Palladium- vs. Peroxide-Promoted Decarbonylation of Neophyl-like Aldehydes[1,2]

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A series of 1-methylbenzocycloalkenyl-1-acetaldehydes has been synthesized, incorporating four-, five-, and six-membered alicyclic rings. Their synthesis and characterization is described. For the purpose of further distinguishing the alternative methods of aldehyde decarbonylation by peroxide vis-á-vis palladium promotion, these aldehydes were subjected to each method. The former method failed completely in the case of the cyclobutyl analogue. The other ring systems exhibited typical neophyl free radical rearrangement, giving rise to 1,1-dimethylbenzocycloalkenes and to 2-methylbenzocycloalkenes with ring expansion. The extent of neophyl rearrangement varied inversely with concentration of the aldehyde. The product from the cyclobutyl compound was a mixture that could not be characterized definitely. The palladium-promoted method succeeded in all cases, although again the cyclobutyl analogue was more resistant to reaction. In this reaction the products were *solely* the 1,1-dimethylbenzocycloalkenes, lending credence to a mechanism that does not involve free radicals, at least beyond the catalyst surface.

The observation[4] that decarbonylation of β-phenylisovaleraldehyde (1) with palladium on carbon proceeded with essentially no rearrangement contrasts markedly with its decarbonylation with di-*tert*-butyl peroxide (DTBP), where rearrangement can be extensive.[5] Furthermore, the latter type decarbonylation of aldehydes 2 is subject to a modest ring size effect, the percentage of phenyl-rearranged product decreasing as the phenyl migration becomes more stereoelectronically demanding in the smaller or more constrained rings.[6] No rearrangement, in fact, was observed in the decarbonylation of benzonorbornene-1-acetaldehyde (3).[7] However, no study has as yet extended the

1

2   m = 2–6

3

4-CHO, m = 1
5-CHO, m = 2
6-CHO, m = 3
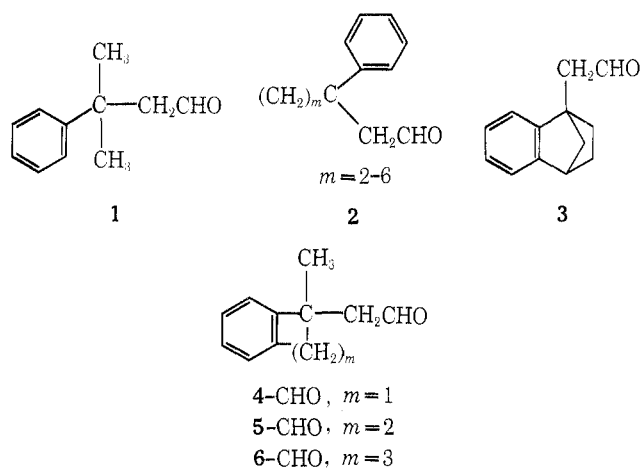
use of palladium-promoted decarbonylation to other rearrangement-prone systems.[8] With this as its background, a study was undertaken on the benzoalicyclic acetaldehydes 4–6-CHO above to compare the rearrangement observed with the two disparate decarbonylation techniques.

Results

The aldehydes 4–6-CHO were synthesized by straightforward procedures which are given in the Experimental Section.

Decarbonylation studies were carried out essentially as earlier described.[8c] The results are shown in Tables I and II.

An additional study was carried out in light of the data in Table I, namely, a study aimed at trapping intermediate acyl radicals with carbon tetrachloride.[9] The results of this study are shown in Table III.

Table I
Peroxide-Induced Decarbonylations

Aldehyde	Concn, M	CO[a]	Hydrocarbon products[b]	Rearrangement
1	6.4[c]	81	65	64
1	1.0[d]	80	69	91
4-CHO	6.0[c]	16	0	
4-CHO	1.0[d]	20	0	
5-CHO	5.9[c,e]	81	76	35
5-CHO	1.0[d]	67	38	86
6-CHO	5.6[c]	74	56	32
6-CHO	1.0[d]	79	24	74

[a] ±2%, by GLC analysis (molecular sieve column, 25°), average of several runs. [b] ±3%, by GLC analysis using calibration data with known mixtures, average of several runs. [c] Neat aldehyde heated at 160° (bath) with three equally spaced additions of DTBP (10 mol %) over 300 min. [d] As in c, except that the reaction was performed in chlorobenzene at 140° (bath) over 900 min. [e] Data from ref 25.

Table II
Palladium-Promoted Decarbonylations[a]

Aldehyde	Time, hr[c]	CO	Hydrocarbon[d]
1	5	92	84, *tert*-butylbenzene
4-CHO	15	34	31, 4-H
5-CHO	3	80	79, 5-H
6-CHO	5	84	82, 6-H

%[b] spans the CO and Hydrocarbon columns.

[a] On neat aldehyde (1–2 mmol) in the presence of palladium on carbon (5%, 100 mg) at 160° (bath). [b] Average of three separate runs, ±5%. [c] Time for disappearance of aldehyde, determined by GLC analysis. [d] Less than 1% (if any) rearranged products was present.

Discussion

The peroxide-induced decarbonylation process is believed to take the course shown in Scheme I. The reaction is well documented[5] and will not be discussed in detail here. The use of 1 along with the others in this study served to calibrate the results, and to allow a more secure comparison with earlier reported data. At 129.7° Rüchardt[10] observed 52% rearrangement to isobutylbenzene and related olefins upon reaction of neat 1 with DTBP, the extent of rearrangement rising both with dilution of 1 and the tem-

Table III
Peroxide-Induced Reaction of Aldehydes and Carbon
Tetrachloride[a]

| Aldehyde	% acyl radical trapped[b]
1	95
4-CHO	0
5-CHO	72
6-CHO	50

[a] Aldehyde (1 M in carbon tetrachloride) and benzoyl peroxide (10 mol %) were refluxed for 5 hr, after which time methanol was added and the mixture was refluxed for an additional 1 hr. [b] As the corresponding methyl ester, ±5%, the average of three separate runs.

perature used. For example, rearrangement at 129.7° rose to 84% with 1 M 1 in o-dichlorobenzene and to 71% at 144.5° with 3 M 1 in the same solvent. Our results with 1 seem quite comparable to these.[11] Moreover, our earlier results[4] with 1 in the palladium-promoted process were again observed here. So it is believed that the conditions and apparatus used are proper for a comparison among the aldehydes of this study in the two types of decarbonylation.

The results in the tables indicate clearly that the benzoalicyclic analogues of 1 behave less satisfactorily in all three types of reactions studied: peroxide-induced decarbonylation, palladium-promoted decarbonylation and peroxide-induced chlorination. Furthermore, while insignificant differences exist between 5- and 6-CHO in these reactions, a startling feature is the gross dissimilarity found with 4-CHO. Only small amounts of carbon monoxide were evolved in the several DTBP-induced reactions of 4-CHO attempted. No 4-H or 7 was ever observed under conditions where less than 1% of each was detectable. Control studies indicated that 60% of these hydrocarbons would be lost through decomposition under reactions conditions, but the failure to detect even 1% of these products argues against their formation at all. The only semicharacterizable product was a viscous oil obtained from chromatography of the reaction residue. Unfortunately, however, the intractable nature of the material precluded any further study.[12] Nonetheless, the acyl radicals formed from 4-CHO obviously underwent decarbonylation with difficulty for some reason, and their presence was therefore sought through chain transfer with carbon tetrachloride,[9] an efficient process with 1 (Table III). Again, a totally negative process was found with 4-CHO. Clearly, acyl radicals from surprisingly slowly (if at all) from this aldehyde. Aldehydes 5- and 6-CHO underwent either type of decarbonylation to similar extents. With both these alicyclic cases, however, the migration of the aryl group via the Ar₁-3 transition state necessary to form 8· and 9· (Scheme I) introduces additional steric strain, causing both to exhibit less rearrangement than does 1 itself in the peroxide process. The lower yield of hydrocarbon in all cases compared to carbon monoxide loss reflects the poor chain nature of these decarbonylations (chain length ~3–10). The radicals formed by loss of carbon monoxide undergo disproportionation and coupling,[10] both of which are termination steps. While it is dangerous to compare different rearrangement percentages in reactions that are not quantitative, it is felt that the rates of disproportionation and coupling in the cases of similar radicals are themselves probably similar and that therefore the rearrangement differences are real.

The mechanism of the heterogeneous palladium-promoted decarbonylation is unknown.[14] However, the results with the present aldehydes concur with the earlier suggestion[4] that neither acyl species R–CO nor alkyl species R· intervene (at least beyond the catalytic surface), as evidenced both by the partial success of the reaction with

Scheme I
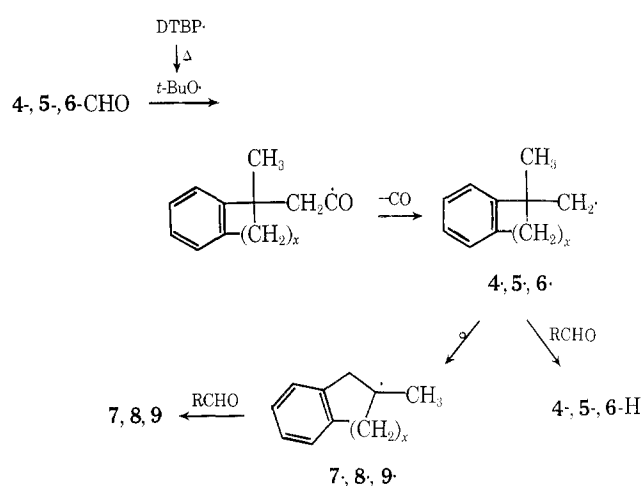
4-CHO and by the total lack of rearranged products from the sensitive precursors 1, 5-, and 6-CHO.

Summary

The present study indicated that palladium-promoted decarbonylation of aldehydes is an efficient, simple, and structurally retentive method, even in sensitive systems. The peroxide-induced technique, on the other hand, is less efficient, more complex, and (as expected) rearrangement prone. Most interestingly, the cyclobutyl analogue has been found to be unexpectedly resistant to both decarbonylation methods, completely failing in the peroxide-induced technique. Further work is needed to determine the cause(s) of this resistance.

Experimental Section

Melting points and boiling points are uncorrected. The former were taken on a Fisher-Johns block. Gas–liquid partition chromatography was performed on a Varian Aerograph A-90P with helium gas as carrier. The columns and temperatures used are cited where appropriate. The following instruments were used to obtain spectra:[17] infrared, Beckman IR 5A; nuclear magnetic resonance, Varian A-60A. The former are given in microns and only significant absorptions are listed. The latter are given in parts per million units (δ) relative to Me₄Si as internal standard. Integration of signals gave values expected for the assigned structure. The usual splitting abbreviations are used. Microanalyses were performed by G. D. Searle Analytical Department or by Micro-Tech Laboratories, both in Skokie, Ill. Spectral and analytical data, together with other selected physical data, are collected in the supplementary tables.[18]

Synthesis of Aldehydes. β-Phenylisovaleraldehyde (1). The aldehyde was available from another study,[4] as was the corresponding methyl ester.

1-Methylbenzocyclobutenyl-1-acetaldehyde (4-CHO). 1-Methylbenzocyclobutene-1-carboxylic acid[1] (0.02 mol) was heated with redistilled thionyl chloride (0.05 mol) in benzene (50 ml). Removal of excess reactants and subsequent distillation afforded the acid chloride[19] 4'- COCl, bp 65° (0.2 mm), 97% yield. Reaction of the acid chloride (0.025 mol) in dry ether (80 ml) with diazomethane (0.07 mol) in dry ether (400 ml) was complete in 2 hr at 25°. The ether was removed by rotary evaporation and the oily, residual diazoketone was dissolved in dry methanol (200 ml). Treatment of this solution with silver benzoate in triethylamine (5 g in 60 ml) over a 3-hr period, as described for this method,[20] led to evolution of nitrogen. The reaction mixture was processed to afford **methyl 1-methylbenzocyclobutenyl-1-acetate, (4-COOMe)**, 79%, bp 88° (0.80 mm).[19] An alternative synthesis of this ester involved reaction of 1-methylbenzocyclobutenyl-1-carbinyl tosylate[1] (4-OTs) with sodium cyanide (1.1 equiv) in dimethyl sulfoxide (25 ml/mmol of tosylate) at 80° for ca. 12 hr. Dilution of the material with water and extraction with ether led to **1-methylbenzocyclobutenyl-1-acetonitrile, (4-CN)**, 49%, bp 100–101° (1.5 mm).[19] Olefinic products which were identical with those observed[1] in the

solvolysis of 4-OTs were also formed in this reaction, rendering it a less satisfactory procedure. Methanolysis of 4-CN (0.04 mol) with water (0.04 mol) in methanol (45 ml) was achieved under reflux as dry hydrogen chloride was bubbled through the solution for 4 hr. Cold brine (50 ml) was added and the solution was extracted with ether. The ether extracts washed until neutral, dried (MgSO₄), and distilled. The ester 4-COOMe was obtained in 78% yield.

Saponification of this ester with 20% ethanolic sodium hydroxide and acidification then gave **1-methylbenzocyclobutenyl-1-acetic acid** (4-COOH), 97%, bp 142° (3.5 mm).[19] The acid was converted to its acid chloride as mentioned above, 97%, bp 111° (4.5 mm).[19] The acid chloride (0.04 mol) was added with stirring to a solution of ethylenimine (0.04 mol) and triethylamine (0.04 mol) in ether (20 ml) at 0°. After 30 min the solution was filtered and combined with an ether wash of the amine hydrochloride precipitate. Ethereal lithium aluminum hydride (8 ml of a 1.25 *M* solution) was then added to the combined ether solution of the aziridide dropwise at 0° over 30 min. Processing the mixture as described[21] gave aldehyde 4-CHO, 80%, bp 82–83° (0.75 mm).[19] The 2,4-dinitrophenylhydrazone was prepared in customary fashion, mp 113°.[19] Heating 4-CHO at 160° either neat or in chlorobenzene produced no significant change in its ir or NMR spectra. See ref 12.

An alternative, attempted synthesis of 4-CHO involved reduction of 4-COOH with ethereal lithium aluminum hydride to 1-**methylbenzocyclobutenyl-1-ethanol** (4-CH₂OH), 98%, bp 100–101° (1.0 mm),[19] followed by conversion to its tosylate (4-CH₂OTs) with *p*-toluenesulfonyl chloride in pyridine in the usual fashion,[22] 90%. The tosylate[19] was an oil that was purified by passage through a short column of alumina. Attempted oxidation of this tosylate with sodium bicarbonate in dimethyl sulfoxide[23] failed. Only dark, ill-defined products resulted.

Another synthesis of 4-CHO proceeded by treatment of 4-COCl with lithium tri-*tert*-butoxyaluminohydride in diglyme using a literature method[24] (65% yield).

1-Methylindanyl-1-acetaldehyde (5-CHO). The aldehyde was prepared as reported.[25] Reaction of the known[25] acid with diazomethane in ether led to **methyl 1-methylindanyl-1-acetate (5-COOMe)**, 94%, bp 122–123° (0.32 mm).[19]

1-Methyltetralyl-1-acetaldehyde (6-CHO). 4-Methyl-4-carboxymethyl-1-tetralone (prepared as reported,[26] 0.25 mol) was heated under reflux in a solution of potassium hydroxide (85% material, 1 mol), hydrazine hydrate (90%, 50 ml), and diethylene glycol (700 ml). Low-boiling material was allowed to escape until the temperature rose to 220°. After 12 hr at this temperature, the material was cooled and then acidified with hydrochloric acid. The solution was extracted several times with benzene and the combined extracts were dried and evaporated to produce **1-methyltetralyl-1-acetic acid** (6-COOH), 86%, mp 72–73° from methanol–water.[19] Reaction of this acid with diazomethane in ether afforded **methyl 1-methyltetralyl-1-acetate**, (6-COOMe), 94%, bp 98–99° (0.1 mm).[19]

Reduction of the above acid on a 20-mmol scale with ethereal lithium aluminum hydride in the well-known fashion gave **2-(1-methyltetralyl)ethanol** (6-CH₂OH), 91.5%, bp 143° (1.5 mm).[19] Reaction of the alcohol with *p*-toluenesulfonyl chloride in pyridine according to the published procedure[22] gave the corresponding tosylate 6-CH₂OTs, 96.5%, an oil purified by low-temperature crystallization from pentane, mp −20°.[19] Oxidation of the purified tosylate (30 mmol) was achieved by reaction with sodium bicarbonate (20 g) in dimethyl sulfoxide (150 ml) at 150°. Nitrogen was bubbled through the hot solution for 5 min and then ice water (200 ml) was added. The material was extracted with ether and processed to yield 6-CHO, 73%, bp 158–159° (10 mm).[19] The 2,4-dinitrophenylhydrazone was made in the usual fashion, mp 171–172°.[19]

Conversion of 6-COOH with thionyl chloride in benzene to the acid chloride was straightforward, 97%, bp 114–115° (0.4 mm).[19] Reaction of this acid chloride with lithium tri-*tert*-butoxyaluminohydride in the reported manner[24] gave 6-CHO in 43% yield. Reduction to 6-CHO by reaction of lithium aluminum hydride and the aziridide[21] from the acid chloride proceeded in 37% yield.

Synthesis of Reference Hydrocarbons. 1,1-Dimethylbenzocyclobutene (4-H). Reduction of 4-OTs (8.25 mmol) with lithium aluminum hydride (8.25 mmol) in ether (50 ml) was performed under reflux (5 hr). The solution was treated carefully with water followed by dilute acid and processed. Distillation afforded 4-H, 80%, bp 60–61° (20 mm), as an oil smelling like *tert*-butylbenzene.[19]

1,1-Dimethylindan (5-H)[27] and **1,1-dimethyltetralin (6-H)[27]** were obtained by the literature method cited, as were **2-methyl-**

indan (7),[27] 2-methyltetralin (8),[25] and **2-methylbenzsuberane (9).[28]**

Decarbonylation Studies. Peroxide-Induced. The general procedure is well documented.[10] Certain details are given in Tables I and III. All-glass apparatus[29] was used in all studies because the use of rubber or silicone septa for peroxide entry or reaction monitoring led to inconsistent results, usually evidenced by extensive induction periods and increased peroxide demand. A brief process description follows. Accurately weighed aldehyde (1–4 mmol, neat or 1 *M* in chlorobenzene) was placed in the apparatus which was then flushed with helium. Di-*tert*-butyl peroxide (10 mol %, redistilled, $d_4{}^{24}$ 0.788) was added and the system was closed. The unit was placed in a 160° bath and the evolved gas collected. Volatile products were not collected but were returned to the reaction mixture. Two equal subsequent DTBP additions were made via a pressurized capillary. After the time period for study, the material in the system was analyzed by GLC: carbon monoxide was determined on a molecular sieves 13X column at 25° and the hydrocarbon products were determined on a series of columns, SE-30, Apiezon L, and Flexol 8N8. Calibration studies were done with mixtures of authentic samples. From the response curves obtained on the mixtures of known hydrocarbons, plus an accurate determination of the reaction mixture volume (±1 μl), calculations gave the amount of each substance present, excluding high molecular weight material for which no GLC data was obtained. In the case of 4-CHO, the viscous reaction residue was chromatographed on silica gel. Benzene eluted chlorobenzene (if any were used) and small amounts of unchanged 4-CHO. Methanol was necessary to elute the viscous yellow oil mentioned in the Discussion.

Because the more volatile hydrocarbon products were returned to the reaction mixture, their stability was determined under reaction conditions. The appropriate pair of hydrocarbons (e.g., 4-H and 7) were made 0.5 *M* in chlorobenzene (4 ml). Di-*tert*-butyl peroxide (0.2 mmol) and an internal standard (biphenyl or *o*-dichlorobenzene) was added and the mixture was heated under reflux for 5 hr. Only the mixture of 4-H and 7 showed significant transformation during this time period; 4-H unchanged, 36%; 7 unchanged, 42%. The other hydrocarbons showed minor changes.

The studies with carbon tetrachloride and benzoyl peroxide (Table III) were carried out as were the DTBP experiments. The methyl esters formed were confirmed and analyzed by GLC on a Reoplex column at 180° by comparison with authentic samples prepared as mentioned above.

Palladium-Promoted. Certain details may be found in Table II. The reactions were performed again in an all-glass apparatus.[29] After the indicated time period (when the aldehyde was consumed), carbon tetrachloride (2 ml) was added and the mixture was carefully filtered to remove the catalyst. Analyses for carbon monoxide and the hydrocarbon products were by GLC as mentioned earlier. Sensitivity experiments indicated that at least 1% (and in some cases less) of rearranged hydrocarbons could be detected on the GLC columns used.

References and Notes

(1) Ring Size Effects in the Neophyl Rearrangement. IX. Part VIII: J. W. Wilt and W. W. Pawlikowski, Jr., *J. Org. Chem.*, **37**, 820 (1972).

(2) Taken from portions of the dissertation of W.W.P., Jr., Loyola University of Chicago, 1970.

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(4) J. W. Wilt and V. P. Abegg, *J. Org. Chem.*, **33**, 923 (1968).

(5) For a review of this well-known rearrangement, see J. W. Wilt in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 8, pp 346–356.

(6) For studies of **2**, cf. J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966), m = 2, 3; J. W. Wilt and H. Philip, *ibid.*, **25**, 891 (1960), m = 4, 5; J. W. Wilt, J. F. Zawadzki, and D. G. Schultenover, *ibid.*, **31**, 876 (1966), m = 6.

(7) J. W. Wilt, H. F. Dabek, Jr., J. P. Berliner, and C. A. Schneider, *J. Org. Chem.*, **35**, 2402 (1970).

(8) For other examples of this reaction, cf. (a) ref 4 and references cited therein; (b) J. S. Matthews, D. C. Ketter, and R. F. Hall, *J. Org. Chem.*, **35**, 1694 (1970); (c) J. W. Wilt and E. Vasiliauskas, *ibid.*, **37**, 1467 (1972).

(9) S. Winstein and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **69**, 2916 (1947); D. E. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).

(10) C. Rüchardt, *Chem. Ber.*, **94**, 2599 (1961).

(11) Rüchardt[10] found that use of chlorobenzene as solvent in the decarbonylation complicated the rearrangement data owing to formation of *p*-chlorotoluene (from DTBP-engendered methyl radical attack). Such a problem was not observed in the cases of **4–6**-CHO, and was corrected in our study of **1** by use of several GLC columns which separated this contaminant from the hydrocarbon products.

(12) Benzocyclobutenes can isomerize thermally to *o*-quinodimethanes.[13] Although no gross change was apparent in the spectra of 4-CHO after heating, slight conversion to an *o*-quinodimethane (and attendant polymerization) cannot yet be totally discounted as a cause of the anomalous behavior observed with this aldehyde.

(13) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958); F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Lett.*, 15 (1962). For a review, cf. I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970).

(14) Based on possibly analogous processes involving homogeneous decarbonylation of aldehydes and acid chlorides with coordinated species,[15] a sequence as shown below may be proposed.

$$RCHO + Pd^0 \underset{\text{oxidative addition}}{\rightleftharpoons} R-\overset{O}{\overset{\parallel}{C}}-Pd-H \rightarrow R-\overset{\overset{O}{\diagup\diagdown}C}{Pd}-H$$

$$RH + Pd^0 \leftarrow RPdH$$

Another mechanistic possibility is a concerted, chelotropic reaction with loss of carbon monoxide and formation of hydrocarbon occuring in the allowed suprafacial manner only in the presence of transition metal catalyst (like palladium).[16]

(15) (a) J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Am. Chem. Soc.*, **89**, 2338 (1967); (b) J. Tsuji and K. Ohno, *ibid.*, **90**, 99 (1968); (c) H. M. Walborsky and L. E. Allen, *Tetrahedron Lett.*, 823 (1970).

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(17) Complete ir and NMR spectra are available in the dissertation of W.W.P., Jr.

(18) See paragraph at end of paper regarding supplementary material.

(19) For further characterization of this compound, see the supplementary tables.

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(28) L. David and A. Kergomard, *C. R. Acad. Sci., Ser. C*, **268**, 986 (1969).

(29) The details of the apparatus are given in the dissertation of W.W.P., Jr.

Reaction of Organoboranes with Lithium Aldimines. A New Approach for the Synthesis of Partially Mixed Trialkylcarbinols[1]

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Partially mixed trialkylcarbinols are produced in good yields via the reaction of dialkylchloroboranes with lithium aldimines followed by treatment with (1) thioglycolic acid, (2) NaOH in diglyme, (3) H_2O_2–NaOH. Primary or secondary alkyl groups are introduced readily. The reaction of trialkylboranes with lithium aldimines also proceeds smoothly, affording the partially mixed trialkylcarbinols on treatment with (1) thioglycolic acid, (2) H_2O_2–NaOH.

In recent years, various procedures for the synthesis of trialkylcarbinols via organoboranes have been developed. Symmetrical trialkylcarbinols are produced from the reaction of trialkylboranes with carbon monoxide,[2] sodium cyanide,[3] or α,α-dichloromethyl methyl ether (DCME).[4] Partially mixed trialkylcarbinols are obtained by treatment of partially mixed trialkylboranes with carbon monoxide,[5] or by treatment of trialkylboranes with 1-lithio-1,1-bis(phenylthio)alkane.[6] On the other hand, totally mixed carbinols are available via the reaction of totally mixed hindered boranes with DCME,[7] or via dialkylmethylvinylboronates.[8] We now report a new approach for the synthesis of partially mixed trialkylcarbinols, where two alkyl groups of the carbinols arise from dialkylchloroboranes and the third is derived from Walborsky's masked acyl carbanions.[9]

Results and Discussion

We previously reported that dialkylchloroboranes (**1**), now readily available via hydroboration with chloroborane–ethyl etherate,[10] reacted with lithium aldimines[9] (**2**) to give unsymmetrical ketones (**5**) on treatment with (1) thioglycolic acid, (2) aqueous alkaline hydrogen peroxide (eq 1).[11]

$$R_2BCl + t\text{-Bu}-N{=}C\overset{R'}{\underset{Li}{\diagup\diagdown}} \xrightarrow{-78°}$$

1   **2**

$$\left[t\text{-Bu}-N{=}C\overset{R'}{\underset{R'}{\diagup}}\underset{}{\searrow}B-R \right] \xrightarrow[\text{1. }HSCH_2CO_2H]{-78°}$$

3

$$\left[t\text{-Bu}-\overset{R'}{\underset{H}{N-C}}\overset{R}{\underset{B-R}{\diagup}} \right] \xrightarrow{\text{2. }H_2O_2\text{-NaOH}}$$
$$\qquad\qquad\qquad SCH_2CO_2H$$

4

$$R'-\overset{\parallel}{\underset{O}{C}}-R + ROH + t\text{-BuNH}_2 \quad (1)$$

5