results are obtained with acyl fluorides–BF_3.[4]

The unusual regioselectivity presented here is specific for the acyl fluoride–BF_3 system. Acyl fluorides–$AlCl_3$ gave product mixtures very similar to those obtained with acyl chlorides–$AlCl_3$, whereas acyl chlorides–BF_3 did not give any acylations. Even though the reasons for the selectivity are unclear, this chemistry offers, for the first time, a method by which a variety of 3-substituted acenaphthenes and 2,6-disubstituted naphthalenes can easily be made.[5,6] We recommend that use of the acyl fluoride–BF_3 reagent be considered whenever it is necessary to modify the isomer distribution of products from a Friedel–Crafts reaction.

Experimental Section

General Methods. Melting and boiling points are uncorrected. IR spectra were taken on a Perkin-Elmer Model 137 spectrophotometer. ^1H NMR spectra were obtained with Varian EM-360 and JEOLCO MH-100 spectrometers and are reported in parts per million (δ) from internal tetramethylsilane, and coupling constants (J) are given in hertz. Mass spectra were recorded with a VG ZAB mass spectrometer in the field-desorption mode. Acyl fluorides were prepared according to Olah and Kuhn.[7]

General Procedure for Acylations. The following procedure for 3-isobutyrylacenaphthene is typical of all the acylations reported in Tables I and II. A solution of 0.020 mol of 1 and 0.025 mol of isobutyryl fluoride[7] in 100 mL of CH_2Cl_2 was treated with dry BF_3 at 0–10 °C for 1 h, warmed to 25 °C, and quenched with water, and the organic phase was dried and stripped to give an oily 15:85 mixture of **2a** and **3a** (VPC). Recrystallization from hexane–ether gave 3.1 g (65%) pure **3a**: mp 75–76 °C; mass spectrum, m/e 224; NMR ($CDCl_3$) δ 7.95 (d, J = 8, 1 H), 7.3–7.75 (m, 4 H), 3.2–3.9 (m, 5 H), 1.25 (d, J = 7, 6 H). Anal. Calcd: C, 85.7; H, 7.19. Found: C, 85.5; H, 7.09.

3-Decanoylacenaphthene (3b) was obtained in 48% yield by fractional crystallization (ethanol) of the crude acenaphthene–decanoyl fluoride product and had the following: mp 43–44 °C; IR (melt) 5.95, 6.82, 7.49, 11.93, 13.2 μm; NMR ($CDCl_3$) δ 7.95 (d, J = 8, 1 H), 7.3–7.8 (m, 4 H), 2.8–3.8 (m, 6 H), 0.8–2.2 (m, 17 H); mass spectrum, m/e 308 (calcd 308). Anal. Calcd. for $C_{22}H_{28}O$: C, 85.7; H, 9.14. Found: C, 85.7; H, 9.24.

3-Acetylacenaphthene (3c) was purified by recrystallization from methanol and had the following: mp 103–105 °C (lit.[3d] mp 103–104 °C); NMR ($CDCl_3$) δ 7.9 (d, J = 8, 1 H), 7.2–7.7 (m, 4 H), 3.2–3.7 (m, 4 H), 2.67 (s, 3 H); mass spectrum m/e 196 (calcd 196).

3-(*p*-Toluyl)acenaphthene (3d): mp 92–94 °C (CH_3OH); IR (mull) 6.00, 6.19, 7.76, 7.88, 8.42, 8.61, 11.71, 13.16 μm; NMR ($CDCl_3$) δ 7.8 (d, J = 8, 1 H), 7.3–7.6 (m, 8 H), 3.4–3.7 (m, 4 H), 2.52 (s, 3 H); mass spectrum, m/e 272 (calcd 272). Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.92. Found: C, 88.1; H, 5.87.

2-Isobutyryl-6-methylnaphthalene (5a): bp 140–150 °C (1.5 mm); IR (neat film) 5.93, 6.10, 7.20, 8.13, 8.34, 8.61, 8.86, 10.08, 12.40 μm; NMR ($CDCl_3$) δ 8.43 (br s, 1 H), 7.2–8.0 (m, 5 H), 3.66 (septet, J = 7, 1 H), 2.60 (s, 3 H), 1.27 (d, J = 7, 6 H); mass spectrum, m/e 212 (calcd 212). Anal. Calcd for $C_{15}H_{16}O$: C, 84.8; H, 7.58. Found: C, 84.6; H, 7.60.

2-Decanoyl-6-methylnaphthalene (5b): mp 54–56 °C (ethanol); IR (mull) 5.96, 8.40, 11.29, 12.12, 13.47, 13.90 μm; NMR ($CDCl_3$) δ 8.44 (br s, 1 H), 7.16–8.1 (m, 5 H), 3.10 (t, J = 7, 2 H), 2.56 (s, 3 H), 0.8–2.1 (m, 17 H); mass spectrum m/e 296 (calcd 296). Anal. Calcd for $C_{21}H_{28}O$: C, 85.1; H, 9.51. Found: C, 84.8; H, 9.61.

2-Acetyl-6-methylnaphthalene (5c): mp 66–68 °C (ethanol–hexane) (lit.[8] mp 66.5 °C); NMR ($CDCl_3$) δ 8.41 (br s, 1 H), 7.2–8.1 (m, 5 H), 2.70 (s, 3 H), 2.52 (s, 3 H).

2-Propionyl-6-methylnaphthalene (5d): mp 60–62 °C (hexane); IR (mull) 5.91, 8.38, 8.83, 10.5, 11.1, 12.2 μm; NMR ($CDCl_3$) δ 8.40 (br s, 1 H), 7.2–8.1 (m, 5 H), 3.00 (q, J = 6.5, 2 H), 2.41 (s, 3 H), 1.19 (t, J = 6.5, 3 H); mass spectrum, m/e 198 (calcd 198). Anal. Calcd for $C_{14}H_{14}O$: C, 84.8; H, 7.11. Found: C, 84.5; H, 7.03.

Acknowledgment. We are grateful to Prof. J. Dunogues, CNRS, France, for supplying representative NMR spectra of substituted acenaphthenes and to Profs. J. S. Swenton, The Ohio State University, and D. C. Baker, University of Alabama, for high-field NMR spectra.

Registry No. 2a, 87969-65-1; **3a**, 87969-66-2; **3b**, 87969-67-3; **3c**, 7434-96-0; **3d**, 87969-68-4; **4**, 91-57-6; **5a**, 73652-97-8; **5b**, 87969-69-5; **5c**, 5156-83-2; **5d**, 69750-34-1; acenaphthene, 83-32-9; isobutyryl fluoride, 430-92-2; decanoyl fluoride, 334-47-4; acetyl fluoride, 557-99-3; *p*-toluyl fluoride, 350-42-5; propionyl fluoride, 430-71-7; phenanthrene, 85-01-8; isobutyrylphenanthrene, 87969-64-0; anthracene, 120-12-7; 9-isobutyrylanthracene, 73633-41-7; 1-isobutyryulanthracene, 87969-70-8; 2-isobutyrylanthracene, 76868-33-2; 5-decanoylacenaphthene, 87969-71-9; 5-acetylacenaphthene, 10047-18-4; 5-*p*-toluylacenaphthene, 87969-72-0.

Supplementary Material Available: NMR spectra of compounds in Tables I and II (10 pages). Ordering information is given on any current masthead page.

(4) Reactions of acyl fluorides–BF_3 with some other polycyclic aromatic compounds were briefly examined. Phenanthrene reacted with isobutyryl fluoride–BF_3 to give two products (VPC, 67:33 ratio); a comparison reaction using isobutyryl chloride–$AlCl_3$ gave four of the five possible products (VPC 2:24:57:16; the last two identical with those from the fluoride reaction; VPC–MS showed that only monoacyl phenanthrenes were present). With anthracene as the substrate, isobutyryl chloride–$AlCl_3$ gave a single product, whereas isobutyryl fluoride–BF_3 suprisingly led to a mixture of all three possible products (VPC 8:30:62). In these cases, isomer separation and regiochemical assignments were not undertaken.

(5) Good regiochemistry can also be achieved by reacting acyl chlorides with anhydrous HF to generate acyl fluorides in situ, followed by the addition of BF_3 and an aromatic substrate. In the case of 2-methylnaphthalene with isobutyryl chloride in HF, followed by BF_3 addition, **5a** was obtained in 80% yield.

(6) Control experiments showed that the reaction products do not isomerize under the reaction conditions.

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Homoallylic Substitution Reactions of 1-Cyclopropyl-1-haloethane: Reaction with Lithium Dialkylcuprates[1]

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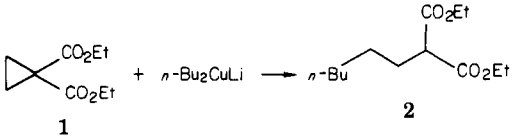
Cationic ring opening reactions of cyclopropane derivatives have been the focus of many studies,[2] but noncationic ring opening by nucleophiles has received only cursory attention. The latter process would be attractive since acid-sensitive substrates and nucleophiles, particularly carbanionic nucleophiles, could be utilized. An example that has found synthetic use involves attack by cuprates or amines on diethyl 1,1-cyclopropanedicarboxylate derivatives, **1**, to give products such as **2**.[3]



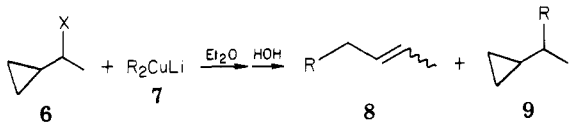
1 2

(1) Presented, in part, at the following: the 12th Northeast Regional Meeting of the American Chemical Society, Burlington, VT, June 1982, ORGN 186 (Hrubiec, R. T.; Smith, M. B.); the 13th Northeast Regional Meeting of the American Chemical Society, Hartford, CT, June 1983, ORGN 149 (Hrubiec, R. T.; Smith, M. B.).

(2) (a) Julia, M.; Mouzin, G.; Descoins, C. *C. R. Hebd. Seances Acad. Sci.* **1967**, *264*, 330. (b) Brady, S. F.; Ilton, M. A.; Johnson, W. S. *J. Am. Chem. Soc.* **1968**, *90*, 2882.

0022-3263/84/1949-0385$01.50/0

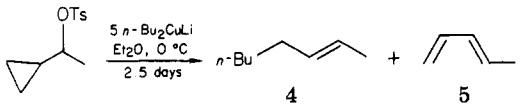
Table I. Reaction of 1-Cyclopropyl-1-haloethane (6) with Lithium Dialkylcuprates 7



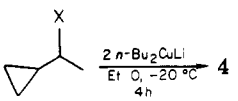
	R	time, h	% 8 (E/Z)[a]	% 9[a]
6a	n-Bu[c]	4.5	80 (2:1)	0[b]
(X = Br)	n-hexyl[c]	4.0	71 (4.5:1)	0[b]
	CH_3[d]	7.0	43 (5:1)	38
	Ph[d]	3.0	43 (5:1)	23
	t-Bu[e]	0.5	10[f]	
6b	n-Bu[c]	96.5	35 (1.4:1)	0[b]
(X = Cl)	n-hexyl[c]	72.0	63 (3.6:1)	0[b]
	CH_3	32.0	30 (4:1)	58
	Ph	91.5	22 (1.8:1)	49

[a] Yields via VPC on a 20-ft, 20% SE-30/Chromoworb W column, utilizing the following internal standards: undecane for 8a, (Z)-2-nonene for 8b, n-heptane for 8c/9c, and n-butylbenzene for 8d/9d. [b] Undetectable by ^1H NMR and VPC. [c] Temperature of reaction, −20 °C. [d] Temperature of reaction, 25 °C. [e] Temperature of reaction, −78 °C. [f] Tentative identification based on VPC/MS analysis.

Since *both* electron-withdrawing groups must be on the cyclopropane ring and the plane of the ring must be orthogonal to *both* carbonyl moieties for optimum reactivity,[3a] this process is limited in scope. A substrate with pedant functionality allowing ring opening but without the requirement of two electron-withdrawing groups would be an interesting as well as useful moiety. Cyclopropylcarbinyl halides appeared to be such a substrate. Facile expulsion of the halide, assisted by the cyclopropane ring, with concomitant nucleophilic attack on the ring, would give the desired homoallylic substitution product. The viability of this concept was demonstrated by Posner when 1-cyclopropylethyl tosylate (3) reacted with lithium di-n-butylcuprate (7a) to give (E)-2-nonene (4) in 49% yield, as well as 23% of (E)-1,3-pentadiene (5).[4] We can now



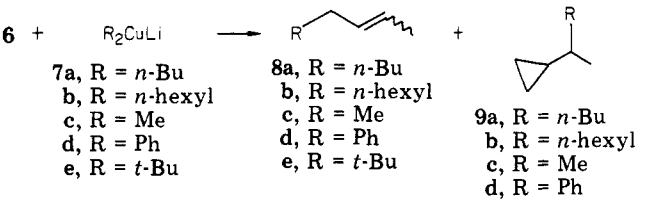
report that cyclopropylcarbinyl halides such as 6 also undergo reaction with 7a to give (E)-2 and (Z)-2 in 80% yield but with no trace of the elimination product 5. We have also examined the reactivity of 1-bromo-1-cyclopropylethane (6a) and 1-chloro-1-cyclopropylethane (6b) with a variety of organocuprates. These results are summarized



6a, X = Br
b, X = Cl

in Table I and clearly indicate important differences in reactivity between 3 and 6, as well as different product distributions that apparently depend upon the reactivity of the organocuprate.

The requisite halides, 6a and 6b, were obtained by treatment of 1-cyclopropyl-1-ethanol with bromine/triphenylphosphine in dimethylformamide or hexachloroacetone/triphenylphosphine, respectively, by methods we have previously reported.[5] The reaction of 6 with organocuprates was found to be facile and produced good yields of substitution products. As previously noted, reaction of 6a with 7a, followed by quenching with water, afforded 80% of 2-nonene (8a). We were unable to detect the



presence of 2-cyclopropylhexane (9a), the direct substitution product. In an analogous manner, lithium di-n-hexylcuprate (7b) reacted with 6a to give 2-undecene (8b) in 71% yield with no trace of 2-cyclopropyloctane (9b). When 6a was allowed to react with lithium dimethylcuprate (7c) or lithium diphenylcuprate (7d), only 43% of 2-hexene (8c) and 43% of 5-phenyl-2-pentene (8d), as well as 39% of 2-cyclopropylpropane (9c) and 23% of 1-cyclopropyl-1-phenylethane (9d), respectively, were obtained. This mixture of homoallylic and direct substitution products from 7c and 7d stand in contrast to the homoallylic substitution product formed exclusively from 7a and 7b. We did not detect the presence of the elimination product, 5, in any of these reactions. As shown in Table I, 8a–d were obtained as a mixture of E and Z isomers, with the E isomer predominating.

We also carried out the reaction of 6a with lithium di-*tert*-butylcuprate (7e). Although this reaction was more facile than those with 7a–d, the formation of a multitude of unidentifiable reaction products with only 10% of what appeared to be 6,6-dimethyl-2-heptene (8e)[6] rendered the reaction unsatisfactory. Organocuprate 7e gives poor yields of substitution products upon reaction with simple alkyl halides,[7] due primarily to the instability of 7e. In all cases, the success of the reaction was strongly dependent upon the stability of 7, which is a function of the reaction temperature.[8] Temperature control was especially important in reactions with 6b, which required longer reaction times and tended to give somewhat lower yields of 8 and/or 9. This is consistent with the reported poorer reactivity of chlorides with organocuprates, as compared to the corresponding bromides,[9] but this may also be a function of the decomposition of the organocuprate. Although elimination and reduction processes have been observed in the decomposition of organocuprates,[8] we were unable to detect the presence of any such products from 6a or 6b. The failure of 6 to produce 5 leads to the conclusion that, in contrast to tosylate 3, elimination is not an important pathway in reactions with cyclopropylcarbinyl halides. It

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is also interesting to note that reaction of the chloride **6b** with **7c** or **7d** gave increased amounts of **9**, relative to identical reactions with the bromide **6a**, which gave primarily **8**.

In general, reaction of organocuprates with **6a** was more facile than with **3**, proceeding at lower temperatures, with shorter reaction times, and requiring fewer equivalents of organocuprate. The yield of 2-nonene from reaction of **6** with **7a** was higher than that from **3** but exhibited reduced stereoselectivity. Further, the chloride **6b** was less reactive than the bromide **6a** in each case, although the product distribution remained essentially unchanged. We noted that highly reactive organocuprates[10] such as **7a** and **7b** reacted with **6** to give, exclusively, the homoallylic substitution product **8**. Less reactive organocuprates[10] such as **7c** and **7d** gave a mixture of both **8** and **9**. We also determined the order of reactivity of **7** with **6** to be *tert*-butyl > *n*-butyl ≃ *n*-hexyl > phenyl > methyl, the same as that observed for reactions of organocuprates with simple alkyl halides.[10] Halide **6** reacts with **7** much faster than the normally sluggish reaction exhibited by many secondary halides.[8,10] This enhancement is undoubtedly due to the presence of the cyclopropane ring.[11] Although the reaction gives products that are analogous to the homoallylic analogue of the well-known S_N2' reaction of allylic halides,[12] the mechanism for the reaction of **6** has not been determined. Posner has suggested that tosylate **3** reacts via direct displacement of the tosyl group, by cuprate, to generate either a copper(II) radical complex or a cuprate(I) cationic complex as an intermediate.[4] Facile rearrangement of this intermediate and oxidative coupling gave 2-nonene.[4] This scheme should apply, generally, to reactions of **6** with organocuprates and clearly implies that S_N2', as applied to allylic systems, is probably not an appropriate mechanistic description. Further study is required, however, to understand the stereochemical and mechanistic details of this reaction as well as the scope of the process with other 1-cyclopropyl-1-haloalkanes.

Experimental Section

All reactions were carried out under an argon atmosphere with all glassware flame dried immediately prior to use. The diethyl ether was distilled from sodium/benzophenone (argon atmosphere). The ^1H NMR spectra were recorded on a Varian EM-360 instrument at 60 MHz or on a Bruker-90 FT instrument at 90 MHz, downfield from tetramethylsilane. The mass spectra were recorded on an AEI MS-9 mass spectrometer or on an HP 5987 VPC/MS instrument, utilizing a 30-m, SE-54 capillary column. The qualitative and quantitative VPC work was accomplished on a Perkin-Elmer 3920-B gas chromatograph, using a 5.9-m, 20% SE-30/Chromosorb W column. Lithium metal, *n*-butyllithium, methyllithium, and phenyllithium were obtained from Alfa. The *n*-hexyllithium was prepared by the methods of Cope and von E. Doering.[13] All alkyllithium solutions were standardized prior to use with diphenylacetic acid by the method of Kofron and Baclawski.[14] The copper(I) bromide was prepared by the methods of Corey and Kende.[15] The 1-cyclopropyl-1-ethanol, *n*-butylbenzene, diphenylacetic acid, copper sulfate pentahydrate, and 1-bromohexane were obtained from Aldrich. (*E*)-2-Nonene, (*Z*)-2-nonene, and (*E*)-2-hexene were obtained from FMI Chemicals.

General Procedures for Reaction of 6 with Lithium Dialkylcuprates 7. Addition of 6.7 mmol of the appropriate alkyllithium[16] to a suspension of 0.48 g (3.36 mmol) of freshly prepared copper(I) bromide[15] in dry ether, at −78 °C, was followed by warming the dark solution to −40 °C for 10–20 min and then to −20 °C for **7a** and **7b** or 25 °C for **7c** and **7d**. This solution was treated with an ether soution of either 0.25 g (1.68 mmol) of 1-bromo-1-cyclopropylethane (**6a**) or 0.176 g (1.68 mmol) of 1-chloro-1-cyclopropylethane (**6b**), dropwise, at the indicated temperature. After the indicated reaction time, the solution was quenched with 4 mL of water and filtered through a Celite pad. The ether layer was separated and dried ($MgSO_4$), and solvents were removed by careful distillation through a 15-cm Vigreux column. Analysis was accomplished by VPC, VPC/MS, and ^1H NMR.

Reaction of Lithium Di-*n*-butylcuprate (7a). (a) With 6a. Addition of **6a** to a solution of **7a** and reaction at −20 °C for 4.5 h gave, after workup, a colorless oil that contained 2-nonene (**8a**): ^1H NMR ($CDCl_3$) δ 0.90 (dist t, 3 H), 1.15–1.60 (m, 8 H), 1.59 (d, 3 H), 1.70–2.1 (m, 2 H), 5.23–5.68 (m, 2 H, C*H*=C*H*); mass spectrum, *m/z* (relative intensity) 126 (45, $M^{+}\cdot$), 55 (100, $M^{+}\cdot - C_5H_{11}$), 56 (45, $M^{+}\cdot - C_5H_{10}$) and 97 (20), 84 (18), 83 (18), 70 (40), 69 (37), 43 (25), 41 (30).

Analysis by VPC with undecane as an internal standard indicated the oil contained 0.17 g (1.35 mmol) of **8a** (80%). Comparison with authentic (*E*)-2-nonene and (*Z*)-2-nonene indicated a 2:1 mixture of (*E*)-**8a**/(*Z*)-**8a**.

(b) With 6b. Addition of **6b** to a solution of **7a** and reaction at −20 °C for 96.5 h gave, after workup, a colorless oil. Analysis by VPC with undecane as an internal standard indicated 0.073 g (0.58 mmol) of a 1.5:1 mixture of (*E*)-**8a**/(*Z*)-**8a** (35%).

Reaction of Lithium Di-*n*-hexylcuprate. (a) With 6a. Addition of **6a** to a solution of **7b** and reaction at −20 °C for 4 h gave, after workup, a colorless oil that contained 2-undecene (**8b**): ^1H NMR ($CDCl_3$) δ 0.9 (dist t, 3 H), 1.15–1.70 (m, 12 H), 1.61 (d, 3 H), 1.70–2.24 (m, 2 H), 5.21–5.65 (m, 2 H, C*H*=C*H*); mass spectrum, *m/z* (relative intensity) 154 (37, $M^{+}\cdot$), 55 (100, $M^{+}\cdot - C_7H_{15}$), 56 (70, $M^{+}\cdot - C_7H_{14}$) and 111 (18), 98 (15), 97 (38), 83 (40), 70 (68), 69 (68), 57 (55), 43 (40), 41 (60).

Analysis by VPC with (*Z*)-2-nonene as an internal standard indicated 0.183 g (1.19 mmol) of a 4.5:1 mixture of (*E*)-**8b**/(*Z*)-**8b** (71%).

(b) With 6b. Addition of **6b** to a solution of **7b** and reaction at −20 °C for 72 h gave, after workup, a colorless oil. Analysis by VPC with (*Z*)-2-nonene as an internal standard indicated 0.164 g (1.06 mmol) of a 3.45:1 mixture of (*E*)-**8b**/(*Z*)-**8b** (63%).

Reaction of Lithium Dimethylcuprate (7c). (a) With 6a. Addition of **6a** to a solution of **7c** and reaction at 25 °C for 7 h gave, after workup, a colorless oil that contained 2-hexene (**8e**) [^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.1–1.6 (m, 2 H), 1.6 (d, 3 H), 1.7–2.2 (m, 2 H), 5.05–5.30 (m, 2 H, C*H*=C*H*); mass spectrum, *m/z* (relative intensity) 84 (75, $M^{+}\cdot$), 69 (34, $M^{+}\cdot - CH_3$), 55 (100, $M^{+}\cdot - C_2H_5$), 56 (30, $M^{+}\cdot - C_2H_4$) and 42 (30), 41 (30)] and 2-cyclopropylpropane (**9c**)[17] [^1H NMR ($CDCl_3$) δ 0.03–0.80 (m, C_3H_5), 1.78 (d, 6 H); mass spectrum, *m/z* (relative intensity) 84 (5, $M^{+}\cdot$), 69 (20, $M^{+}\cdot - CH_3$), 56 (100, $M^{+}\cdot - C_2H_4$) and 55 (15), 43 (12), 41 (43)].

Analysis by VPC with *n*-heptane as an internal standard indicated 0.061 g (0.72 mmol) of **8c** (43%) as a 5:1 mixture of (*E*)-**8c**/(*Z*)-**8c**, by comparison with authentic (*E*)-2-hexene, as well as 0.054 g (0.64 mmol) of **9c** (38%).

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(b) With 6b. Addition of **6b** to a solution of **7c** and reaction at 25 °C for 32 h gave, after workup, a colorless oil. Analysis by VPC with *n*-heptane as an internal standard indicated 0.043 g (0.51 mmol) of a 4:1 mixture of (*E*)-**8c**/(*Z*)-**8c** (30%) as well as 0.082 g (0.97 mmol) of **9c** (58%).

Reaction of Lithium Diphenylcuprate (7d). (a) With 6a. Addition of **6a** to a solution of **7d** and reaction at 25 °C for 3 h gave, after workup, a colorless oil that contained 1-phenyl-3-pentene (**8d**)[18] [^{1}H NMR ($CDCl_3$) δ 1.63 (d, 2 H), 2.20–2.92 (m, 4 H), 5.14–5.40 (m, 2 H, *CH*=*CH*), 7.1–7.8 (m, 5 H); mass spectrum, *m*/*z* (relative intensity) 166 (12, $M^{+\cdot}$), 91 (100, $M^{+\cdot} - C_4H_7$)] and 1-cyclopropyl-1-phenylethane (**9d**)[19] [^{1}H NMR ($CDCl_3$) δ 0.03–0.58 (m, 5 H, C_3H_5), 1.42 (d, 3 H), 7.1–7.8 (m, 5 H); mass spectrum, *m*/*z* (relative intensity) 146 (14, $M^{+\cdot}$), 131 (55, $M^{+\cdot} - CH_3$), 105 (100, $M^{+\cdot} - C_3H_5$) and 118 (76), 117 (97), 91 (62)]. Analysis by VPC with *n*-butylbenzene as an internal standard indicated 0.105 g (0.72 mmol) of a 5:1 mixture of (*E*)-**8d**/(*Z*)-**8d** (43%) as well as 0.056 g (0.38 mmol) of **9d** (23%).

(b) With 6b. Addition of **6b** to a solution of **7d** and reaction at 25 °C for 91.5 h gave, after workup, a colorless oil. Analysis by VPC with *n*-butylbenzene as an internal standard indicated 0.054 (0.37 mmol) of a 2:1 mixture of (*E*)-**8d**/(*Z*)-**8d** (22%) and 0.122 g (0.83 mmol) of **9d** (49%).

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Registry No. **6a**, 80204-20-2; **6b**, 10524-06-8; **7** (R = *n*-Bu), 24406-16-4; **7** (R = *n*-hexyl), 73303-09-0; **7** (R = CH_3), 15681-48-8; **7** (R = Ph), 23402-69-9; **7** (R = *t*-Bu), 23402-75-7; (*E*)-**8** (R = *n*-Bu), 6434-78-2; (*Z*)-**8** (R = *n*-Bu), 6434-77-1; (*E*)-**8** (R = *n*-hexyl), 693-61-8; (*Z*)-**8** (R = *n*-hexyl), 821-96-5; (*E*)-**8** (R = CH_3), 4050-45-7; (*Z*)-**8** (R = CH_3), 7688-21-3; (*E*)-**8** (R = Ph), 16091-23-9; (*Z*)-**8** (R = Ph), 16487-65-3; **8** (R = *t*-Bu), 87970-30-7; **9** (R = CH_3), 3638-35-5; **9** (R = Ph), 16510-30-8.

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Equilibrium Constant for Pyruvic Oxime Formation[1]

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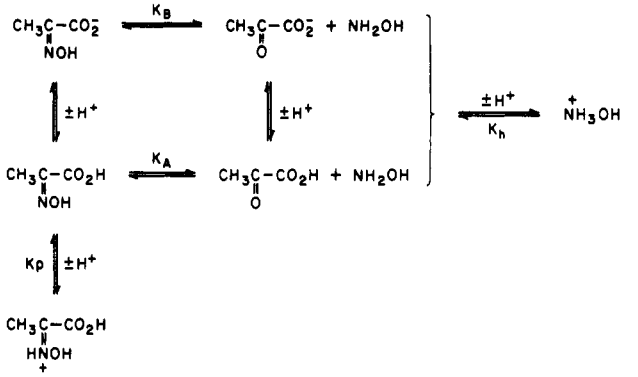
The pathway for conversion of pyruvic oxime (2-oximinopropanoic acid) to nitrite by a soil bacterium (*Alcaligines* sp.)[2,3] is currently under study in this laboratory[4,5] and in this regard the value for the equilibrium formation constant of pyruvic oxime is relevant. A survey of the literature revealed some discrepancies in estimates of oxime formation constants. Jencks,[6] using data of Conant and Bartlett,[7] reported equilibrium constants for formation of acetone oxime (1.06×10^6 M^{-1}) and pyruvic semicarbazone (1.96×10^5 M^{-1}), and using Conant and Bartlett's data, we calculate a value of 3.09×10^2 M^{-1} for acetone semicarbazone formation. If we make the reasonable assumption that acetone and pyruvate exhibit similar selectivity toward semicarbazide and hydroxylamine, we can predict that the equilibrium constant for pyruvic oxime formation, K_B of Scheme I, should be about 7×10^8 M^{-1} at 25 °C. Sharon and Katchalsky,[8] using data of Roe and Mitchell,[9] calculated equilibrium constants for oxime formation at room temperature for acetaldehyde, acetone, vanillin, and diethyl ketone. A value of approximately 1×10^3 M^{-1} was obtained in each case. We find this result rather surprising in light of the wide range of values reported for other equilibrium additions to carbonyl compounds.[6,7,10-13] Fisher et al.[14] claim to have measured the pyruvic oxime equilibrium constant, K_B, spectrophotometrically and reported a value of 2.2×10^4 M^{-1} at 25 °C and pH 6.

Scheme I



From a study[15] of the basis of a colorimetric assay[16] for pyruvic oxime we had reason to believe that the formation constant reported by Fisher et al.[14] considerably underestimated the true value. To determine the formation constant of pyruvic oxime, we took advantage of the fact that hydrolysis of pyruvic acid oxime is favored in dilute acid due to protonation of hydroxylamine. The equilibrium concentrations of released hydroxylamine as a function of acid strength were determined by means of a modification of the indooxine (5-[(8-hydroxy-5-quinolyl)-imino]-8(5*H*)-quinolone) assay.[16]

Results and Discussion

Hydrolysis of pyruvic oxime (1.07×10^{-2} M) in 0.05 M phosphate buffer at pH 4.55 and 100 °C (pH 6.43 at 25 °C) was followed spectrophotometrically through formation of indooxine. The absorbance at 710 nm increased to an equilibrium value and showed first-order kinetics with a half-time of 8 min. This value implies that at room

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