similar to the type of situation[7] in which alkyl rearrangement has been shown to occur. With this in mind we prepared the dimethyl derivative IX and examined its mass spectrum. The base peak in this spectrum (Figure 3 (lower quadrants)) is due to benzylic cleavage to give the dimethyltropylium ion of mass 119, while the relative abundance of the anticipated alkyl rearrangement ion s of mass 118 is small at 70 ev but increases at low electron energies (Figure 3 (lower left)). However the mass spectrum of 5-phenyl-5-methyl-2-hexanone-4,4-d_2 (X) showed no shift of the *m/e* 118 peak to *m/e* 120 as would be expected if the alkyl rearrangement X → t were operative. It seems, therefore, that alkyl and other groups suffer migration to carbonium ion centers,[8] but not to radical ion sites.[9]

Experimental Section[10]

7-Phenyl-2-heptanone (III).—The Grignard reagent from 5-phenylpentyl bromide (2.3 g; prepared by ethylene oxide chain extension[11] of hydrocinnamyl bromide followed by bromination with 48% HBr–concentrated H_2SO_4) and magnesium (0.23 g) in ether was treated with acetaldehyde (0.6 ml) in ether and worked up in the usual way. Oxidation of the resulting alcohol with Jones reagent[12] gave 7-phenyl-2-heptanone which was purified by vpc on Apiezon L at 190° (retention time of 10 min).

6-Phenyl-2-hexanone (V).—Following the above procedure, using the Grignard derivative of 4-phenylbutyl bromide (from LAH reduction of 4-phenylbutyric acid followed by bromination in the usual manner) gave 6-phenyl-2-hexanone (V), purified by vpc on Apiezon L at 185° (retention time 14 min).

5-Phenyl-2-pentanone (VI).—This compound was prepared by the same procedure outlined for III, using hydrocinnamyl bromide as a starting material. Purification of the product was carried out by vpc on an Apiezon L column at 175° (retention time of 11 min).

3-(2-Oxocyclopentyl)propionate (VII) and 2-methyl-3-(2-oxocyclopentyl)propionate (VIII).—Both compounds were prepared by the Stork enamine procedure[13] employing alkylation of cyclopentanone pyrrolidine enamine with methyl acrylate and methyl methacrylate, respectively. The compounds were purified by vpc on Apiezon L at 180° (retention times of 5 and 5.5 min).

5-Phenyl-5-methyl-2-hexanone (IX).—β-Phenylisovaleric acid, prepared by the method of Dippy and Young,[14] was reduced with LAH to the alcohol and brominated using 48% HBr–concentrated H_2SO_4 (4:1). Treatment of the Grignard reagent of this bromide with acetaldehyde and subsequent oxidation (as for III, V, and VI) gave the required ketone IX, which was purified by vpc on a 20% polybutylene glycol column at 170° (retention time 12.5 min). The structure of the compound was verified by nmr and mass spectrometry.

The 4-d_2 derivative (X) was prepared by NaOD–MeOD exchange of the methyl ester of β-phenylisovaleric acid (esterification being carried out with diazomethane) followed by $LiAlH_4$ reduction, bromination, and Grignard reaction as outlined above for the nondeuterated compound.

Registry No.—III, 14171-88-1; V, 14171-89-2; VI, 2235-83-8; VII, 10407-36-0; VIII, 14128-60-0; IX, 14128-61-1.

[7] C. Djerassi, A. M. Duffield, F. Komitsky, and L. Tökes, *J. Am. Chem. Soc.*, **88**, 860 (1966). For a general review of alkyl rearrangements see P. Brown and C. Djerassi, *Angew. Chem.*, **79**, 481 (1967).

[8] R. G. Cooks and D. H. Williams, *Chem. Commun.*, 51 (1967) have established a generalized pattern for the migration of hydroxyl and alkoxyl groups to carbonium ion centers.

[9] R. R. Arndt and C. Djerassi, *ibid.*, 578 (1965).

[10] Conditions for operation of the Atlas CH-4 mass spectrometer were: inlet line temperature, 150°; reservoir temperature, 90°; ion source temperature, 200° (except compounds IX and X which were run at 175°); ionizing current, 10 μA; electron voltage as specified. For the A.E.I. MS-9: inlet line and ion source temperature, *ca.* 200°; ionizing current, 100 μA; electron voltage as specified. Processes for which metastable ions were observed are marked with an asterisk (*) in the text. High resolution measurements were carried out where necessary to determine the composition and homogeneity of relevant peaks.

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Benzylic Chlorides in the Darzens Reaction

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The alkoxide-promoted reactions between four *para*-substituted benzyl chlorides and five carbonyl compounds have been studied. *p*-Nitrobenzyl chloride and benzaldehyde was the only combination of reactants that yielded an epoxide; all other pairs gave ethers or stilbenes. The factors influencing the course of these reactions are discussed.

The Darzens reaction, as usually applied, involves the base-promoted condensation of an aldehyde or ketone with an α-halo ester to produce an α,β-epoxy ester. The general scope mechanism of this reaction have been reviewed up to 1954.[2,3] The reaction has also been extended to benzylic halides in a few cases. Kleucker[4] obtained two isomeric epoxides and a small amount of 4,4′-dinitrostilbene when *p*-nitrobenzyl chloride was condensed with cinnamaldehyde or furfural in methanol using potassium carbonate as the base. Bergmann and Hervey[5] made a more extensive study of this reaction; however, in most cases yields of epoxides were not reported. Benzyl chloride with *p*-nitrobenzaldehyde and methanolic potassium hydroxide gave predominantly *p*-nitrobenzyl methyl ether. Hanna and co-workers[6] obtained nearly quantitative yields of 4,4′-dinitrostilbene when *p*-nitrobenzyl chloride was treated with alkali in aqueous acetone. Feldstein and Vander Werf[7] treated benzyl chloride with *p*-chlorobenzaldehyde in attempts to prepare *p*-chlorostilbene oxide; however in ethereal sodium methoxide a chlorohydrin was obtained while with sodium ethoxide in butyl ether the product was *p*-chlorobenzoic acid in 67% yield. When benzaldehyde was condensed with *p*-chlorobenzyl chloride in the

[1] To whom inquiries should be addressed.

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[3] M. Ballester, *Chem. Rev.*, **55**, 283 (1955).

[4] E. Kleucker, *Chem. Ber.*, **55**, 1634 (1922).

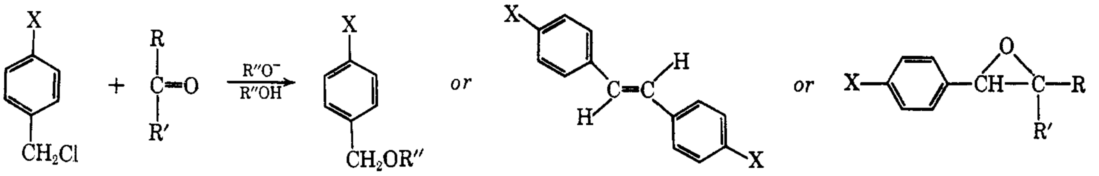
[5] E. Bergmann and J. Hervey, *ibid.*, **62**, 893 (1929).

[6] S. B. Hanna, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 217 (1961).

[7] A. Feldstein and C. A. Vander Werf, *J. Am. Chem. Soc.*, **76**, 1626 (1954).

TABLE I

REACTIONS OF BENZYLIC HALIDES WITH CARBONYL COMPOUNDS[a]



A B C

Reaction	X	Carbonyl compound	Product	Yield, %
1	H	Acetone	A[b]	78
2	H	Benzaldehyde[c]	A[d]	31
3	Cl	Benzaldehyde[e]	A[f]	83
4	p-$ClCH_2C_6H_4O$	Benzaldehyde[g]	A[h]	91[i]
5	NO_2	Formaldehyde[j]	B	99[i]
6	NO_2	Propionaldehyde	B[k]	65[i]
7	NO_2	Benzaldehyde	B, C	1.1,[i] 94[i]
8	NO_2	Acetone	B	98[i]
9	NO_2	Acetophenone[l]	B	23[i,m]

[a] Ethanol (95%) was used as the solvent; the base used was NaOH except in reaction 2 where potassium *t*-butoxide in *t*-butyl alcohol was used; $R'' = C_2H_5$ except in reaction 2 where $R'' = C(CH_3)_3$. [b] A trace of benzyl alcohol was also found. [c] Six per cent was recovered. [d] Yield based on benzyl chloride. The remainder consisted of benzoic acid (44% based on benzaldehyde), dibenzyl ether (38% based on benzyl chloride or benzaldehyde), and benzyl benzoate (13% based on benzaldehyde). [e] Fifty-eight per cent was recovered. [f] A trace of unidentified alcohol was also found. [g] Thirty-three per cent was recovered. [h] The product was the di(ethyl ether). Benzyl alcohol (5%) was also found. [i] Crude yield. [j] Aqueous formaldehyde was used. [k] *p*-Nitrotoluene (13%) was also isolated. [l] Excess acetophenone was used as the solvent. [m] More stilbene was present but was not isolated.

presence of potassium carbonate in methanol, *p*-chlorobenzaldehyde was obtained.

In the studies of the Darzens reaction with benzylic halides thus far, the benzylic halide has generally been of the nitrobenzyl or benzhydryl type while the carbonyl component has generally been an aromatic aldehyde or ketone. The current study was undertaken to further explore the scope of the Darzens reaction in preparing epoxides from benzylic chlorides and to extend the reaction to other aldehydes and ketones, especially in the aliphatic series.

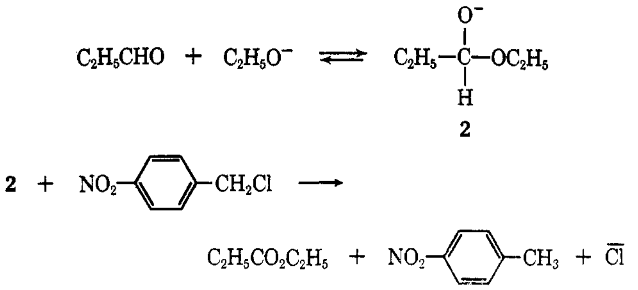
Results and Discussion

The results of this study are summarized in Table I. In the first four reactions simple displacement of chloride by the alkoxide has occurred. The variety of products in the second reaction can be explained on the basis of a Cannizzaro-type (Tischtschenko–Claisen)[8] reaction involving benzaldehyde and the *t*-butoxide ion followed by reaction of the resulting benzyloxy ion with benzyl chloride and benzaldehyde. The benzoic acid in the above reaction probably originated from thermal decomposition of *t*-butyl benzoate during distillation near 200°. Pfannl[9] reported that heating *t*-butyl benzoate at 213° gave benzoic acid and isobutylene.

The high yield of *p*-chlorobenzyl ethyl ether in the third reaction is in contrast to the results of Feldstein and Vander Werf[7] who reported the isolation of *p*-chlorobenzaldehyde from this reaction when potassium carbonate in methanol was employed.

Each of the reactions employing *p*-nitrobenzyl chloride (5–9) gave mainly *trans*-4,4′-dinitrostilbene (**1**) except when benzaldehyde was the carbonyl component, wherein the desired epoxide was found in 94% yield. The results in reaction 8 are analogous to the reaction of Hanna and co-workers[6] mentioned above. These results may be due to a combination of electronic and steric effects. If the carbanion–halohydrin mechanism[10–12] suggested for epoxide formation is correct, one would expect the reaction to be facilitated by electron-withdrawing groups, such as the phenyl group, attached to the carbonyl group. In acetophenone the carbonyl group may be too hindered to undergo attack by the nucleophile; also the electron-releasing inductive effect of the methyl group would reduce the electrophilicity of the carbonyl carbon atom.

The isolation of *p*-nitrotoluene in reaction 6 is rather unexpected. A possible explanation for its formation may be a hydride-type displacement. This



hydride transfer is somewhat analogous to the Cannizzaro reaction noted above.[8] Ethyl propionate was not specifically identified; however, it is quite likely that it would undergo further condensation under the reaction conditions.

An attempt was made to trap the proposed *p*-nitrophenylcarbene intermediate[6] in the formation of 4,4′-dinitrostilbene (**1**) by reaction with cyclohexene. However, no cyclopropane derivative was found, *trans* **1** being the only product.

It appears, based on previously published results and

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(10) G. Hahn, *Chem. Ber.*, **62**, 2485 (1929).

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the current effort, that several factors are involved in determining the course of the Darzens reaction between benzylic halides and aldehydes or ketones. Benzylic halides with weakly acidic benzylic protons are consumed *via* displacement by alkoxide in alcohol. Depending on the carbonyl component, even relatively reactive benzylic halides such as *p*-nitrobenzyl chloride are usually converted to stilbene derivatives. Thus it appears that the nature of the carbonyl acceptor is of considerable importance, for in the cases reported to date where the electron density and steric hindrance on the carbonyl carbon atom are low, epoxide formation occurs. Conversely, when the partially positive nature of the carbonyl carbon is decreased by hyperconjugative or inductive effects, condensation to the epoxide is unfavorable. A detailed study of the effect of bases or solvents was not conducted; however in view of the results of Feldstein and Vander Werf[7] it would not be surprising to observe considerable influence by the solvent or base.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 137 Infracord, and ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. The gas-liquid partition chromatography (glpc) data were obtained on a Beckman GC-2A or F & M Model 500. Melting points were determined in capillary tubes and are uncorrected. Ethanol (2B, 95%) was used as the solvent unless otherwise specified.

Reaction of Benzyl Chloride with Acetone and Sodium Hydroxide in Ethanol.—A solution of sodium hydroxide (22.0 g, 0.55 mole) in 400 ml of ethanol was added over a period of 30 min to a stirred solution of benzyl chloride (63.3 g, 0.50 mole) and acetone (29.0 g, 0.50 mole) in 100 ml of ethanol. After stirring the mixture at reflux for 6 hr, 450 ml of the solvent was distilled, and 300 ml of water was added. After acidification, the organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic solutions were dried over anhydrous sodium sulfate. Distillation gave 53.2 g (78%) of benzyl ethyl ether, bp 182–184°, $n^{27}\text{D}$ 1.4916–1.4934. The infrared spectrum was identical with that of an authentic sample[13-15] except for the presence of a weak band at 2.89 μ. Glpc analysis by comparison with authentic samples showed the presence of a few per cent of benzyl alcohol in addition to benzyl ethyl ether.

Reaction of Benzyl Chloride with Benzaldehyde and Potassium *t*-Butoxide in *t*-Butyl Alcohol.—A solution of benzyl chloride (63.3 g, 0.50 mole) and benzaldehyde (53.1 g, 0.50 mole) was added over a period of 10 min to a stirred solution of potassium *t*-butoxide, prepared under nitrogen from potassium (21.5 g, 0.55 g-atom) and 500 ml of *t*-butyl alcohol. After stirring at reflux for 3 hr, the reaction mixture was worked up as above. Distillation gave 23.7 g of distillate (bp 120–190°). Analysis by glpc (Silicone gum rubber column) showed the presence of benzaldehyde, benzyl chloride, and *t*-butyl benzyl ether. The retention times were identical with those of the authentic compounds.[16]

The distillation residue on cooling, deposited 20.6 g of crystals, whose infrared spectrum was identical with that of an authentic sample of benzoic acid. Distillation of the mother liquor gave more of the above components in addition to benzyl benzoate and dibenzyl ether, which were identified by comparison of their glpc retention times and infrared spectra with those of authentic samples. No *t*-butyl benzoate was found in any fractions. The total isolated amounts were 3.1 g of benzaldehyde, 3.9 g of benzyl chloride, 25.3 g of *t*-butyl benzyl ether, 25.44 g of benzoic acid, 6.3 g of benzyl benzoate, and 35.4 g of dibenzyl ether.

Reaction of *p*-Chlorobenzyl Chloride with Benzaldehyde and Sodium Hydroxide in Ethanol.—A solution of *p*-chlorobenzyl chloride (3.22 g, 0.20 mole), benzaldehyde (23.4 g, 0.22 mole), and sodium hydroxide (8.8 g, 0.22 mole) in 300 ml of ethanol was stirred at reflux for 4 hr. Infrared analysis of the distilled product indicated a mixture of benzaldehyde, *p*-chlorobenzyl ethyl ether,[17] and an unidentified alcohol. Glpc analysis (silicone rubber column) showed the presence of benzaldehyde (13.6 g, 58% recovery) and *p*-chlorobenzyl ethyl ether (28.3 g, 83% yield). The retention times on a Carbowax 20 M column were identical with those of the known compounds. Absent from the reaction mixture were *p*-chlorobenzyl chloride, *p*-chlorobenzaldehyde, ethyl benzoate, and benzyl ethyl ether.

Reaction of Bis(α-chloro-*p*-tolyl) Ether (3) with Benzaldehyde and Sodium Hydroxide in Ethanol.—A solution of sodium hydroxide (8.8 g, 0.22 mole) in 200 ml of ethanol was added over a period of 30 min to a stirred suspension of **3** (26.7 g, 0.10 mole) and benzaldehyde (23.4 g, 0.22 mole) in 100 ml of ethanol. The mixture was stirred at reflux for 4 hr and worked up as above. Distillation gave the following fractions: (a) 7.7 g (33% recovery), bp 66–67° (9 mm), identified as benzaldehyde by infrared analysis; (b) 2.1 g, bp 125° (0.2 mm), identified as *ca.* 50% benzyl alcohol (5% yield) by infrared analysis; and (c) 18.9 (66%), bp 132–138° (0.1 mm), $n^{21}\text{D}$ 1.5432 (lit.[18] $n^{25}\text{D}$ 1.5405), identified as bis(α-ethoxy-*p*-tolyl) ether (**4**). The infrared spectrum of the distillation residue (7.0 g) indicated it to be mainly **8**. The total yield of crude **4** was 25.9 g (91%).

Reaction of *p*-Nitrobenzyl Chloride with Acetone and Sodium Hydroxide in Ethanol. Preparation of *trans*-*p*,*p*-Dinitrostilbene (1).—A solution of sodium hydroxide (8.8 g, 0.22 mole) in 200 ml of ethanol was added over a period of 15 min to a stirred suspension of *p*-nitrobenzyl chloride (34.3 g, 0.20 mole) and acetone (11.6 g, 0.20 mole) in 400 ml of ethanol and stirred at reflux for 6 hr. The reaction mixture was diluted with 500 ml of water, acidified, and filtered. The solid (17.0 g, 63%) was recrystallized from aqueous dimethyl sulfoxide and from acetone to give bright yellow-orange needles of **1**: mp 292.5–293.5° (with sublimation), lit.[19] melting point ranged from 280 to 305°.

Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.21; H, 3.72; N, 10.37. Found: C, 62.56; H, 3.78; N, 10.20.

The aqueous filtrate was extracted with methylene chloride, the combined extracts were washed with water and dried. On removal of the solvent, an additional 9.5 g of crude *trans* **1** was obtained. The total yield of crude *trans* **1** was 26.5 g (98%).

Repetition of this experiment using excess acetone as the solvent and powdered sodium hydroxide as the base again gave *trans* **1** in a crude yield of 98%.

Reaction of *p*-Nitrobenzyl Chloride with Formaldehyde and Sodium Hydroxide in Aqueous Ethanol.—A solution of sodium hydroxide (8.8 g, 0.22 mole) in 200 ml of ethanol was added to a stirred suspension of *p*-nitrobenzyl chloride (34.3 g, 0.20 mole) and 37% aqueous formaldehyde (17.9 g, 0.22 mole) in 100 ml of ethanol over a period of 15 min. After stirring at reflux for 4 hr, the reaction mixture was worked up as in the preceding reaction. The total yield of crude *trans* **1** was 27.0 g (99%).

Reaction of *p*-Nitrobenzyl Chloride with Propionaldehyde and Sodium Hydroxide in Ethanol.—A solution of sodium hydroxide (8.8 g, 0.22 mole) in 200 ml of ethanol was added over a period of 30 min to a stirred suspension of *p*-nitrobenzyl chloride, (34.3 g, 0.20 mole) and propionaldehyde (12.8 g, 0.22 mole) in 100 ml of ethanol. After stirring at reflux for 4 hr, the mixture was processed as above. A total of 17.7 g (66%) of crude **1** was obtained. Distillation of the mother liquor gave 2.8 g of material which was shown by infrared analysis to be mainly *p*-nitrotoluene (13%). Carbonyl and hydroxyl impurities were present. Another fraction [5.6 g; bp 110–150° (0.4 mm); $\lambda_{\max}^{\text{neat}}$ 2.85 (m), 3.39 (s), 3.69 (m), 5.81 (s), 5.95 (s), 6.26 (s) μ] was not identified.

Infrared analysis of the starting chloride (*p*-nitrobenzyl chloride) showed no trace of *p*-nitrotoluene.

Reaction of *p*-Nitrobenzyl Chloride with Benzaldehyde and Sodium Hydroxide in Ethanol.—A solution of sodium hydroxide (8.8 g, 0.22 mole) in 200 ml of ethanol was added to a stirred suspension of *p*-nitrobenzyl chloride (34.3 g, 0.20 mole) and benzaldehyde (23.4 g, 0.22 mole) in 100 ml of ethanol over a 45-min period. The mixture was stirred at reflux for an additional 2 hr and processed as above. A small amount of the stilbene (**1**)

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(13) J. B. Senderens, *Compt. Rend.*, **178**, 1412 (1924).

(14) J. v. Braun, *Chem. Ber.*, **43**, 1350 (1910).

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(0.6 g, 1.1%) was filtered. The organic layer of the filtrate was separated, and the aqueous layer was extracted with methylene chloride. The solvent from the combined organic solutions was distilled, and on cooling, the residue was solidified (45.3 g, 94%). Recrystallization three times from ethanol gave 15.8 g, (33%) of p-nitrostilbene oxide, mp 122–124.5°. The infrared spectrum was identical with that of the authentic sample (mp 125.5–126.5°) prepared according to the procedure of Bergmann and Hervey.[5]

Reaction of p-Nitrobenzyl Chloride with Acetone and Sodium Hydroxide.—A solution of p-nitrobenzyl chloride (34.3 g, 0.20 mole) in 50 ml of acetophenone was added to a stirred suspension of powdered sodium hydroxide (8.8 g, 0.22 mole) in 50 ml of acetophenone over a period of 30 min. The mixture was stirred at 100° for 3 hr, and, upon cooling, 100 ml of water was added. After acidification, 6.2 g (23%) of 1 was filtered. Infrared analysis of the syrup remaining after removing most of the acetophenone indicated the presence of mainly 1 in addition to acetophenone.

Reaction of p-Nitrobenzyl Chloride with Sodium Hydroxide in Cyclohexene.—A solution of p-nitrobenzyl chloride (34.3 g, 0.22 mole) in 400 ml of cyclohexene was added from a steam-heated funnel over a period of 20 min to a stirred suspension of powdered sodium hydroxide (8.8 g, 0.22 mole) in 100 ml of cyclohexane. After stirring at reflux for 4 hr and subsequent cooling, 100 ml of water was added and acidified. The remaining solid was filtered and extracted with hot cyclohexene to give 11.7 g (75% yield) of *trans* 1. The infrared spectrum was identical with that of the authentic sample. The organic layer of the filtrate was separated, and the aqueous layer was extracted with 50 ml of cyclohexene. The combined organic extracts, after drying over anhydrous calcium sulfate and distillation of the solvent, gave, on cooling, 25.1 g of crystals, mp 60–65°. Two recrystallizations from benzene–heptane gave 5.0 5 (15% recovery) of p-nitrobenzyl chloride. The infrared spectrum was identical with that of the authentic sample except for the presence of additional maxima at 12.61 and 13.23 μ (Nujol). From the combined mother liquors was obtained an additional 9.5 g of p-nitrobenzyl chloride. The total recovery of p-nitrobenzyl chloride was 14.5 g (42%).

Registry No.—**1**, 100-44-7; **3**, 104-83-6; **4**, 2362-18-7; **5**, 100-14-1; acetone, 67-64-1; benzaldehyde, 100-52-7; formaldehyde, 50-00-0; propionaldehyde, 123-38-6; acetophenone, 98-86-2; *trans-p,p*-dinitrostilbene 2501-02-2.

Carbene and Carbenoid Chemistry. IV. The Effect of Halide Ions on Chloro- and Bromocarbenoid Addition Reactions[1]

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cis- and *trans*-7-chloronorcaranes were the major cyclopropyl products from the reaction of cyclohexene with methylene chloride and methyllithium prepared from methyl chloride or bromide. Small amounts of *cis*- and *trans*-7-methylnorcaranes were also produced; use of methyl bromide gave small amounts of *cis*- and *trans*-7-bromonorcaranes. In contrast, methyllithium prepared from methyl iodide or from methyl chloride with lithium iodide added gave primarily the methylnorcaranes with smaller amounts of norcarane and the chloronorcaranes. 2,3-Dimethyl-2-butene gave 3-chloro-1,1,2,2-tetramethylcyclopropane and pentamethylcyclopropane on reaction with methylene chloride and methyllithium prepared from methyl iodide. The reaction of cyclohexene with methylene bromide and methyllithium prepared from either methyl bromide or iodide gave norcarane as the principal cyclopropyl product, accompanied by lesser amounts of the 7-bromo derivatives. The corresponding reaction with bromoform gave primarily 7,7-dibromonorcarane with smaller amounts of the 7-bromo derivatives. Methylene iodide was formed from the reaction of methylene bromide and methyllithium prepared from methyl iodide, but added lithium iodide was necessary for the formation of methylene iodide from methylene chloride and methyllithium. Probable reaction pathways are discussed to account for the above observations.

The reaction of methylene chloride with an alkyllithium in the presence of an olefin usually gives a chlorocyclopropane,[2] presumably *via* an intermediate carbenoid species.[2a,c,3] Recently several reports have appeared describing anomalies which result when this reaction is carried out with methyllithium prepared from methyl iodide. We reported earlier that the reaction of styrene, methylene chloride, and n-butyllithium prepared from n-butyl bromide gave the expected *cis*- and *trans*-1-chloro-2-phenylcyclopropanes.[4] However when the reaction was repeated with methyllithium which was prepared from methyl iodide, phenylcyclopropane and *cis*-1-methyl-2-phenylcyclopropane[5–7] were obtained, but no trace of the chlorophenylcyclopropanes was found.[4] Similarly, the reaction of cyclooctatetraene, methylene chloride, and methyl-

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[3] (a) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962); (b) *ibid.*, **87**, 4270 (1965); (c) H. Heaney, *Organometal. Chem. Rev.*, **1**, 27 (1966); (d) G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967).

[4] W. L. Dilling, *J. Org. Chem.*, **29**, 960 (1964).

[5] In our original paper[4] the stereochemistry of the 1-methyl-2-phenylcyclopropane was not specified. Analysis of the nmr spectrum of this compound strongly suggests that it is the *cis* isomer.[6] The position of the methyl resonance (−0.82 ppm) is in good agreement with the data published for methyl groups *cis* to phenyl rings.[7] For example the *cis* (to phenyl) methyl resonance of 1,1-dimethyl-2-phenylcyclopropane occurs at −0.77 ppm while the *trans* methyl occurs at −1.20 ppm.[7] The singlet character of the phenyl resonance[4] is also in accord with the *cis* stereochemistry.[7] The phenyl resonance for *cis*-1-chloro-2-phenylcyclopropane is also a singlet while the *trans* isomer is a multiplet.[4] Finally the benzylic proton resonance supports the *cis* assignment; primary coupling constants of *ca.* 6.1, 8.5, and 8.5 cps.[4] The fact that none of the coupling constants is in the 3–5-cps range lends support to the proposal that this isomer is the *cis* isomer. One would expect the coupling constant between the benzylic proton and the proton on the methyl-bearing carbon to be in the 3–5-cps range for the *trans* isomer. From the published spectra[4] of the benzylic protons of the *cis*- and *trans*-1-chloro-2-phenylcyclopropanes it can be seen that the *cis* isomer has coupling constants of 7.7, 7.7, and 9.1 cps while the *trans* isomer has coupling constants of 3.3, 7.6, and 8.9 cps. The coupling constants involved in the benzylic proton of the methylphenylcyclopropane are closer in magnitude to those of the *cis*-chlorophenylcyclopropane than to the *trans* isomer. Apparently the coupling constant of the benzylic proton to the *trans* methylene proton in both of the chlorophenylcyclopropanes and the phenylmethylcyclopropane is larger than usual (in the range of 6.1–9.1 cps).

[6] See R. A. Moss, *J. Org. Chem.*, **30**, 3261 (1965).

[7] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).