

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

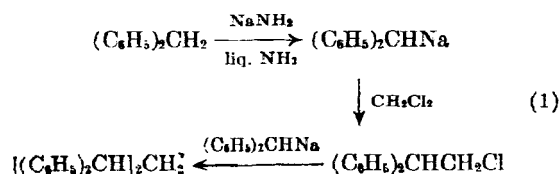
## Reactions of Alkali Diphenylmethides with Certain Polyhalides. Displacement on Halogen or Hydrogen<sup>1</sup>

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Sodium and potassium diphenylmethides in liquid ammonia reacted with chloroform to form diphenylmethane and cyanide ion and with carbon tetrachloride or bromotrichloromethane to give tetraphenylethane, diphenylmethane, and cyanide ion. The initial reactions are considered to involve displacement on hydrogen and halogen respectively. Evidence is presented that the cyanide ion arises through the intermediate formation of dichlorocarbene, which was isolated as its cyclohexene adduct in the absence of ammonia.

Sodium diphenylmethide, prepared from sodium amide and diphenylmethane in liquid ammonia and a little ether, has previously been shown to undergo alkylation with alkyl and benzyl halides,<sup>2</sup> and two-fold alkylation with methylene halides.<sup>3</sup> The reaction may be illustrated with methylene chloride (Equation 1).



some unidentified material was produced. The cyanide ion was identified qualitatively by the Prussian blue test and by effecting the benzoin condensation, for which cyanide ion is considered specific.<sup>4</sup> The cyanide ion was determined quantitatively as described in a laboratory manual.<sup>5</sup> Since the polyhalides immediately discharged the characteristic red color of the diphenylmethide ion, they were added in ether solution to the reagent until the reaction mixtures became essentially colorless; the number of molecular equivalents of the reagent neutralized by one molecular equivalent of each polyhalide was measured. The results are summarized in Table I.

TABLE I  
REACTION OF POLYHALIDES WITH ALKALI DIPHENYLMETHIDES IN LIQUID AMMONIA

Polyhalide	M	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHM Equivalents Neutralized	Tetraphenyl- ethane Yield, %	Diphenylmethane Recovered, %	Cyanide Ion Yield, %
CCl <sub>4</sub>	K	4	0	85	92 <sup>c</sup>
CCl <sub>4</sub>	Na	3.6	0	96	— <sup>d</sup>
CCl <sub>4</sub>	K	5	23, <sup>a</sup> 89 <sup>b</sup>	47, <sup>a</sup> 78 <sup>b</sup>	85 <sup>c</sup>
CCl <sub>4</sub>	Na	4.5	23, <sup>a</sup> 89 <sup>b</sup>	48, <sup>a</sup> 80 <sup>b</sup>	— <sup>d</sup>
BrCCl <sub>3</sub>	K	5	34, <sup>a</sup> 86 <sup>b</sup>	48, <sup>a</sup> 80 <sup>b</sup>	71 <sup>c</sup>
BrCCl <sub>3</sub>	Na	4.8	34, <sup>a</sup> 86 <sup>b</sup>	51, <sup>a</sup> 85 <sup>b</sup>	— <sup>d</sup>
C <sub>6</sub> H <sub>5</sub> CCl <sub>3</sub>	Na	3	66-68	8-13	—

<sup>a</sup> Conversion yield. <sup>b</sup> Yield based on Scheme B. <sup>c</sup> See Ref. 5 for quantitative method. <sup>d</sup> Gave strong positive Prussian blue test.

Sodium diphenylmethide and potassium diphenylmethide have now been found not to produce direct alkylation products with chloroform, carbon tetrachloride, or bromotrichloromethane. Instead, the products were diphenylmethane and cyanide ion with the first halide, and diphenylmethane, 1,1,2-tetraphenylethane and cyanide ion with the two latter halides. These two hydrocarbons were also obtained with benzotrichloride, but no cyanide ion was observed; instead

The reactions with chloroform and carbon tetrachloride or bromotrichloromethane may be rationalized by Schemes A and B, respectively. The initial step in Scheme A involves displacement on hydrogen (acid-base reaction) and that in Scheme B, displacement on halogen. The former displacement regenerates diphenylmethane, whereas the latter forms benzhydryl halide which alkylates unchanged diphenylmethide ion to give tetraphenylethane. The second component in both initial displacements would be the trichlorocarbanion, which loses chlo-

(1) Supported by the Office of Ordnance Research, U. S. Army, and National Science Foundation.

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

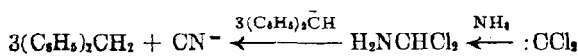
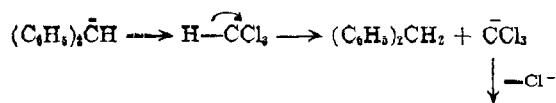
(3) C. R. Hauser, C. F. Hauser, and P. J. Hamrick, Jr., *J. Org. Chem.*, **24**, 397 (1959).

(4) See J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1956, p. 257.

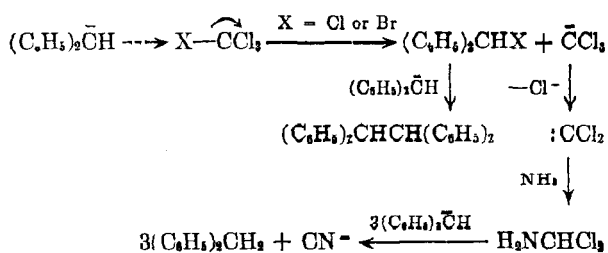
(5) F. Charlot and D. Bezier, *Quantitative Inorganic Analysis*, tr. by R. C. Murray, John Wiley and Sons, Inc., New York, 1957, p. 380.

ride ion to give dichlorocarbene. This reactive intermediate adds ammonia, followed by dehydrochlorination and neutralization of the resulting hydrogen cyanide. The total number of molecular equivalents of diphenylmethide ion neutralized by one molecular equivalent of the polyhalide would be four in Scheme A and five in Scheme B; these values are in excellent agreement with those observed (see Table I).

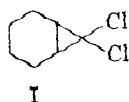
## SCHEME A



## SCHEME B



An attempt to capture dichlorocarbene as its cyclohexene adduct I<sup>6</sup> was unsuccessful in liquid ammonia. Thus when several molecular equivalents of the olefin were added to potassium diphenylmethide in this medium followed by chloroform, none of I was isolated. Since an 85% yield of cyanide ion was obtained, the carbene evidently reacted preferentially with ammonia, a large excess of which was present.



Adduct I was isolated, however, when a suspension of potassium diphenylmethide in cyclohexene was treated with two molecular equivalents of chloroform, carbon tetrachloride, or bromotrichloromethane. The results are summarized in Table II. Besides the products listed in Table II, some residue was produced, suggesting that part of the reagent reacted with the olefin. Despite the special conditions employed to remove the ammonia (see Experimental), a little ammonia appeared to remain, since yields of 1-5% of cyanide ion were found. Carbonation of certain of the reaction mixtures after addition of the polyhalide showed that the diphenylmethide ion was largely consumed, since very low yields (0.1-4%) of diphenylacetic acid were obtained.

(6) See W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

TABLE II  
REACTIONS OF POLYHALIDES WITH POTASSIUM  
DIPHENYLMETHIDE IN CYCLOHEXENE

Polyhalide	Adduct I Yield, %	Tetra- phenyl- ethane Yield, %	Diphenyl- methane Recovered, %
CCl <sub>4</sub>	11-15	—	40-79
CCl <sub>2</sub>	26	17	62
BrCCl <sub>2</sub>	17	17	40

These results show that the diphenylmethide ion reacts differently with methylene chloride, chloroform and carbon tetrachloride, involving displacements on carbon, hydrogen, and chlorine respectively (see Equation 1, Scheme A and Scheme B).

The analogous displacement on the hydrogen of chloroform by hydroxide ion in water (acid-base reaction) has been postulated,<sup>7</sup> and displacements on a chlorine of carbon tetrachloride and on the bromine of bromotrichloromethane with phenyllithium<sup>8</sup> and butyllithium<sup>9</sup> have been observed (lithium-halogen interchanges). The last reaction was shown to produce dichlorocarbene, which was isolated as I.<sup>9</sup>

While many metal-halogen interchanges involving organolithium reagents are known,<sup>8-10</sup> only a few such reactions with organosodium reagents appear to have been reported previously. One has involved butylsodium and  $\alpha$ -bromonaphthalene to form, after carbonation,  $\alpha$ -naphthoic acid (28%),<sup>11</sup> and another sodio ethyl isobutyrate and benzenesulfonyl chloride in ether to give sodium benzenesulfinate and ethyl  $\alpha$ -chloroisobutyrate (60%).<sup>12</sup>

Besides the present examples, certain other reactions in liquid ammonia have produced products that appear to arise through sodium-halogen interchange. One of these involved the formation of tetraphenylethane as a side reaction product in the alkylation of disodiophenylacetate with benzhydriol bromide.<sup>13</sup>

EXPERIMENTAL<sup>14</sup>

Reactions of polyhalides with alkali diphenylmethides (Table I). A. With potassium diphenylmethide. To a stirred solution of 0.1 mole of potassium amide in 200 ml. of com-

(7) See Ref. 4, p. 132.

(8) G. Wittig and H. Witt, *Ber.*, **74**, 1474 (1941).

(9) W. T. Miller, Jr., and C. S. Youn Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959).

(10) See R. G. Jones and H. Gilman, *Org. Reactions*, **VI**, 339 (1951).

(11) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(12) B. E. Hudson, Jr., Ph.D. Thesis, Duke University (1941).

(13) C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 4942 (1956).

(14) Melting points and boiling points are uncorrected.

mercial anhydrous liquid ammonia<sup>15</sup> was added a solution of 16.8 g. (0.1 mole) of diphenylmethane in an equal volume of anhydrous ether, and the resulting deep red solution of potassium diphenylmethide was stirred for 15 min. To the stirred reagent (0.1 mole) was added dropwise solutions of weighed samples (7 to 10 g.) of the polyhalide in 50 ml. of ether until the color was discharged. The amount of halide added was determined by difference in the volumes of the original and unadded solutions. The ammonia was allowed to evaporate as more ether was added. When the mixture had come to room temperature water was added, and the resulting reaction mixture was worked up as described below.

In the experiment with chloroform, the two layers of the reaction mixture were separated. The ethereal layer was dried over anhydrous sodium sulfate, and the solvent removed. The residue was distilled *in vacuo* to give diphenylmethane, b.p. 84–87° at 1 mm.,  $n_D^{20}$  1.5744. The aqueous layer of the reaction mixture was diluted to 250 ml., and 10-ml. aliquots were analyzed quantitatively for cyanide ion.<sup>5</sup>

In the experiments with carbon tetrachloride and bromotrichloromethane the reaction mixtures were filtered. The solid on the funnel was recrystallized twice from chloroform to give 1,1,2,2-tetraphenylethane, light tan needles, m.p. 211–212°. This melting point was not depressed on admixture with an authentic sample of this hydrocarbon. The two layers of the aqueous-ethereal filtrate of the reaction mixture were separated. The aqueous layer was analyzed for cyanide ion as indicated above. The ethereal layer was dried and the solvent removed. The residue was distilled *in vacuo* to give diphenylmethane, b.p. 86–88° at 1.2 mm.,  $n_D^{20}$  1.5742. The residue remaining in the flask was recrystallized to give more tetraphenylethane, m.p. 211–212° after several recrystallizations with chloroform.

B. *With sodium diphenylmethide.* This reagent (0.2 mole) was prepared from 0.2 mole each of sodium amide and diphenylmethane in 400 ml. of liquid ammonia and about 40 ml. of ether as described previously.<sup>3</sup> To the stirred red reagent was added measured ethereal solutions of the polyhalide until the color was discharged, as described above for the potassium reagent. After adding ammonium chloride the resulting reaction mixtures were worked up to give diphenylmethane, b.p. 133–134° at 11 mm., and tetraphenylethane, m.p. 211–212° (except in the experiment with chloroform). The latter hydrocarbon was identified both by

the mixed melting point method and by comparison of its infrared spectrum with that of an authentic sample.

In the experiments with chloroform, carbon tetrachloride, and bromotrichloromethane, positive Prussian blue tests were obtained from the aqueous layers of the filtrates of the reaction mixtures.

In another experiment with carbon tetrachloride, the ammonia was replaced by ether and the latter solvent then evaporated. To the resulting residue was added 200 ml. of 95% ethanol and 10 g. of benzaldehyde, and the mixture was stirred for 2 hr. The precipitated crystals of tetraphenylethane (20%) were removed by filtration. The brown ethanolic filtrate was reduced in volume and cooled to give 4.3 g. (43%) of benzoin, m.p. 136–137° after one recrystallization from ethanol. The melting point was not depressed on admixture with an authentic sample of benzoin, and the infrared spectra of the two samples were identical. More benzoin and some diphenylmethane appeared to be present in the dark residual material.

*Reactions of polyhalides with potassium diphenylmethide in cyclohexene* (Table II). The reagent (0.1 mole) was prepared as described above, and the liquid ammonia evaporated as an equal volume of ether was added. The resulting ethereal suspension was refluxed for 3 hr. to remove dissolved ammonia, more ether being added occasionally to maintain constant volume. Cyclohexene (200 ml.) was then added, and the ether, about 50 ml. of the cyclohexene, and traces of ammonia were removed *in vacuo* at 50°. The resulting brown suspension in cyclohexene was cooled in an ice bath. To the stirred suspension was added during 30 min. a solution of the polyhalide (0.2 mole) in cyclohexene. After removing the ice bath the reaction mixture was stirred for 4 hr., and then shaken with water. The two layers were separated. The organic layer was dried over sodium sulfate, concentrated and distilled. A fraction boiling up to 84° at approximately 1 mm. was collected and shown to contain adduct I by its infrared spectrum and low index of refraction. Further purification by vapor phase chromatography gave a pure sample of 7,7-dichloronorcaradiene (I), identical by infrared spectrum and index of refraction with an authentic sample.<sup>6</sup> The expected hydrocarbons were isolated in the usual manner (see Table II). Also an appreciable amount of residue was obtained.

The experiments with carbon tetrachloride and chloroform were repeated and the reaction mixtures were treated with Dry Ice. There was obtained, besides the expected hydrocarbons and adduct I, only very low yields (0.1–4%) of diphenylacetic acid.

DURHAM, N. C.

(15) See C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).