leading to pockets of highly substituted resin was not the cause of this chelation was demonstrated by carrying out the above experiments with the same result using a phosphine-substituted "popcorn" copolymer[1] prepared from styrene (0.9 mmol), *p*-bromostyrene (0.1 mmol), and divinylbenzene (0.002 mmol). The most plausible explanation is that the polymer chain is sufficiently mobile, especially when the resin is solvent swelled, to bring nonadjacent sites together.[9]

In cases where tertiary phosphines are not displaced and monosubstitution is kinetically favored resin chelation does not result. For example, treatment of $[Rh(COD)Cl]_2$ with **1** yielded a 1:1 resin complex by splitting the chloro bridge. Similarly 1 equiv of **6** reacted with 2 equiv of **1** under mild conditions (C_6H_6, 25°) to form the 1:1 complex **7** (ν_{CO} 2022, 1965; ν_{NO} 1750). However, further heating (70°, 24 hr, diglyme) converted **7** into the 1:2 complex **8** (ν_{CO} 1940; ν_{NO} 1700 cm^{-1}).[10]

$RhCl(P(C_6H_5)_3)_2(C_2H_4)$ **4**

$MClL_3$ **5a**, L = **1**; M = Rh; **b**, L = **1**; M = Ir

$Co(NO)(CO)_3$ **6**

$Co(NO)(CO)_2L$ **7**, L = **1**

$Co(NO)(CO)L_2$ **8**, L = **1**

$Rh_4(CO)_{10.5}L_{1.5}$ **9**, L = **1**

The resin-bonded complexes exhibit normal reactions. For example, **3b** reacts with *p*-nitrobenzoyl azide to afford a resin-bound N_2 complex, ν_{N_2} 2095. Treatment of **3b**, **5a**, or **5b** with hydrogen afforded the spectral changes expected for oxidative addition. The resin-bound mononuclear hydrogenation catalysts **5a**,**b** were superior to their homogeneous analogs only in catalyst lifetime and ease of product separation.

Novel polynuclear catalysts were prepared by treating **1** with the readily substituted $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$.[11] Aerial oxidation (accelerated by light) led to the disappearance of ν_{CO}; H_2 (1 atm, THF) afforded active metal particles of extremely small size, presumably 4 and 6 Rh atoms, respectively. The substance derived from $Rh_6(CO)_{16}$ catalyzed the hydrogenation of arenes at 25° and 1 atm of H_2, exhibiting reactivity and substrate selectivity similar to Engelhard's 5% Rh/Al_2O_3,[12] whereas that derived from $Rh_4(CO)_{12}$ exhibited diminished activity which we attribute to $Rh_6(CO)_{16}$ formed spontaneously in solutions of $Rh_4(CO)_{12}$. Evidence that the polymer prevents aggregation is afforded by comparing reactions of these catalysts with CO: from the Rh_4 catalyst over 50% of the Rh was removed as $Rh_4(CO)_{12}$; from the Rh_6 catalyst a small amount of $Rh_4(CO)_{12}$ and much $Rh_6(CO)_{16}$ were obtained at <40 psi; and from 5% Rh/Al_2O_3[13] only a barely detectable amount of $Rh_4(CO)_{12}$ was obtained after 24 hr at >1000 psi. Polymer-free $Rh_4(CO)_{11}(P(C_6H_5)_3)$ similarly oxidized and reduced also catalyzed arene reduction but failed to give $Rh_4(CO)_{12}$ upon CO treatment suggesting that irreversible aggregation to larger metal units occurred without the use of the polymeric ligand.

Acknowledgments. We are indebted to Rohm and Haas Company for experimental polymer samples and to Professor M. Boudart for experimental aid and R. Bacskai, Chevron Research Company, for advice. This work was supported by the National Science Foundation Grant No. GP 20273X.

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[9] More highly cross-linked polystyrene resins were employed: Biobeads SX-12 and Rohm and Haas XAD-2 and XE-305. Substantial amounts of phosphine could only be introduced into XE-305 but 2 mequiv of triphenylphosphine was liberated for each milliequivalent of **2b** taken up.

[10] (a) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 657 (1963); (b) E. M. Thorsteinson and F. Basolo, *Inorg. Chem.*, **5**, 1691 (1966).

[11] (a) R. Whyman, *Chem. Commun.*, 230 (1970); (b) B. L. Booth, M. J. Else, R. Fields, and R. N. Hazeldine, *J. Organometal. Chem.*, **27**, 119 (1971).

[12] P. N. Rylander and L. Hasbrouck, "Technical Bulletin," Vol. X, No. 2, Engelhard Industries, Murray Hill, N. J., 1969, p 50.

[13] Hydrogen adsorption studies of this catalyst by H. Uchida showed 43% dispersion. Assuming a cubic shape, this corresponds to an average particle size of 40 or 80 Å corresponding to each surface Rh taking up one or two H atoms.

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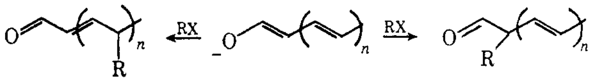
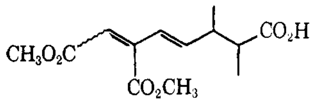
New Synthetic Reactions. Transfer Alkylations

Sir:

Enolates derived from unsaturated carbonyl systems are potentially ambident in their behavior toward carbon alkylation.[1] Conceptually, an alkylating agent may add at the α, γ, ϵ, etc., carbon (eq 1); practically C-alkylation occurs selectively at the α-carbon—the carbon bearing the highest negative charge density. In conjunction with synthetic studies directed toward sesquiterpene antibiotics, we required large quantities of diester acid **1**. Thus, we desired a reaction introducing an α-methylacetic acid unit at one of the more remote positions (*i.e.*, γ, ϵ, etc.) in a polyenolate. Here we wish to report a convenient solution to this problem.

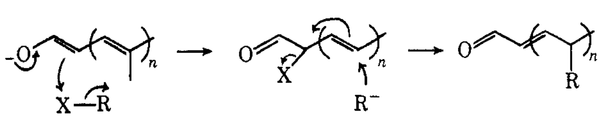


(1)



1

Equation 2 exemplifies the concept. Treatment of a polyenolate with an alkyl halide that undergoes displacement at halogen generates a carbanion and a new 2-halo-β,γ-unsaturated ketone. Recombination of these partners by S_N2' like attack generates net γ or ϵ alkylation. We term this process transfer alkylation. The appropriate choice of an alkylating agent is crucial. Bromomalonates are ideal because of their ability to act as bromonium sources and their ease of conversion to acetic acids. Three bromomalonates (**2**, **3**, and **4**) were screened.[2-4]



(2)

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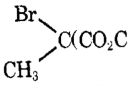
[1] (a) For a discussion of enolate alkylation, see: H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 190–192. (b) This reaction may also be termed an oxidative Michael reaction.



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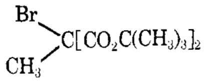

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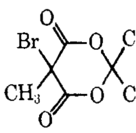
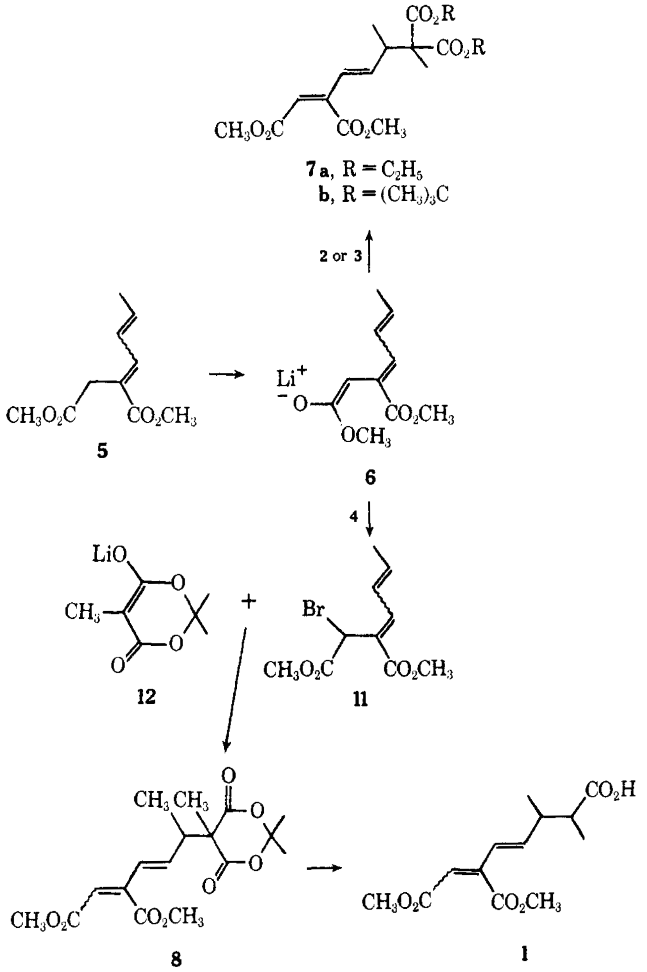


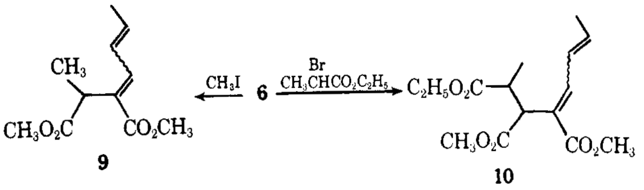
4

Addition of methyl 3-carbomethoxy-3,5-heptadienoate (**5**)[4,5] to a −78° THF–hexane solution of lithiodiisopropylamide generated the trienolate **6** (see Scheme I). Addition of the resultant solution to bromomalonate **2** at −78° followed by warming to room temperature produced **7a** in 67% yield as a 3.5:1 mixture of maleate and fumarate.[4] Use of the *tert*-butyl ester **3** reduced the yield of transfer alkylation product **7b** to 31%; oxidative dimers of **6** became the major products (43% yield). Utilizing the cyclic malonate **4** in a THF–HMPA solvent mixture generated a 66% isolated yield of **8** in addition to 9% of starting material.[4]

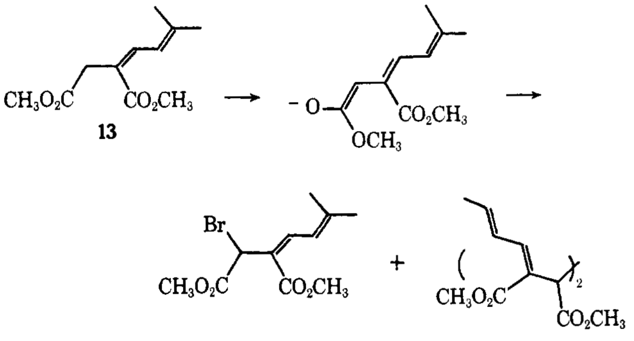
Scheme I



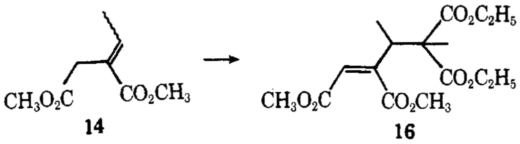
Several observations support the pathway outlined in eq 2 as the major course for formation of the observed products. Direct alkylation of **6** with methyl iodide or ethyl 2-bromopropionate yielded only the expected 2-alkylated compounds **9** and **10**, respectively.[4]

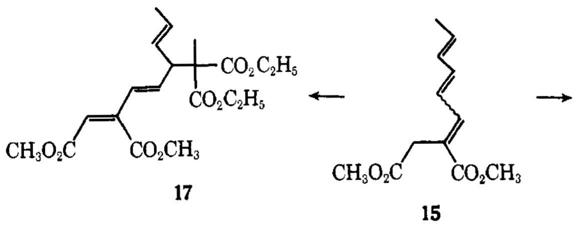


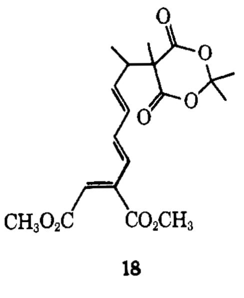
More definitive evidence arises from a careful study of the alkylation of trienolate **6** with **4**. Carrying out the alkylation in THF led to the precipitation of the lithium salt of the cyclic malonate **12** and isolation of the intermediate bromide **11**. Subsequent addition of HMPA effected redissolution of **12** and S_N2'' alkylation (*i.e.*, Michael addition followed by bromide expulsion). Blocking Michael addition by *gem*-alkyl substitution effectively inhibits reaction. Thus, the trienolate from dienoate **13** generated only the corresponding bromide and the oxidative dimer.



To assess the generality of this new reaction, we have extended it to enoate **14** and the trienoate **15**. Although







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(2) Bromomalonate **2** (bp 56–59° (0.2 mm)) was obtained in approximately 85% yield by brominating diethyl methylmalonate with molecular bromine and calcium carbonate in chloroform. Di-*tert*-butyl 2-bromo-2-methylmalonate (**3**, bp 62–64° (0.1 mm)) was prepared in 61% yield by quenching di-*tert*-butyl 2-lithio-2-methylmalonate with molecular bromine. The cyclic ketal **4** was generated in 73% yield by treating the corresponding malonate[3] in chloroform with molecular bromine and anhydrous sodium fluoride.

(3) K. Pihlaja and M. Seilo, *Acta Chem. Scand.*, **22**, 3053 (1968).

(4) All new compounds have been completely characterized by infrared, nuclear magnetic resonance, ultraviolet, and mass spectroscopy. Elemental compositions have also been obtained for all new compounds.

(5) Compounds **5** (bp 68–70° (0.01 mm)), **13** (bp 99–102° (0.4 mm)), **14** (bp 60–65° (0.2 mm)), and **17** (bp 105–110° (0.03 mm)) were prepared in 76, 60, 81, and 77% yield, respectively, by the condensation of the appropriate aldehyde with the sodium salt of dimethyl dimethylphosphonosuccinate. This phosphonate was obtained by the direct condensation of trimethyl phosphite with the monomethyl ester of acid. See, for example: R. G. Harvey, *Tetrahedron*, **22**, 2561 (1966); R. S. Ludington, U. S. Patent 3,400,102 (1968); *Chem. Abstr.*, **69**, 78112*g* (1968).

alkylation of the anion of **14** proceeds well with **2** to give a 52% yield of the transfer alkylated product **16**, reaction with **4** led only to oxidative dimers. Trienoate **15** shows a remarkable selectivity depending on the choice of bromomalonate. Thus, reaction of the trienolate derived from **15** with **1** generated only the product of 1,6 addition, **17**, in 56% isolated yield as a 2:1 mixture of the fumarate and maleate, respectively, whereas, the similar reaction with **4** generated a 38% isolated yield of the 1,8 product **18** as a 2:1 mixture of maleate and fumarate.

Synthetically the attributes of the cyclic malonate **4** make it the preferred transfer alkylating agent. It is a highly crystalline solid, mp 85–86°, that is easily prepared and purified by recrystallization from isopropyl alcohol. Furthermore, dissolution of the products of transfer alkylation with **4** in trifluoroacetic acid at 25° followed by removal of the solvent *in vacuo* effects selective hydrolysis to the malonic acid which may be decarboxylated by warming in DMSO. Thus, utilizing this sequence, a sample of the fumarate isomer of **8** was converted to **1** in 82% yield.

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(6) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.

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Synthesis with Nitrogen Atoms

Sir:

Reaction of atomic nitrogen with organic compounds in the gas phase is characterized by extensive breaking of carbon–carbon bonds.[1] The usual products from olefins are HCN and small amounts of hydrocarbons. The course of these reactions can be very complex, with possible involvement of excited molecular nitrogen, atomic nitrogen, atomic hydrogen, and other radicals resulting from fragmentation of primary products.

One anticipates a simpler chemistry in the condensed phase. Little work has been published on the reactions of atomic nitrogen in solution and at low temperatures.[2] We report here that in the condensed phase some *gem*-dihalo olefins react with nitrogen atoms with minor production of HCN and with the major product being halogenated nitrile; carbon–carbon bond cleavage is not the major reaction.

"Active" nitrogen, which is mainly ground-state (quartet) atomic nitrogen, was generated by pumping molecular nitrogen, from which oxygen was removed over copper at 500°, through a 2450-MHz microwave discharge. The flow rate of nitrogen atoms was measured calorimetrically by catalyzed recombination of the atoms on copper oxide coated copper washers.[3] Reaction with substrate was accomplished by bubbling the atomic nitrogen stream through liquid olefin cooled to a few degrees above its melting point. Most reaction takes place in the condensed phase, since reaction flames[1] are not seen before the nitrogen reaches substrate, and the yellow nitrogen afterglow is extinguished after the substrate. The molar ratio of halo olefins to atomic nitrogen was greater than 90:1. The yields of nitrogenous products account for 70–95% of the atomic nitrogen reaching the substrate (see Table I).

Reaction of vinylidene halides with nitrogen atoms occurs in high yield to produce haloacetonitriles. These reactions do not involve cleavage of the carbon–carbon double bond as a major reaction. With substrates which do not have a *gem*-dihalo group, cleavage

$$H_2C{=}CX_2 + N \longrightarrow X{-}CH_2{-}CN$$
$$H_2C{=}CRX + N \longrightarrow HCN,\ RCN,\ \text{etc.}$$

of the double bond predominates, producing either HCN or other nitriles (C_6H_5–CN, Cl_3C–CN, NC–CN, etc). These observations can be explained readily.

Free radicals have been reported[4] to add preferentially to the CH_2 end of 1,1-dichloroethylene. Such an addition of nitrogen atoms would be expected to give HCN as the major nitrogen-containing product (Scheme I), but in fact, $ClCH_2CN$ is the largest product. The preferred formation of $ClCH_2$–CN requires another reaction route, probably other than addition at the nonmethylene carbon since there is no instance of preferred Markovnikov-type addition of radicals.[4]

Table I. Relative Percentages of Nitrogenous Products[a]

Substrate	Reaction temp, °C	HCN	$ClCH_2$–CN	ClCN	$BrCH_2$–CN	Other nitriles
$H_2C{=}CCl_2$	−126	7.5	91.8	0.7		[b]
$H_2C{=}C(Cl)Br$	−96	10.1	29.3	4.2	56.4	BrCN (trace)
$H_2C{=}CBr_2$	−78	47.3			52.7	BrCN (trace)
$H_2C{=}C(CN)Cl$	−73	36.5	Trace			$(CN)_2$ (63.5%); $CH_2(CN)_2$ (trace)
$H_2C{=}C(CCl_3)Cl$	−78	49.6	28.6			Cl_3C–CN (21.8%)[c]
$H_2C{=}C(C_6H_5)Cl$	−23	51.8		0.6		C_6H_5–CN (47.6%)[d]
cis-ClCH=CHCl	−78	90.7	8.6	0.7		[b]

[a] Products were identified by comparison of vpc retention times with authentic samples, and by infrared and nmr spectroscopy and mass spectroscopy. [b] No Cl_2CH–CN detected. [c] No Cl_3C–CHCl–CN or Cl_3C–CH_2–CN detected. [d] No C_6H_5–CH_2–CN detected.

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(1) A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York, N. Y., 1968.

(2) N. N. Lichtin and C. T. Chen, *J. Amer. Chem. Soc.*, **93**, 5922 (1971).

(3) For the principles of this method, see: B. Bak and J. Rastrup-Andersen, *Acta Chem. Scand.*, **16**, 111 (1962); E. M. Levy and C. A. Winkler, *Can. J. Chem.*, **40**, 686 (1962); J. E. Morgan and H. I. Schiff, *ibid.*, **41**, 903 (1963). The accuracy of the calorimetric method has been verified by the "titration" of atomic nitrogen with nitric oxide. Details of this method will be published elsewhere.

(4) For addition of various radicals to haloethylenes, see: R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953) (CF_3); J. E. Francis and L. C. Leitch, *Can. J. Chem.*, **35**, 500 (1957) (Br·); and J. F. Harris, Jr., *J. Amer. Chem. Soc.*, **84**, 3148 (1962), and F. S. Dainton and B. E. Fleischfressen, *Trans. Faraday Soc.*, **62**, 1838 (1966) (Cl·).