pointed out. In this connection an nmr study involving 4-*tert*-butylcyclohexanone and 4-*tert*-butylcyclohexanone-*cis-3,5,5-d*$_3$ (axial 3D) and their $AlCl_3$ complexes was undertaken. Figure 2 illustrates the 60-MHz nmr spectra of the ketones and their $AlCl_3$ complexes as 1 *M* solutions in benzene (τ 2.73). The low-field doublets of the trideuterated ketone (τ 7.69, J_{gem} = -13.4 Hz) and complex (τ 7.42, J_{gem} = -17.0 Hz) are assigned to equatorial protons on C-2 and C-6. The assignments are based on the following facts: (1) the signals integrate to two protons in each case, (2) the signals appear basically as doublets in the nondeuterated compounds,[23a] (3) the widths of the signals are relatively narrow owing to axial–equatorial H–D vicinal coupling constants,[23b] and (4) the relatively large shift of these protons in going from ketone to complex. The high-field doublets of the trideuterated ketone (τ 8.14, J_{gem} = -13.4 Hz)[24] and complex (τ 8.10, J_{gem} = -17.0 Hz) are assigned to the axial protons on C-2 and C-6. These assignments are based on the following facts: (1) the signals intergrate to two protons in each case, (2) the signals give a complex splitting pattern in the nondeuterated compounds,[23a] (3) the widths of the signals are relatively broad owing to axial–axial H–D vicinal coupling constants,[23b] and (4) the relatively slight shift of these protons in going from ketone to complex.

The nmr spectra of ketone and ketone–$AlCl_3$ show nonflexible conformations displaying axial and equatorial protons on C-2 and C-6. The spectra are consistent with a very high population of the chair form of the ketone and ketone–$AlCl_3$. The spectra do not rule out the possibility of an equilibrium between the chair conformation and certain nonchair conformations, where the equilibrium is in the direction of a high predominance of the chair form. Unfortunately, the spectra do not allow predictions regarding detectable limits of nonchair conformers.

Registry No.—$(CH_3)_3Al$, 75-24-1; $(C_2H_5)_3Al$, 97-93-8; $(C_6H_5)_3Al$, 841-76-9; CH_3MgBr, 75-16-1; C_6H_5MgBr, 100-58-3; 4-*tert*-butylcyclohexanone, 98-53-3; 3,3,5-trimethylcyclohexanone, 873-94-9; 2-methylcyclopentanone, 1120-72-5; 3-methylcyclopentanone, 1757-42-2; *cis*-3,4-dimethylcyclopentanone, 19550-72-2.

Acknowledgment.—We are grateful to Dr. A. C. Huitric for helpful comments concerning the interpretation of the nmr spectra shown in Figure 2.

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[23] (a) W. F. Trager and A. C. Huitric, *Tetrahedron Lett.*, 825 (1966); (b) A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964).

[24] A JEOL H4 100 spectrometer was used to obtain 100-MHz nmr spectra for all samples. In this case a distinct doublet at τ 8.14 was observed.

Reaction of Alkali Metal Diphenylmethides with 1,1-Dichloroalkanes. Conjugate Addition to 1,1-Diphenylalkenes

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The reaction of sodium diphenylmethide (**1′**) with methylene chloride was previously considered to proceed by a twofold alkylation to give 1,1,3,3-tetraphenylpropane (**3**). The reaction is shown to proceed by a single alkylation to give diphenylethyl chloride, which is dehydrohalogenated to diphenylethylene. Conjugate addition of **1′** to the latter olefin, followed by neutralization, gives **3**. Conjugate addition of **1′** to other 1,1-diphenylalkenes is not observed. Alkali triphenylmethides react similarly with methylene chloride, except that elimination is not possible, and the monoalkylation product does not react further.

Previously, sodium diphenylmethide in liquid ammonia was shown to react with α,ω-dihaloalkanes including methylene chloride and ethylene chloride, to give the tetraphenylalkanes corresponding to twofold alkylation of the halide by the anion, although the triphenylmethide ion reacted but once with methylene chloride to give triphenylethyl chloride.[2]

Subsequently, sodium and potassium diphenylmethide were shown to undergo quite different reactions with chloroform (proton abstraction) and carbon tetrachloride (displacement on halogen).[3] Also, methylene iodide was shown to iodinate certain organometallic compounds,[4] and ethylene bromide and iodide were shown to react with **1′** differently than did the chloride.[5] It thus seemed important to reexamine the reaction of the alkali diphenylmethides with the methylene halides.

When potassium diphenylmethide (**1′**) was treated with 0.5 molar equiv of methylene chloride, the orange color, as previously noted,[2] was not discharged, but a substantial excess of halide did discharge the color. Work-up of this reaction mixture gave almost none of the expected tetraphenylpropane (**3**), but gave 1-chloro-2,2,4,4-tetraphenylbutane (**4**), in 40% conversion. Gas chromatography indicated a small amount of tetraphenylpropane (about 15%), but showed a 35% recovery of diphenylmethane (**1**). Three mechanisms were considered to explain these results; path C, Scheme I, was shown to be correct.

When hydrocarbon **3** was treated with ammoniacal potassium amide, a red color indicative of an anion was observed, but, when the color was discharged by methylene chloride, starting material was largely recovered, indicating a slight extent of ionization. This rules out path A, Scheme I, since diphenylmethide must be an even weaker base than amide ion. Path B, Scheme I,

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[1] NSF Undergraduate Research Participant, summer, 1971.

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[3] C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, *J. Org. Chem.*, **26**, 2627 (1961).

[4] R. L. Gay, T. F. Crimmins, and C. R. Hauser, *Chem. Ind.* (*London*), 1635 (1966).

[5] W. G. Kofron and C. R. Hauser, *J. Amer. Chem. Soc.*, **90**, 4126 (1968).

SCHEME I

$$\text{Path A } \mathbf{2} + \mathbf{1'} \longrightarrow \mathbf{3};\ \mathbf{3} + \mathbf{1'} \longrightarrow \mathbf{3'};\ \mathbf{3'} + \mathrm{CH_2Cl_2} \longrightarrow \mathbf{4}$$

$$\text{Path B } \mathbf{2} + \mathbf{1'} \longrightarrow \mathbf{2'};\ \mathbf{2'} + \mathbf{2} \longrightarrow \mathbf{4}$$

$$\text{Path C } \mathbf{2} + \mathbf{1'} \longrightarrow (\mathbf{2'}) \longrightarrow \mathbf{5};\ \mathbf{5} + \mathbf{1'} \longrightarrow \mathbf{3'};\ \mathbf{3'} + \mathrm{CH_2Cl_2} \longrightarrow \mathbf{4};\ \text{or } \mathbf{3'} + \mathrm{NH_4^+} \longrightarrow \mathbf{3}$$

$$\text{Overall: } 3\ \mathbf{1'} + \mathrm{CH_2Cl_2} \xrightarrow{\mathrm{NH_4^+}} \mathbf{3} + \mathbf{1}$$

$$2\ \mathbf{1'} + \mathrm{CH_2Cl_2} \xrightarrow{\mathrm{NH_4^+}} {}^1/_3\ \mathbf{4} + {}^1/_3\ \mathbf{3} + {}^2/_3\ \mathbf{1}$$

$$\underset{\mathbf{1}}{\mathrm{(C_6H_5)_2CH_2}} \xrightarrow{\mathrm{NH_2^-}} \underset{\mathbf{1'}}{\mathrm{(C_6H_5)_2\bar{C}H}} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{\mathbf{2}}{\mathrm{(C_6H_5)_2CHCH_2Cl}}$$

$$\underset{\mathbf{2'}}{\mathrm{(C_6H_5)_2\bar{C}CH_2Cl}}$$

$$\underset{\mathbf{3}}{\mathrm{(C_6H_5)_2CHCH_2CH(C_6H_5)_2}} \quad \underset{\mathbf{3'}}{\mathrm{(C_6H_5)_2CHCH_2\bar{C}(C_6H_5)_2}}$$

$$\underset{\mathbf{4}}{\mathrm{(C_6H_5)_2CHCH_2C(C_6H_5)_2CH_2Cl}} \quad \underset{\mathbf{5}}{\mathrm{(C_6H_5)_2C{=}CH_2}}$$

appeared unlikely, since the β-halo anion (**2′**) would probably eliminate halide; in agreement with this, treatment of **2** with 1 molar equiv of **1′** gave both **3** (51%) and **5** (47%). Treatment of **5** with **1′** did result in a change in color from orange (**1′**) to red (other alkyldiphenylmethide ions have colors more red than **1′**), and treatment of this mixture with methylene chloride resulted in a 62% yield of **4**. When this experiment was repeated, but with methylene chloride omitted and the adduct neutralized with ammonium chloride, **3** was obtained in 52% yield. If Scheme I's path C is correct, then formation of **3** must also involve an intermediate dehydrohalogenation of **2** to **5**. The stoichiometry of this pathway would then be a 3:1 ratio of **1′** to methylene chloride, and not 2:1 as previously assumed. Reexamination of the original report suggests no disagreement with this stoichiometry, even though the reported yield of **3** was 72% (67% would be the maximum by Scheme I). If $^1/_2$ molar equiv of methylene chloride is used, $^1/_3$ molar equiv will react to form **3′**, leaving $^1/_6$ molar equiv of methylene chloride to alkylate **3′** to give **4**. The remainder of the **3′** imparts the observed color to the solution and is converted to **3** upon work-up. While only 67% of **1** is converted to solid products (**3** and **4**), the molecular weight of **4** is increased 14% over **3**; thus the total amount of solid would give an apparent yield of approximately 72%. The chloro compound (**4**) is more soluble than **3**, and on recrystallization pure **3** is obtained. When the alkylation of **1′** was carried out with $^1/_3$ molar equiv of methylene chloride, followed by neutralization with ammonium chloride after 20 min, **3** was obtained in 61% yield (41% conversion).

A similar conjugate addition of **1′** has been observed with 1,1-dichloro-2,2-diphenylethylene.[6] This suggests that such a reaction might be a convenient route to 2-alkyl-1,1,3,3-tetraphenylpropanes, since 1,1-diphenylalkenes are readily available from benzophenone, and since 1,1-dichloroalkanes other than methylene chloride are not alkylated by **1′**.[5] However, several 1,1-diphenylalkenes failed to react with **1′** to give adducts. Apparently the alkene is deprotonated by **1′** to form an allylic anion, which does not react further with **1′**, and on work-up the starting materials are recovered. The formation of the anion from 1,1-diphenylpropene with potassium amide was demonstrated by carbonation to give 4,4-diphenyl-3-butenoic acid (eq 1). Thus the

$$\mathrm{(C_6H_5)_2C{=}CHCH_3} \xrightarrow{\mathrm{NH_2^-}} \mathrm{(C_6H_5)_2C{=}CH\bar{C}H_2} \xrightarrow{\mathrm{CO_2,\,H^+}} \mathrm{(C_6H_5)_2C{=}CHCH_2COOH} \qquad (1)$$

conjugate addition of **1′** is only observed with alkenes such as **5**, which do not have allylic protons.

The original report suggests that sodium triphenylmethide undergoes reaction with methylene chloride to give 1,1,1-triphenyl-2-chloroethane.[2] This halide and the analogous bromide were prepared from the methylene halide and sodium triphenylmethide.[7,8] The chloride was shown to be thermally unstable, rearranging to triphenylethylene with loss of hydrogen chloride,[7] and, when converted with sodium to the 1,1,1-triphenylethyl anion, undergoing rearrangement to 1,1,2-triphenylethane.[8] When the alkylation of potassium triphenylmethide with methylene chloride was carried out in liquid ammonia, triphenylethyl chloride could be obtained in 52% yield, even though the halide was added to the anion solution. In fact, the halide was not dehydrohalogenated and was recovered even when refluxed in ether with 1 equiv of potassium triphenylmethide, or when stirred at room temperature in ether with 1 equiv of potassium amide.

Experimental Section

Reactions of Potassium Diphenylmethide and Methylene Chloride. A. General Procedure.—Potassium diphenylmethide was prepared in liquid ammonia as previously described.[5] Unless otherwise indicated, methylene chloride in ether was added to the anion solution. A general procedure is described in detail; the other reactions were similar, and the yields are summarized in Table I.

TABLE I

REACTIONS OF **1′** WITH METHYLENE CHLORIDE[a]

Mole ratio of **1′**:CH₂Cl₂	Product (conversion, %) [yield, %][c]
2	**1** (31)[93]
	3 (28)[85]
	4 (28)[85]
	5 (5.3)
3	**1** (20)[60]
	3 (41)[61]
	4 (1)
	5 (trace)
0.1[b]	**1** (18)
	5 (18)
	2 (47)

[a] The potassium salt was used; results were similar whenever reactions were repeated with the sodium salt. [b] Inverse addition. [c] The conversion is the amount of **1′** converted to the indicated product; the yield is that based on the overall stoichiometry of Scheme I.

B. Reaction of Potassium Diphenylmethide with 0.5 Molar Equiv of Methylene Chloride.—To 0.1 mol of potassium diphenylmethide was added 4.25 g (0.05 mol) of methylene chloride. After 20 min the color was discharged by the addition of ammonium chloride, the ammonia was evaporated, and the residue was stirred with ether and water. The ethereal solution was separated, washed with dilute hydrochloric acid, water, and brine, dried over magnesium sulfate, and evaporated. The

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[6] F. B. Kirby, W. G. Kofron, and C. R. Hauser, *J. Org. Chem.*, **28**, 2176 (1963).

[7] J. C. Charlton, I. Dostrovsky, and E. D. Hughes, *Nature (London)*, **167**, 987 (1951).

[8] E. Grovenstein, *J. Amer. Chem. Soc.*, **79**, 4985 (1957).

residue was stirred with hexane and filtered. The solid (6.75 g) was recrystallized from hexane to give 5.6 g (28% conversion of anion) of 1-chloro-2,2,4,4-tetraphenylbutane, mp 121–122°.

Anal. Calcd for $C_{28}H_{25}Cl$: Cl, 8.93. Found: Cl, 9.06.

The hexane filtrate was evaporated and the residual oil was distilled at 2 mm to give 5.2 g (31% recovery) of diphenylmethane, bp 89–96°. The still pot residue was crystallized in hexane and recrystallized from methanol to give 5.1 g (28% conversion) of 1,1,3,3-tetraphenylpropane, mp 139.5–141.5°. Diphenylethylene was detected in the combined mother liquors by gas chromatography (estimated 0.95 g, 5.3% conversion).

Reaction of Potassium Diphenylmethide with 1,1-Diphenylethylene.—To a solution of 0.05 mol of potassium diphenylmethide in 120 ml of liquid ammonia was added an ethereal solution of 9 g (0.05 mol) of 1,1-diphenylethylene. The dark red solution was stirred for 20 min and 3 g of ammonium chloride was added. The ammonia was evaporated and the residue was stirred with ether and water. The ethereal solution was separated, washed, dried, and evaporated to give 17.4 g of solid. Recrystallization from ethanol and hexane gave 9 g (52%) of tetraphenylpropane, mp 139–140°. Another 5.4 g of lower melting product was obtained from the mother liquor. In another experiment, 5.4 g (0.03 mol) of 1,1-diphenylethylene in ether was added to 0.03 mol of potassium diphenylmethide, and the deep red solution was stirred for 30 min. An ethereal solution of 2.6 g (0.03 mol) of methylene chloride was added. The color was slowly (25 min) discharged. Work-up as above gave 7.4 g (62%) of tetraphenylchlorobutane, 2.3 g (22%) of tetraphenylpropane, and 15% each of diphenylmethane and diphenylethylene.

Reaction of 1,1-Diphenyl-1-propene with Potassium Amide.—To a solution of 0.025 mol of potassium amide in 100 ml of liquid ammonia was added an ethereal solution of 4.85 g (0.025 mol) of 1,1-diphenyl-1-propene. The ammonia was replaced with ether, and the deep red solution was poured onto Dry Ice. Water was added and the aqueous layer was separated and acidified. The solid was recrystallized from carbon tetrachloride to give 3 g (50%) of 4,4-diphenyl-3-butenoic acid, mp and mmp 118–119°.[9]

Reaction of Potassium Triphenylmethide with Methylene Chloride.—To a solution of 0.025 mol of potassium triphenylmethide, prepared from 0.025 mol of potassium amide and 6.1 g (0.025 mol) of triphenylmethane in liquid ammonia, was added 2.4 g (0.028 mol) of methylene chloride. The color was not discharged after 40 min. Ammonium chloride was added to discharge the color and the ammonia was evaporated. The residue was stirred with ether and water and the ethereal layer was separated, dried over magnesium sulfate, and evaporated. The residue was recrystallized from methylene chloride–ethanol to give 3.8 g (52%) of 1-chloro-2,2,2-triphenylethane, mp 99–100°. The experiment was repeated, except that after the methylene chloride had been added and the solution stirred for 20 min an ammoniacal solution of 0.025 mol of potassium amide was added, and the mixture was stirred until the ammonia had evaporated (about 1.5 hr). Work-up as above afforded only triphenylethyl chloride (53%), and triphenylethylene could not be detected.

Registry No.—**1,** 101-81-5; **1′,** 10060-17-0; **3,** 36171-50-3; **4,** 40139-28-4; **5,** 530-48-3; methylene chloride, 75-09-2; 1,1-diphenyl-1-propene, 778-66-5; potassium amide, 17242-52-3; 4,4-diphenyl-3-butenoic acid, 7498-88-6; potassium triphenylmethide, 1528-27-4; 1-chloro-2,2,2-triphenylethane, 33885-01-7.

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[9] W. S. Johnson, J. W. Petersen, and W. P. Schneider, *J. Amer. Chem. Soc.*, **69**, 74 (1947).

Kinetic Isotope Effects in the Oxidation of Alcohols by Silver Carbonate

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The kinetic isotope effect resulting from the silver carbonate oxidation of a variety of alcohols has been determined by a convenient double labeling technique which may be utilized for similar determinations in other systems. The method is especially suitable to systems where reproducible direct kinetic measurements are not possible. The theory strengths and limitations of the method are discussed and its validity is experimentally verified.

The importance of kinetic isotope effects in the study of organic reaction mechanisms is well known and has been extensively reviewed.[1] Frequently the mere existence or absence of a kinetic isotope effect is a sufficient clue for the differentiation among many theoretically plausible mechanistic alternatives.

The study of kinetic isotope effects is also useful in establishing the magnitude of errors involved in tracer experiments and in providing experimental verification of theoretical calculations regarding the nature of the transition states in various types of bond-breaking processes.

The above applications as well as the general methods for evaluating kinetic isotope effects have been elegantly discussed and reviewed by Raaen and his coauthors.[2]

However, kinetic isotope effects in chemical reactions are frequently difficult to measure because of the problems involved in obtaining sufficiently reproducible direct kinetic data on individual isotopic species. This difficulty is particularly evident in heterogeneous reaction systems, where it may prove impossible to maintain even an approximate control over all the significant reaction variables.

Frustration over attempts to obtain such direct kinetic data for the oxidation of alcohols by silver carbonate on Celite,[3] a combination known as Fetizon's reagent,[4] led us to utilize a double isotopic labeling technique which permits different isotopic species to be studied in a single reaction mixture and the determination of the kinetic isotope effect without a concurrent determination of the kinetics of the reaction.

It must be emphasized that theoretical treatments relating kinetic isotope effects to the isotopic composition of reactants and products have been previously described.[5] Also the use of one isotope as a

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[1] C. J. Collins and N. S. Bowman, "Isotope Effects in Chemical Reactions," ACS Monograph 167, Van Nostrand-Reinhold, Princeton, N. J., 1970.

[2] V. F. Raaen, G. A. Ropp, and H. R. Raaen, "Carbon 14," McGraw-Hill, New York, N. Y., 1968, pp 47–83.

[3] F. J. Kakis, "On the Mechanism of the Oxidation of Alcohols by Silver Carbonate," 7th Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 1971.

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