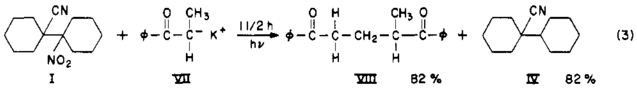
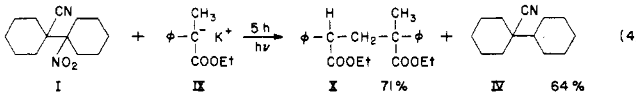
Whereas β-nitro nitrile I and propiophenone anion (VII) react completely in $1^1/_2$ h (eq 3), the anion of acetophenone does not react under the same conditions.



(3)

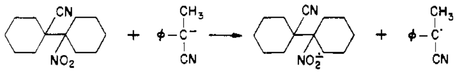
In the same way, the reaction of the anion of α-methylphenylacetic ester (IX) with β-nitro nitrile I is 80–85% complete in 5 h (eq 4); but with anion of the ethyl ester of phenylacetic acid, there is no detectable reaction in 5 h.



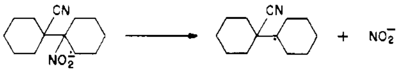
(4)

These puzzling results become readily intelligible on the basis of a chain mechanism which is exemplified by eq 5–8.[3]

INITIATION


(5)

CHAIN PROPAGATION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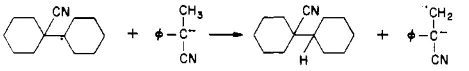
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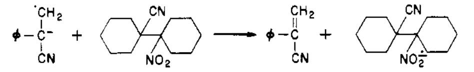
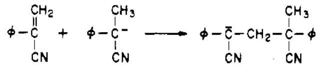

(8)

The α-cyanostyrene then enters into a Michael addition with the starting anion II to give III (eq 9).


$$\phi-\underset{CN}{\overset{CH_2}{\overset{\|}{C}}} + \phi-\underset{CN}{\overset{CH_3}{C^-}} \longrightarrow \phi-\underset{CN}{\bar{C}}-CH_2-\underset{CN}{\overset{CH_3}{C}}-\phi \qquad (9)$$

Clearly, the chain sequence of eq 5–8 is not possible with the anions of benzyl cyanide, fluorene, 9-phenylfluorene, acetophenone, and ethyl phenylacetate. presumably, a methyl group is not unique—ethyl and isopropyl, for example, should, in principle, produce the same result although the Michael addition may well prove much slower than for the methyl cases.[4]

The view that these are indeed chain reactions involving free radicals and radical anions is supported by the fact that they are inhibited by 20 mol % of di-*tert*-butyl nitroxide and by *m*-dinitrobenzene. Also, in conformity with the proposed mechanism, the 9-methylfluorene dimer has the structure VI rather than that of the symmetrical dimer. Although β-nitro nitrile I was employed in most of our studies, other β-nitro nitriles exhibit the same behavior.[5] The cyano group is not necessary for these reactions; α-nitrocumene, $C_6H_5C(NO_2)Me_2$, reacts with V in the same way as I, albeit at a much slower rate.

The following is a typical procedure. Under N_2, 0.188 g (0.0047 mol) of dry KH was dissolved in 20 mL of dry, degassed Me_2SO and to this solution was added a solution of 9-methylfluorene (0.923 g; 0.0052 mol) in 10 mL of dry, degassed Me_2SO. The resulting red solution was transferred via a cannula to a solution of I (0.543 g; 0.0023 mol) in 5 mL of Me_2SO. After the reaction mixture was stirred for $1^1/_2$ h under N_2 with exposure to two 20-W ordinary fluorescent lights, the resulting red solution was poured into 300 mL of cold H_2O and extracted with diethyl ether. The extracts were washed with H_2O and dried ($MgSO_4$), and the ether was removed. The white solid that remained was flash chromatographed on silica gel by using pentane–chloroform (9:1). This gave 0.873 g of white crystals; mp 175–177 °C. Recrystallization from hexane afforded 0.835 g (93% yield) of VI, mp 175–176 °C (lit.[6] mp 175–176 °C). ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 3 H), 2.18 (d, 2 H), 3.12 (t, 1 H), and 6.56–7.82 (complex multiplet, 16 H). MS: *m/e* 358 (20.14), 193 (7.63), 179 (100), and 165 (26.95). These values accord with the published values.[6] When the red reaction solution is quenched with D_2O, the product is the 9-deuteriofluorene corresponding to VI. This is clear from the NMR spectrum: the triplet at δ 3.12 vanishes and the doublet at δ 2.18 becomes a singlet. At least 90% of the product is the 9-deuteriofluorene.

Further elution with pentane–chloroform (3:1) gave 0.390 g of a white solid; mp 63–66 °C. Recrystallization from methanol afforded 0.369 g (84% yield) of IV; white crystals, mp 67–68 °C. ^{1}H NMR ($CDCl_3$): δ 1.16 (m, 8 H), 1.56–2.10 (complex multiplet, 12 H). IR ($CDCl_3$): 2225 cm^{-1} (CN). Anal. Calcd for $C_{13}H_{21}N$: C, 81.62; H, 11.07; N, 7.32. Found: C, 81.75; H, 11.20; N, 7.29.

Acknowledgment. We thank the National Science Foundation, Merck and Co., Inc., and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

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Received December 1, 1987

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[3] Chain termination presumably results from combination, and disproportionation, of the radicals.

[4] These and other obvious extensions of this new chain sequence are being explored.

[5] All new compounds were characterized by elemental analyses, NMR, IR, and mass spectra.

[6] Guthrie, R. D.; Wesley, D. P.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5780.

Indium in Organic Synthesis: Indium-Mediated Allylation of Carbonyl Compounds

Summary: Indium-mediated allylation of a variety of ketones and aldehydes afforded excellent yields of the corresponding homoallylic alcohols under very mild reaction conditions.

Sir: There has been growing interest in the use of metallic elements in synthetic chemistry, among which Li,[1] Mg,[1]

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[1] Katzenellenbogen, J. A.; Lenox, R. S. *J. Org. Chem.* **1973**, *38*, 326.

[2] Ruppert, J. F.; White, J. D. *J. Org. Chem.* **1976**, *41*, 550. Pétrier, C.; Luche, J.-L. *J. Org. Chem.* **1985**, *50*, 910.

[3] Hiyama, T.; Sawahara, M.; Obayashi, M. *Chem. Lett.* **1983**, 1237. Hiyama, T.; Sawahara, M.; Obayashi, M. *Nippon Kagaku Kaishi* **1984**, 1022.

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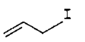
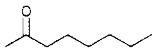
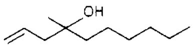
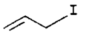
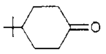
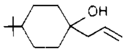
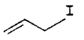
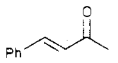
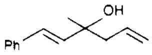
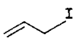
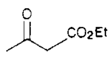
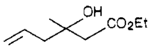
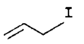
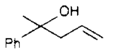
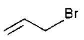
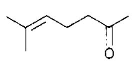
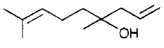
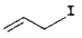
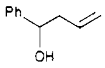
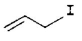
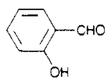
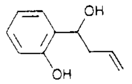
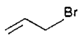
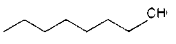
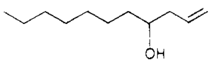
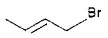
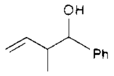
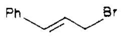
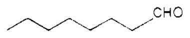
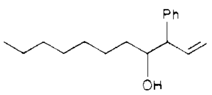
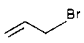
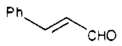
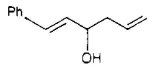
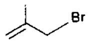
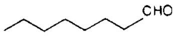
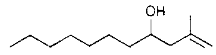
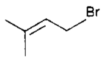
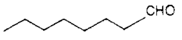
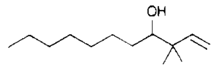
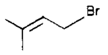
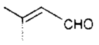
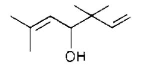
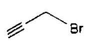
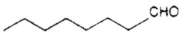
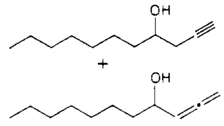
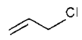
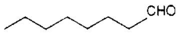
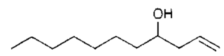
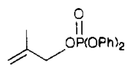
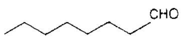
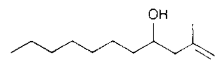
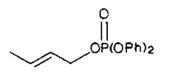
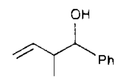
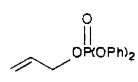
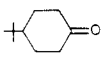
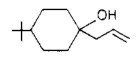
Table I. Indium-Mediated Allylation of Carbonyl Compounds[a]

allyl halide	carbonyl compd	product	yield,[b] %
			89
			89[c]
			92
			57
	PhCOCH$_3$		91
			81
	PhCHO		87
			98
			76
	PhCHO		94[d]
			90
			95
			75
			70
			75
			72[e]
			10[f]
			64[g]
	PhCHO		54[g,h]
			62[g,i]

[a] All the reactions were carried out by using allyl halide (3 mmol), carbonyl compound (2 mmol), and indium (3 mmol) in DMF (4 mL) for 1 h at room temperature. [b] Based on carbonyl compound. [c] Axial:equatorial = 83:17. [d] Erythro:threo = 66:34. [e] Acetylene:allene = 62:38. [f] Reaction time 20 h. [g] With lithium iodide (3 mmol), reaction time 15 h. [h] Erythro:threo = 58:42. [i] Axial: equatorial = 82:18.

Zn,[2] Mn,[3] Sn,[4] Sb,[5] Ce,[6] Pb,[7] and Bi[8] were successfully used for allylation of carbonyl compounds.[9] Here we describe the allylation of ketones and aldehydes using metallic indium, which proceeds smoothly under very mild conditions to afford homoallylic alcohols in excellent yields.

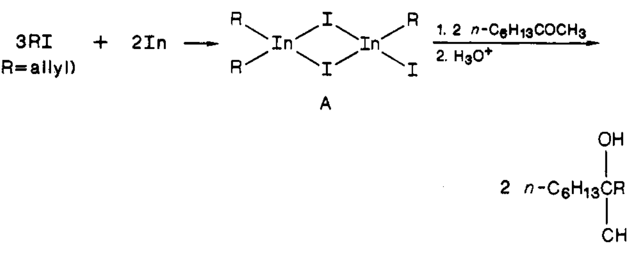
A typical experimental procedure is as follows: To a suspension of an indium powder[10] (345 mg, 3 mmol) in DMF (3 mL) was added a mixture of allyl iodide (504 mg, 3 mmol) and acetophenone (240 mg, 2 mmol) in DMF (1 mL). An exothermic reaction occurred immediately. The

Table II. Yields of 4-Methyl-1-decen-4-ol with Various Ratios of Indium:Allyl Iodide:2-Octanone

molar ratio, indium:allyl iodide:2-octanone	yield,[a,b] %
3:3:2	89 (100)
2:3:2	84 (100)
2:2:2	64 (67)
2:3:3	58 (67)
1:3:2	48 (50)

[a] Based on 2-octanone. [b] Figures in parentheses refer to the theoretical yields expected from Scheme I.

Scheme I



mixture was stirred at room temperature for 1 h, and then the reaction was quenched by the addition of diluted hydrochloric acid. The product was extracted with ether and purified by column chromatography on silica gel to afford 2-phenyl-4-penten-2-ol (196 mg, 91% yield). Results for other carbonyl compounds are listed in Table I. Allylic bromides are equally reactive, however, the reactivity of allyl chloride is markedly depressed. Allylic phosphates themselves are much less reactive, but with an equimolar amount of lithium iodide, moderate yields of products were attained. Various types of ketones and aldehydes are allylated in high yields, but ester and cyano groups were not susceptible to allylation by the present method. It is worthy of note that even the substrates having active hydrogen such as ethyl acetoacetate and salicylaldehyde could be readily allylated in good yields. The present allylation is highly regiospecific; allylic halides react only at the γ-position, and α,β-unsaturated carbonyl compounds give regiospecific 1,2-addition products. On the other hand, propargyl bromide gave a mixture of the acetylenic and allenic products. 4-*tert*-Butylcyclohexanone gave the axial alcohol predominantly (axial:equatorial, 8:2), and the reaction of benzaldehyde with crotyl bromide afforded a mixture of the erythro and threo alcohols in the ratio of 66:34.

In order to clarify the intermediate indium species of this reaction, we carried out the indium-mediated coupling of allyl iodide and 2-octanone with various molar ratios of indium:allyl iodide:2-octanone, and the yields of the product were examined. The results (Table II) show that the stoichiometric ratio of this reaction is 2:3:2, suggesting the intermediacy of the sesquiiodide[11,12] A and two-thirds of the allyl group being transferred to the carbonyl compound (Scheme I).

Indium-mediated synthetic reactions have been scarecely studied.[14] The present allylation of carbonyl compounds is superior to the existing ones using other metals in regard to its generality, high yields, and mildness of reaction conditions. Further mechanistic studies and extension of this interesting reaction are now under way.

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(10) Indium powder, stabilized by 0.5% of MgO, was obtained from Nakarai Chemicals Co. Ltd. and used as received.

(11) The reactions of indium metal and alkyl halides (RX) were reported,[13] in most cases of which were isolated sesquihalides $R_3In_2X_3$.

(12) The reaction of indium metal and allyl iodide in DMF in the absence of carbonyl compounds gave an organoindium species as a viscous oil after removal of the solvent. The compound showed absorptions of 472, 387, 168, and 148 cm^{-1} in the far infrared region. The ^{1}H NMR spectrum (DMF-d_7, −30 °C) revealed two sets of allyl signals with a 2:1 intensity ratio: δ 1.75 (d, J = 8 Hz, 4 H, CH$_2$), 2.02 (d, J = 8 Hz, 2 H, CH$_2$), 4.40–4.79 (m, 6 H, =CH$_2$), and 5.94 (m, 3 H, =CH). These data are consistent with the formulation of $R_3In_2I_3$ (R = allyl). The organoindium compound thus obtained reacted with 2-octanone to give an 86% yield of the coupling product. Further structural elucidation on this compound is now in progress.

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Triphenylsulfonium Salt Photochemistry. New Evidence for Triplet Excited State Reactions

Summary: Direct and sensitized photolysis of triphenylsulfonium salts can generate the triplet state which yields diphenyl sulfide as the major photoproduct. Triplet sensitization is observed in the presence of ketones with E_T > 74 kcal/mol, and the efficiency of sensitization correlates qualitatively with increasing E_T of the sensitizer. In contrast, the singlet excited state yields mainly (phenylthio)biphenyls in addition to diphenyl sulfide.

Sir: Triphenylsulfonium salts are increasingly used as photoinitiators for acid-catalyzed processes in resist applications.[1,2] The proposed mechanisms for photodecomposition involve homolysis to generate the diphenylsulfinyl radical cation and phenyl radical, or heterolysis to phenyl cation and diphenyl sulfide.[3,4] Each pathway ultimately yields diphenyl sulfide and generates acid. Recently we reported a new decomposition pathway from direct photolysis of triphenylsulfonium salts in solution which yields (phenylthio)biphenyls (**3–5**) as the major products by rearrangement, in addition to the escape product diphenyl sulfide (**2**) (Scheme I).[5] These rearrangement products

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