁾ A. V. Grosse and V. N. Ipatieff, J. Org. Chem., 8, 438 (1943).

⁽¹²⁾ T. H. Vaughn, J. Am. Chem. Soc., 55, 3454 (1933).
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Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 117.

Reactions of Alkali Diphenylmethides with 1,1-Dihalides and 1,1,1-Trihalides. In Table II are summarized the results obtained from the reactions with various halides. The details of typical experiments are described below.

A. Reaction with 1,1-Dichloroethane. A solution of 2.5 g (0.025 mol) of 1,1-dichloroethane in ether was added to 0.05 mol of ammoniacal potassium diphenylmethide. The ammonia was evaporated, and the residue was stirred with ethanol and filtered. The ethanolic solution was combined with an acidic solution of 5 g of 2,4-dinitrophenylhydrazine in ethanol. The yellow dinitrophenylhydrazone of acetaldehyde, mp and mmp 168° (after recrystallization from ethanol), weighed 0.62 g (11%).

B. Reaction with 1,1,1-Trichloroethane. An ethereal solution of 2.23 g (0.017 mol, 0.33 mole equiv) of 1,1,1-trichloroethane was added to 0.05 mol of potassium diphenylmethide in 200 ml of liquid ammonia. The acetaldehyde dinitrophenylhydrazone, isolated as above, weighed 0.45 g (12%); mp and mmp 168° after recrystallization from ethanol.

C. Reaction with α, α, α -Trichlorotoluene. To a solution of 0.05 mol of potassium diphenylmethide in 200 ml of liquid ammonia was added 3.29 g (0.017 mol) of α,α,α -trichlorotoluene. The benzaldehyde dinitrophenylhydrazone, isolated as above, was recrystallized from ethanol-ethyl acetate to give 1.24 g (26%) of orange crystals, mp and mmp 235-237°

Reaction of Potassium Diphenylmethide with N-Bromosuccinimide. To a solution of 0.02 mol of potassium diphenylmethide, prepared by addition of a solution of 3.36 g (0.02 mol) of diphenylmethane in tetrahydrofuran to 0.02 mol of potassium amide in 100 ml of liquid ammonia, was added a solution of 1.78 g (0.01 mol) of Nbromosuccinimide in tetrahydrofuran. The orange color gradually disappeared. The mixture was stirred as the ammonia evaporated, and the residue was stirred with carbon tetrachloride and filtered. Evaporation of the carbon tetrachloride gave 2.74 g (82%) of tetraphenylethane, mp and mmp 210°. The material insoluble in carbon tetrachloride was stirred with acetone and enough concentrated hydrochloric acid to make the mixture slightly acidic, and the mixture was filtered. The acetone was evaporated, the residue was stirred with acetone and filtered, and the solution was concentrated and chilled, to give 0.76 g (76%) of succinimide, mp and mmp 125-127°.

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Structure of the Diquinone Resulting from Oxidation of β -Naphthoquinone

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Abstract: A yellow compound, $C_{20}H_{10}O_5$, formed in good yield on oxidation of β -naphthoquinone with ferric chloride was reported by Hooker and Fieser¹ in a paper of 1936 to yield β,β -dinaphthyl on zinc dust distillation and on this evidence was regarded as the hydroxydinaphthyldiquinone 6a rather than 6. Later British work, however, showed that β , β -dinaphthyl could have been formed by rearrangement of the initially formed α , α or α , β isomer. We have now found that comparison of the nuclear magnetic resonance spectrum with those of the model compounds 7 and 8 shows conclusively that the structure is 6 and not 6a. Compound A, obtained by oxidation as one of six transformation products described by Hooker and Fieser, is inferred on infrared evidence to have the structure 10, and this is amply confirmed by the nuclear magnetic resonance of the acetate methyl ester, as shown in Figure 1. The decarboxylation of A to the methyl compound C can be followed by continuous recording of the nmr spectrum in hot pyridine. Orange compound D and red compound F, obtained by the reaction of concentrated sulfuric acid on A and on C, are characterized by formation and by nonformation of a bisulfite addition compound as the β -naphthoquinone 11 and the α,β -unsaturated α -naphthoquinone lactone 15.

This investigation is an extension of work reported in a paper written by L. F. F. as junior author¹ and published in 1936, a year after the death of the senior author, Samuel C. Hooker. This English-born chemist, after taking the Ph.D. degree with Bamberger at Munich after just 1 year of research, had, in 1885, become chief chemist for the Franklin Sugar Refining Co. in Philadephia.² A Philadelphian importer of South American bethabarra wood, valued for the preparation of fine fishing rods and bows on account of its remarkable elasticity, invited young German-trained Hooker to investigate a yellow substance which occurs in the grain of the wood.3 Greene and Hooker4 isolated the pigment and identified it as the known but in-

completely characterized substance lapachol, then regarded by Paternò⁵ as the 2-hydroxy-3-(α-alkenyl)-1,4-naphthoquinone 1. Hooker found the chemistry

of lapachol a fascinating subject for spare-time research and he gained the experimental cooperation of various

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