with water, sodium carbonate solution, water, and saturated sodium chloride solution, then dried by filtering through a layer of anhydrous sodium sulfate. The product recovered from the extracts was fractionated at 4 mm. pressure to yield: (1) 0.9 g., b.p. 126–130°, n_D^{25} 1.4508; (2) 2.5 g., b.p. 130°, n_D^{25} 1.4508; (3) 1.6 g., b.p. 159–163°, n_D^{25} 1.4610.

Fractions 1 and 2 were taken as the yield of unsaturated esters (VII and VIII), wt. 3.4 g. (55%). For analysis, there was used a center cut, b.p. 130°/4 mm., n_D^{25} 1.4508.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.33; H, 11.89. Found: C, 75.64; H, 11.78.

On quantitative hydrogenation in acetic acid, with platinum oxide catalyst, consumption of hydrogen was one millimole per 254 mg. of ester (calcd. mol. wt. is 254). The ultraviolet spectrum showed a rapidly rising absorption as the wave length was decreased below 220 mμ until at 200 mμ, ε was 6280. Carbonyl absorption in the infrared was at 5.75 μ. In gas chromatography, a single symmetrical peak was observed (*cf.* data below on recovered lactone).

The principal constituent of Fraction 3 in the above distillation was starting lactone, but there was also present some unsaturated ester and a third component which appears to have the γ-lactone structure. Infrared absorption was at 5.66 μ and at 5.76 μ. In gas phase chromatography in the 2 m. × 9 mm. column at 226°, helium flow of 145 ml./min., three bands with the following retention times and per cents of total area were observed: 10′ 00″ (18.5%), 14′ 04″ (18.0%), 17′ 51″ (63.5%). For the unsaturated ester, retention time was 9′ 50″, and for the starting lactone retention time was 17′ 50″; so the intermediate band presumably represents γ-lactones.

Ozonolysis of unsaturated ester mixture. Ozone, flowing at the rate of 0.29 mmole/min., was passed for 4.2 min. into a dichloroethylene solution of 305 mg. (1.2 mmole) of the unsaturated ester mixture. Temperature of the reaction was −20°. After the reaction had stood for about 20 min., water was added, and the mixture was heated at 80° with stirring for 30 min.[12] The organic phase was separated, solvent was distilled, and the residue was used for gas phase chromatography in the 3 m. × 15 mm. column. Chromatograms were recorded at 190°, 200°, and 227°, but results at 200° recorded in Fig. 1 were most informative.

Saponification of the unsaturated ester mixture. A 2.0-g. sample of the unsaturated ester mixture was saponified by heating under reflux for 2.5 hr. with 3*M* equivalents of potassium hydroxide in 10% solution in ethanol. The reaction mixture was diluted with water, acidified and extracted. Distillation of the product at 4-mm. pressure yielded 0.3 g., b.p. 156–161.5°, n_D^{25} 1.4591, and 0.9 g., b.p. 161.5–163.5°, n_D^{25} 1.4592. Both fractions absorbed bromine in carbon tetrachloride solution and showed infrared absorption at 5.86 μ. Titration gave an equivalent weight of 240, which is the calculated value for the unsaturated acid.

A mixture of 0.5 g. of the unsaturated acid and 60 ml. of 2*N* sulfuric acid was heated to boiling for 2 min. The cooled solution was extracted with three portions of ether, and the extracts were washed with water and sodium carbonate solution. Material recovered from the ether after carbonate extraction amounted to 50 mg. and showed infrared absorption at 5.66 μ, 5.77 μ, and 5.86 μ. Acid recovered from the sodium carbonate extract showed an infrared spectrum identical with that of the starting material.

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(12) Experiments in these laboratories on methyl oleate by Dr. Peter Tavs have shown that this procedure gives a high yield of carbonyl compounds from the ozonide, with 5% or less of acids.
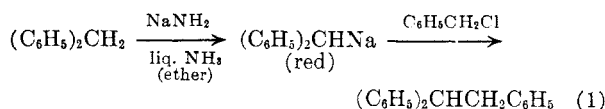
Twofold Alkylations of Sodium Diphenylmethide with Methylene Halides to Form Bisbenzhydrylmethylene Hydrocarbons. Alkylations of Sodium Triphenylmethide[1]

CHARLES R. HAUSER, CHARLES F. HAUSER, AND PHILLIP J. HAMRICK, JR.

Sodium diphenylmethide in liquid ammonia entered into a twofold type of alkylation with methylene chloride and certain higher methylene halides to form the corresponding bisbenzhydrylmethylene hydrocarbons in good yields. These results are of both theoretical and practical interest. Similar results were obtained with sodium triphenylmethide and certain methylene halides.

It has recently been shown[2] that sodium diphenylmethide, prepared from diphenylmethane and sodium amide in liquid ammonia and ether, can be alkylated in excellent yields with various alkyl halides in this medium. The reaction may be illustrated with benzyl chloride, which rapidly discharged the red color of the reagent (Equation 1).

$$(C_6H_5)_2CH_2 \xrightarrow[\substack{\text{liq. NH}_3 \\ \text{(ether)}}]{\text{NaNH}_2} (C_6H_5)_2CHNa \xrightarrow{C_6H_5CH_2Cl} (\text{red})$$

$$(C_6H_5)_2CHCH_2C_6H_5 \quad (1)$$

It has now been found that sodium diphenylmethide can enter into a twofold alkylation with certain methylene halides to form the corresponding bisbenzhydrylmethylene derivatives in good yields. For example, treatment of this reagent with half of a molecular equivalent of methylene chloride produced hydrocarbon I in 72% yield. This reaction presumably involves the intermediate formation of the corresponding monohaloalkyl derivative (Equation 2).

(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) C. R. Hauser and P. J. Hamrick, Jr., *J. Am. Chem. Soc.*, **79**, 3142 (1957). Also see C. B. Wooster and N. W. Mitchell, *J. Am. Chem. Soc.*, **52**, 688 (1930); C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **54**, 2419 (1932).
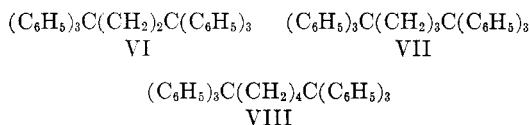
TABLE I

BISBENZHYDRYLMETHYLENE HYDROCARBONS FROM SODIUM DIPHENYLMETHIDE AND METHYLENE HALIDES

Hydro-carbon	Yield,[a] %	M.P., °C.	Lit., M.P.	Analysis				Molecular Weight	
				Calcd.		Found		Calcd.	Found
				C	H	C	H		
I	72	141–142[b]	135[c]	93.05	6.94	92.87	6.64	348	344
II	93	124–125[d]	120–121[c]	92.77	7.23	92.65	7.21	362	360
III	85	74–75[b]	74–75[e]	92.51	7.49	92.48	7.30	377	371
IV	90	123–125[b]	123–124[f]	92.26	7.74	92.31	7.68	391	389

[a] In general, these yields were based on the combined weights of several fractions, each of which melted at the recorded value or slightly lower. [b] Recrystallized from 95% ethanol. [c] Ref. 3. [d] Recrystallized from 1:4 benzene–petroleum ether. [e] Ref. 5. [f] Ref. 6.

$$(C_6H_5)_2CHNa \xrightarrow[\text{liq. NH}_3]{\text{ClCH}_2\text{Cl}} (C_6H_5)_2CHCH_2Cl \xrightarrow{(C_6H_5)_2CHNa}$$
(ether)

$$(C_6H_5)_2CHCH_2CH(C_6H_5)_2 \quad (2)$$
I

Similarly, sodium diphenylmethide underwent the twofold type of alkylation with ethylene chloride, trimethylene bromide, and tetramethylene chloride to give hydrocarbons II, III, and IV in yields of 93%, 85%, and 90%, respectively. The results are summarized in Table I.

$$(C_6H_5)_2CH(CH_2)_2CH(C_6H_5)_2 \quad (C_6H_5)_2CH(CH_2)_3CH(C_6H_5)_2$$
II   III

$$(C_6H_5)_2CH(CH_2)_4CH(C_6H_5)_2$$
IV

The hydrocarbons I–IV have previously been obtained by various methods. Hydrocarbon I was produced in unreported yield by the reduction of 1,1,3,3-tetraphenylpropene with sodium in liquid ammonia and in practically quantitative yield, by the reduction of tetraphenylallene with this reagent.[3] Hydrocarbon II was formed as a by-product (best yield 35%) in the reduction of 1,1-diphenylethylene with certain metals in liquid ammonia.[4] Hydrocarbon III was prepared in over 50% yield by the reduction of 1,1,5,5-tetraphenylpentadiene-1,4 with phosphorous and iodine.[5] Hydrocarbon IV was obtained in unreported yield from 1,1,6,6-tetraphenylhexanediol-1,6 through its dimethyl ether which was cleaved with sodium-potassium alloy in ether, followed by hydrolysis.[6]

It can be seen from Table I that the melting points of our products III and IV agreed with the literature values but that the melting points of our products I and II were slightly higher than the earlier values. It is to be noted that the melting points of the homologous series I to IV pass through a minimum.

It can further be seen from Table I that our products gave satisfactory analyses and molecular weights.

It seems unlikely that any of the products isolated were o- or p-ring derivatives which might have arisen from alkylations involving o- or p-resonance forms of the diphenylmethide ion, since such derivatives were evidently not obtained in the previous alkylations with benzyl chloride and other alkyl halides.[2]

The present type of two-alkylation of sodium diphenylmethide furnishes a convenient method for the synthesis of the homologous series of hydrocarbons I–IV and presumably for that of certain higher members of this series. With the exception of the reaction with methylene chloride where a red color was still present after 40 min., the reactions studied appeared to be completed within a few minutes as indicated by the discharge of the characteristic red color of the diphenylmethide ion.

It is of interest that, although ethylene chloride and especially the intermediate monohalide represented in Equation 2 have relatively reactive β-hydrogens, these halides underwent largely the substitution type of reaction to form the alkylation products and not much dehydrohalogenation (β-elimination). These observations further illustrate the considerable tendency of sodium diphenylmethide to exhibit nucleophilic displacement on carbon rather than β-elimination even though the diphenylmethide ion is a relatively strong base.[7]

Alkylations of sodium triphenylmethide. Like sodium diphenylmethide, sodium triphenylmethide may be prepared from triphenylmethane and sodium amide in liquid ammonia and ether and alkylated in this medium. As an example of a simple alkylation, this reagent was benzylated to form hydrocarbon V in 99% yield (Equation 3).

$$(C_6H_5)_3CH \xrightarrow[\text{liq. NH}_3]{\text{NaNH}_2} (C_6H_5)_3CNa \xrightarrow{C_6H_5CH_2Cl}$$
(ether)   (red)

$$(C_6H_5)_3CCH_2C_6H_5 \quad (3)$$
V

Hydrocarbon V has previously been obtained in equally high yield from benzylmagnesium chloride and triphenylchloromethane.[8]

(3) C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **56**, 1133 (1934).

(4) H. Gilman and J. C. Bailie, *J. Am. Chem. Soc.*, **65**, 267 (1943).

(5) G. Wittig and B. Obermann, *Ber.*, **68B**, 2214 (1935).

(6) B. Wittig and M. Leo, *Ber.*, **63A**, 943 (1930).

(7) See ref. 2 and C. R. Hauser, C. F. Hauser, and P. J. Hamrick, Jr., *J. Org. Chem.*, **23**, 1713 (1958).

(8) M. Gomberg and L. H. Cone, *Ber.*, **39**, 1461 (1906).

TABLE II

BISTRIPHENYLMETHYLMETHYLENE HYDROCARBONS FROM SODIUM TRIPHENYLMETHIDE AND METHYLENE HALIDES

Hydro-carbon	Yield,[a] %	M.P., °C.	Lit., M.P.	Calcd. C	Calcd. H	Found C	Found H
VI	78	94–95[b]	. .	93.34	6.66	93.45	6.67
VII	84	150–151[c]	. .	93.14	6.86	93.12	6.67
VIII	49	207–208[d]	189[e]	92.94	7.06	92.99	6.86

[a] In general these yields were based on the combined weights of several fractions, each of which melted at the recorded value or slightly lower. [b] Recrystallized from 95% ethanol. [c] Recrystallized from 1:4 ethyl acetate–ethanol. [d] Recrystallized from 1:2 ethyl acetate–ethanol. [e] Ref. 9.

Also, sodium triphenylmethide evidently underwent the twofold type of alkylation with ethylene chloride, trimethylene bromide, and tetramethylene chloride to give hydrocarbons VI, VII, and VIII in yields of 78%, 84%, and 49%, respectively. The results are summarized in Table II.

$$(C_6H_5)_3C(CH_2)_2C(C_6H_5)_3 \quad (C_6H_5)_3C(CH_2)_3C(C_6H_5)_3$$
VI   VII

$$(C_6H_5)_3C(CH_2)_4C(C_6H_5)_3$$
VIII

Apparently hydrocarbons VI and VII have not previously been described. Hydrocarbon VIII has been prepared[9] from the 1,4-addition of triphenylmethyl radicals to 1,3-butadiene followed by reduction over Adams catalyst. The yields in these two steps were 10% and 80%, respectively.

It can be seen from Table II that the melting point of our product VIII was considerably higher than the earlier value.

It can further be seen from Table II that all three of our products VI–VIII gave acceptable analyses. Unfortunately these hydrocarbons were too insoluble in the ordinary solvents for satisfactory molecular weight determinations by the boiling point elevation method.

It was possible that one or more of our products VI–VIII were in reality o- or p-ring–substituted derivatives such as IX or X, which might have arisen from alkylations involving a p-resonance form of the triphenylmethide ion.

X

IX
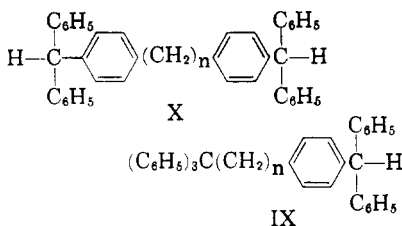
This now seems doubtful, however, since the addition of these products to sodium amide in liquid ammonia failed to produce colors which might have been expected had they had the active methinyl hydrogen of structures IX and X. On the other hand, the addition of the hydrocarbons

I–IV to sodium amide in liquid ammonia produced red colors.

The twofold alkylations with sodium triphenylmethide appeared to be completed somewhat more slowly than the corresponding twofold alkylations with sodium diphenylmethide as indicated by the time of fading of the characteristic red colors of the two reagents.

Moreover, whereas sodium diphenylmethide gave a good yield of hydrocarbon I with methylene chloride, sodium triphenylmethide failed to undergo satisfactorily the corresponding twofold alkylation with this halide under similar conditions. The latter reagent may have formed the monohaloalkyl derivative XI, since several workers[10] have observed that this halide can be obtained in good yield by the action of methylene chloride on an ethereal solution of sodium triphenylmethide prepared from triphenylchloromethane and sodium or sodium amalgam.
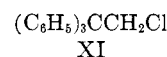
$$(C_6H_5)_3CCH_2Cl$$
XI

It should be mentioned that the monochlorides, $(C_6H_5)_3CCH_2CH_2Cl$ and $(C_6H_5)_3CCH_2CH_2CH_2Cl$, have also apparently been obtained by Charlton, Dostrovsky, and Hughes[10] from ethereal sodium triphenylmethide and ethyl chloride and trimethylene chlorobromide, respectively. The former monochloride and the bromide corresponding to the latter monochloride were presumably formed as intermediates in our preparations of hydrocarbons VI and VII, respectively.

EXPERIMENTAL[11]

Twofold alkylations of sodium diphenylmethide with methylene halides. To a stirred suspension of 0.1 mole of sodium amide in 300 ml. of commercial, anhydrous liquid ammonia[12] was added 16.8 g. (0.1 mole) of diphenylmethane in 50 ml. of anhydrous ether. The resulting dark red sodium diphenylmethide solution was stirred for 10 min. To this stirred reagent was added 0.05 mole of methylene chloride,

(9) J. B. Conant and B. F. Chow, *J. Am. Chem. Soc.*, **55**, 3475 (1933).

(10) J. Charlton, I. Dostrovsky, and E. Hughes, *Nature*, **167**, 987 (1951); E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957); H. E. Zimmerman and F. J. Smentowski, *J. Am. Chem. Soc.*, **79**, 5455 (1957).

(11) Melting points were taken on a Fisher-Johns melting point apparatus. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(12) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, VIII, 122 (1954).

ethylene chloride, trimethylene bromide, or tetramethylene chloride in 100 ml. of anhydrous ether, and the stirring continued for 35–40 min. In the experiment with methylene chloride, the reaction mixture was still deeply colored (cherry red) after this time but in the experiments with the other three halides the red color faded and a yellow or tan suspension was produced within a few minutes. The liquid ammonia was evaporated on the steam bath as an equal volume of ether was added. The resulting ethereal suspension was cooled and shaken with water. The two layers were separated. The aqueous layer was extracted with ether and the ethereal extract combined with the original ethereal layer. The ethereal solution was dried over Drierite, and the solvent removed. The residue was recrystallized from appropriate solvents to give the hydrocarbons I–IV. The data for these compounds are summarized in Table I. The molecular weights were estimated by boiling point elevations in chloroform solution.[13]

Benzylation of sodium triphenylmethide. This reagent (0.1

(13) We are indebted to Mr. W. F. Owens, Jr., of Wake Forest College for these determinations.

mole) was prepared as described below, and its alkylation with a molecular equivalent of benzyl chloride was effected essentially as described recently[2] for the corresponding alkylation of sodium diphenylmethide. There was obtained a 99% yield of 1,1,1,2-tetraphenylethane (V), m.p. 143–144° after recrystallization from benzene and petroleum ether. The reported melting point for this hydrocarbon is 144°.[8]

Twofold alkylations of sodium triphenylmethide with methylene halides. To a stirred suspension of 0.1 mole of sodium amide in 300–400 ml. of liquid ammonia[12] was added 24.4 g. (0.1 mole) of triphenylmethane in 50–100 ml. of anhydrous ether. The resulting dark red solution was stirred for 10 min. To this stirred reagent was added 0.05 mole of ethylene chloride, trimethylene bromide, or tetramethylene chloride in 50–100 ml. of anhydrous ether, and the stirring continued for 50–90 min. (Dry Ice condenser). The red color of the reagent was discharged within 15–45 min. The reaction mixture was worked up as described above for the experiments with sodium diphenylmethide. The results are summarized in Table II.

DURHAM, N. C.

Synthesis of Some Octenoic Acids

JAMES A. KNIGHT AND JAMES H. DIAMOND[1]

The preparation and properties of *trans*-4- and -6- and of *cis*-3-, -4-, and -6-octenoic acids are reported in this paper. The previously reported isomers, *trans*-3- and *cis*-2-octenoic acids, are also reported in this paper. The *cis* acids were prepared by the catalytic semihydrogenation of the corresponding octynoic acids. The *trans* acids were obtained either directly or indirectly starting with a *trans* alkenoic acid obtained by a Knoevenagel condensation. Physical properties, including infrared spectra, were determined for all of the acids and most of the intermediates. The infrared spectra of the *trans* compounds showed strong absorption in the region of 10.2–10.35 microns. None of the *cis* compounds showed absorption in this region.

The isomeric unbranched octenoic acids were needed in a study of the ionization constants of unsaturated fatty acids. Of the eleven isomers, the following acids are reported in the literature: *trans*-2-,[2,3] *trans*-3-,[4] *trans*-5-,[5] *cis*-2,[2] *cis*-5-[5] and 7-octenoic acid.[6,7] The preparation and properties of the unreported isomers, *trans*-4- and -6- and *cis*-3-, -4-, and -6-octenoic acids, are presented in this paper. Due to the method of preparation of *trans*-3-octenoic acid and the lack of agreement of physical constants for *cis*-2-octenoic acid, the preparation and properties of these acids are also included. The physical properties of the acids are given in Table I.

The *cis* octenoic acids were prepared by catalytic semihydrogenation of the corresponding octynoic acids. Hydrogenation of acetylenic compounds in the presence of catalytic substances is reported to give predominantly *cis* ethylenic compounds.[8-11] This method has been used to prepare unsaturated acids[5,6] and hydrocarbons[12] having a *cis* configuration. In this work, W-5 Raney nickel[13] which had been aged five to six months was used as the catalyst, and dry thiophene-free benzene was found to be the most suitable solvent. In previous studies[5,14] a sharp decrease in the rate of hydrogenation was reported to occur after one molar equivalent of hydrogen had been absorbed. In

(1) Abstracted in part from the M.S. thesis of James H. Diamond. Present address: Hastings Chemical Division, Minnesota Mining and Manufacturing Company, Saint Paul, Minn.

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(5) D. R. Howton and R. H. Davis, *J. Org. Chem.*, **16**, 1405 (1951).

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(8) L. Crombie. *Quart. Revs. (London)*, **6**, 128 (1952).

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(11) A. W. Johnson, *The Chemistry of Acetylenic Compounds, The Acetylenic Fatty Acids*, Volume II, Longsman, Green and Co., New York, 1950, pp. 41–7.

(12) B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 3156 (1953).

(13) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

(14) G. F. Hennion, W. A. Schroeder, R. P. Lu, and W. B. Scanlon, *J. Org. Chem.*, **21**, 1142 (1956).