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NUCLEOPHILIC SUBSTITUTION IN ORGANOMERCURY HALIDES BY A FREE RADICAL CHAIN PROCESS^{*,**}

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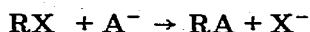
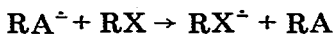
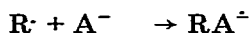
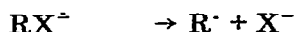
Summary

Primary and secondary alkylmercury halides react with the salts of secondary nitroalkanes to afford tertiary nitroalkanes, mercury metal, and halide ion. The reaction is light initiated and is strongly inhibited by radical scavengers. Cyclic products resulted from the reaction of 1-chloromercury-5-hexene establishing the 5-hexen-1-yl radical as an intermediate. A chain mechanism involving radical ions is proposed to account for these substitution reactions. Aryl- and 1-alkenylmercury halides are either unreactive towards nitronate ions or are reductively symmetrized to the bis[organo]mercury compounds and mercury metal. Alkyl mercurials are unreactive towards nucleophiles other than nitronate ions or, in the case of benzylmercury chloride, may be reduced to bibenzyl.

Introduction

The ions-radical chain mechanism for nucleophilic substitution in aliphatic [1,2] and aromatic systems (Scheme 1) has been labeled S_{RN}^1 [3]. In a preliminary communication we described the substitution reaction of alkylmercury halides with nitronate ions (eq. 1) and proposed that an S_{RN}^1 process was oper-

SCHEME 1

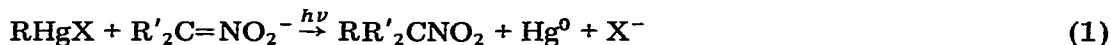


^{*} In honor of Professor Henry Gilman for his many years of outstanding research and teaching in the field of organometallic chemistry.

^{**} Electron Transfer Processes, Part 28. For Part 27 see G.A. Russell, B. Mudryk and M. Jawdosiuik, *J. Amer. Chem. Soc.*, 103 (1981) 4610.

^{***} National Science Foundation Undergraduate Research Participant, (1978).

ative [4]. With all other reported aliphatic systems the substrate (RX in Scheme 1) contains a nitro or activated benzyl substituent at the reaction



center. Radical pairs may result from electron transfer between anions and alkyl halides not containing a nitrosubstituent, but S_{RN}^1 chains have not been observed [5]. Except for nitro- or cyano-activated benzyl derivatives [6], only tertiary structures have been employed in the aliphatic S_{RN}^1 process. These generally have the structure $(\text{R})_2\text{C}(\text{X})\text{NO}_2$ where $\text{X} = \text{Cl}, \text{Br}, \text{NO}_2, \text{CN}, \text{CO}_2\text{Et}, \text{COAr}, \text{SO}_2\text{R},$ or R^* . Reaction 1 is the only reported S_{RN}^1 reaction involving attack of a nucleophile on an organometallic substrate ** and one of the few known direct reductive coupling reactions of an anion and an organomercurial ***.

In our preliminary communication we reported that reaction 1 was initiated by light and inhibited by free radical scavengers. Although these observations are consistent with an S_{RN}^1 formulation, mechanisms involving S_{H}^2 processes instead of radical ions were not rigorously excluded. Herein we describe the scope and limitations of reaction 1 and provide firm evidence for the operation of an S_{RN}^1 process.

Results and discussion

Examples of reaction 1 are given in Table 1. Primary and secondary alkylmercury chlorides, bromides, and iodides coupled with the anions of 2-nitropropane and nitrocyclohexane under sunlamp irradiation to afford tertiary nitroalkanes in generally good yields. Electronic effects appear to be important in determining the reactivity of an organomercurial. Thus α -ketomercurials or benzylmercury halides were converted to products in less than two hours at room temperature while simple alkylmercury halides required 17 hours or more. Methylmercury chloride and the anion of 2-nitropropane yielded only 2% of the expected *tert*-nitrobutane after 40 hours of sunlamp irradiation. Allylmercury chloride which might be expected to exhibit high reactivity afforded only a 50% yield of the expected nitroalkane after 24 hours. The appearance of resinous material in the workup suggests that polymerization of the mercurial and/or product occurred. Aryl- and vinylmercury halides proved either unreactive with nitronate ions or were symmetrized to the bis[organo]-

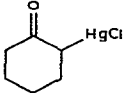
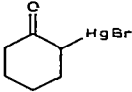
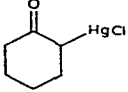
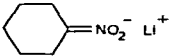
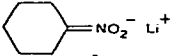
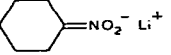
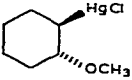
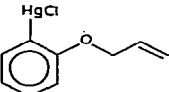
* The nitro group is usually retained in the radical but in the cases where $\text{X} = \text{CN}, \text{CO}_2\text{Et}, \text{COAr}$ the nitro group is lost [1c, 2b, 2c].

** Certain metallate anions ($\text{ArTe}^-, \text{ArSe}^-, \text{Co}(\text{CO})_4^-$) appear to react with aryl halides by the S_{RN}^1 process [7].

*** The reduction of alkylmercury salts by hydride transfer agents, typified by sodium borohydride, involves the stoichiometric metathesis of the organomercury salt to an organomercury hydride followed by radical chain elimination of the mercury salt [8]. Sulfinato and dialkyl phosphite anion react photochemically with 1-alkenylmercury halides to form α, β -unsaturated sulfones and phosphonates by a chain reaction not involving the 1-alkenyl radical [9].

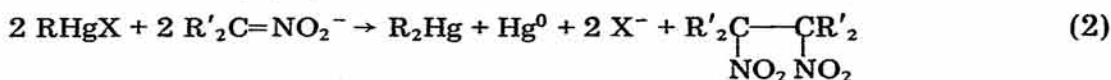
TABLE I

 REACTIONS OF ORGANOMERCURY HALIDES WITH NITRONATE SALTS IN Me₂SO TO FORM NITRO COMPOUNDS (reaction 1)

RHgX	R' ₂ C=NO ₂ ⁻ M ⁺	Time (h) ^a	RR' ₂ CNO ₂ (% Yield)
	Me ₂ C=NO ₂ ⁻ Li ⁺	1	56 ^{b, c}
	Me ₂ C=NO ₂ ⁻ Li ⁺	1	68 ^d
		2	60
PhCH ₂ HgCl		2	87
PhCH ₂ HgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	2	100 ^{b, c, e}
PhCH ₂ HgCl	MeCH=NO ₂ ⁻ Li ⁺	2	~5 (40) ^f
n-C ₆ H ₁₃ HgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	37	90
n-C ₆ H ₁₃ HgBr	Me ₂ C=NO ₂ ⁻ Li ⁺	70	50
n-C ₆ H ₁₃ HgI	Me ₂ C=NO ₂ ⁻ Li ⁺	70	80
cyclo-C ₆ H ₁₁ HgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	34	76
cyclo-C ₆ H ₁₁ HgCl		60	84
Me ₂ CHHgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	17	63 ^b
CH ₂ =CHCH ₂ HgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	24	50
	Me ₂ C=NO ₂ ⁻ Li ⁺	47	14.5 ^g
cyclo-C ₅ H ₉ CH ₂ HgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	41	35
cyclo-C ₅ H ₉ CH ₂ HgCl	Me ₂ C=NO ₂ ⁻ K ⁺	40	47
CH ₂ =CH(CH ₂) ₄ HgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	48	35 ^h
CH ₂ =CH(CH ₂) ₄ HgCl	Me ₂ C=NO ₂ ⁻ K ⁺	21	48 ^h
MeHgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	40	~2 ⁱ
Me ₃ CHgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	4	0
Me ₃ CCH ₂ HgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	21	~5 ^j
PhHgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	15	0 ⁱ
(E)-Me ₃ CCH=CHHgCl	Me ₂ C=NO ₂ ⁻ Li ⁺	16	0 ^k
	Me ₂ C=NO ₂ ⁻ Li ⁺	23	0 ^l

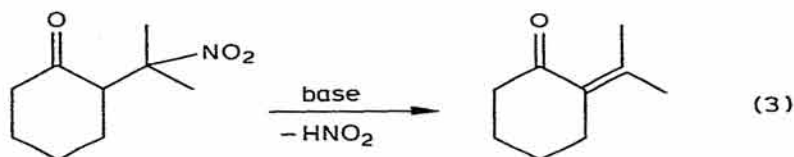
^a Reactions were performed in nitrogen-purged solvents at ambient reaction temperatures (25–45°C) with irradiation from a 275 watt sunlamp positioned 4 to 8 inches from the Pyrex reaction flask. ^b Little or no *tert*-nitroalkane resulted when the reaction was performed with 3 to 5 mole percent di-*t*-butyl nitroxide added. ^c The *tert*-nitroalkane was not formed when the reaction was performed in the dark. ^d DMF solvent. ^e *tert*-Nitroalkane was not formed when the reaction was performed in Me₂SO saturated with molecular oxygen at 760 Torr. ^f 2-Methyl-2-nitro-1,3-diphenylpropane. ^g *Cis* and *trans* isomers were formed (*cis* : *trans* = 1 : 8). ^h Only the cyclized products 1-cyclopentyl-2-methyl-2-nitropropane and 2-cyclohexyl-2-nitropropane (25 : 1 ratio) were formed. The indicated yield is for the sum of these products. ⁱ A trace of 2,3-dimethyl-2,3-dinitrobutane was isolated. ^j Irradiation in a Rayonet RPR-100 reactor equipped with 350 nm bulbs. GC-MS indicated the formation of bis[neopentyl]mercury. ^k Bis[(*E*)-3,3-dimethyl-1-butenyl]mercury (82%) and 2,3-dimethyl-2,3-dinitrobutane (52%) were isolated. ^l Bis[*o*-allyloxyphenyl]mercury (17%) and 2,3-dimethyl-2,3-dinitrobutane (39%) were isolated.

mercury compound with the concomitant appearance of mercury metal and nitronate dimer (eq. 2).



In one example the halogen on mercury affected the outcome of the reaction. The 2-halomercurycyclohexanones afforded β -nitro ketones for halogen = Cl, Br. For the case halogen = I a rapid reaction occurred with the anion of 2-nitropropane in which mercury metal precipitated, but workup of the organic product yielded an unstable iodine-releasing residue which was not investigated further. Another iodide, *n*-hexylmercury iodide, coupled with the anion of 2-nitropropane in 80% yield.

β -Nitro ketones such as I readily eliminate the elements of nitrous acid when treated with base (eq. 3) to yield an α,β -unsaturated ketone. This formal controlled cross-Claisen condensation has also been achieved by the coupling of enolate ions with α -halo nitroalkanes [10].



Sterically hindered alkylmercurials afford drastically lowered yields of nitroalkanes with nitronate ions. Thus *trans*-2-methoxy-1-chloromercury cyclohexane and the lithium salt of 2-nitropropane gave only a 14.5% yield of product in a *trans/cis* ratio of 8/1. Neopentylmercury chloride only yielded a trace (5%) of nitroalkane and a trace of bis[neopentyl]mercury after prolonged irradiation in a Rayonet reactor at 350 nm. A tertiary mercurial, *t*-butylmercury chloride, decomposed with loss of mercury metal when irradiated in solution with the lithium salt of 2-nitropropane, but no coupling product was formed.

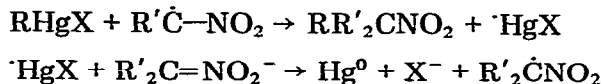
The use of the salt of nitroethane, a primary nitroalkane, in a reaction with benzylmercury chloride (Table I) afforded mostly 2-methyl-2-nitro-1,3-diphenylpropane. Evidently the first-formed product, a secondary nitroalkane, was deprotonated and reacted further with a molecule of benzylmercury chloride.

Reaction 1 failed to proceed in the dark. No attempts were made to ascertain the quantum yield in this photostimulated process, but for favorable cases it must be quite high (e.g., $>10^3$). Reaction 1 was strongly inhibited by the presence of small amounts of di-*t*-butyl nitroxide (3–5 mole percent based on mercury), an efficient radical scavenger, and by the use of oxygen-saturated solvent. Reaction 2 was also photostimulated and did not appear to be inhibited by di-*t*-butyl nitroxide although the presence of a stoichiometric amount of the radical scavenger prevented the formation of a nitronate dimer.

A key experiment was the reaction between 1-chloromercury-5-hexene and the anion of 2-nitropropane. Only cyclized nitroalkanes were formed (Table 1). Rearrangement of the 5-hexen-1-yl moiety is diagnostic for the free radical intermediate [11]. The anion does not cyclize [12] and the cation closes exclusively to the thermodynamically favored six-membered ring [13].

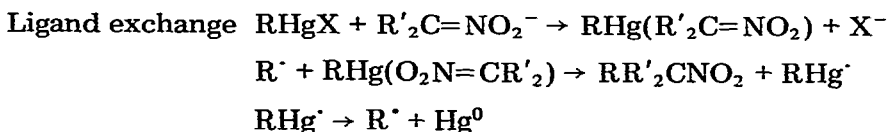
Observation of the 5-hexen-1-yl rearrangement rules out mechanistic Scheme 2 in which the chain carrying radical is derived from oxidation of the nitronate anion.

SCHEME 2



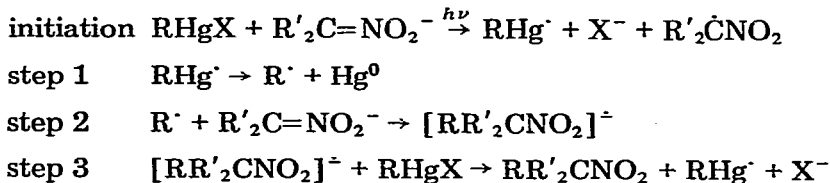
Scheme 3 utilizes the alkyl radical derived from the mercurial, but requires ligand metathesis of mercury. This exchange of nitronate ion for halide is not observed (see the Experimental section).

SCHEME 3



The mechanism of reaction 1 thus appears best represented by Scheme 4, a modified S_{RN}^1 process. The nature of photoinitiation is not certain but appears not to involve simple homolysis of the organomercurial, since simple alkylmercury halides do not absorb light above ~ 310 nm and more energetic light was filtered by the use of Pyrex glassware. No charge-transfer complex was detected

SCHEME 4

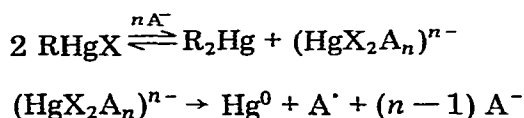


between the mercurial and the nitronate salt. Therefore, electron transfer to the mercurial from a photoexcited nitronate ion ($\lambda_{\text{max}} = 352$ nm for lithium 2-nitropropanate in DMSO) may be the general mode for chain initiation. Chain propagation step 1 has ample literature precedent as a key step in the thermal decomposition of organomercury hydrides [10] and has been estimated to be endothermic by approximately 7 kcal mol^{-1} for $\text{R} = \text{alkyl}$ [14]. Step 2 is common to S_{RN}^1 processes involving nitronate ions [1,2]. Step 3, an electron transfer process, appears reasonable in light of the strong reducing power of a tertiary nitroalkane radical anion ($E_{\text{ox}}^0 = 1.6$ to 1.8 V vs SCE in glyme) [15].

Although step 1 in Scheme 4 is expected to be rapid for $\text{R} = \text{alkyl}$, this process may be highly endothermic for $\text{R} = \text{vinyl}$ or $\text{R} = \text{aryl}$. For $\text{R} = \text{ethenyl}$ the

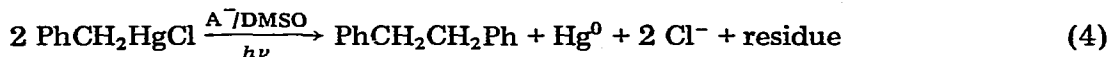
heat of dissociation of RHg^\cdot has been estimated to be $19 \pm 6 \text{ kcal mol}^{-1}$ [14]. Thus in light of Scheme 4 the failure of aryl- and vinylmercury halides to couple with nitronate ions is not surprising. Although reductive symmetrization of some organomercury salts are believed to occur via reduction of the mercurial to the organic free radical [16], we do not believe the symmetrizations of vinyl and aryl mercurials by nitronate anions involves the vinyl or aryl radicals. Thus, the symmetrizations (reaction 2) of (*E*)-3,3-dimethyl-1-butenylmercury chloride, or *o*-allyloxyphenylmercury chloride were not prevented by the presence of di-*t*-butyl nitroxide and no rearrangement of the *o*-allyloxyphenyl moiety occurred*. The symmetrization reaction 2 may result from reduction of an equilibrium concentration of mercuric halide (Scheme 5). Mercury(II)chloride is reduced by $\text{Me}_2\text{C}=\text{NO}_2^-$ in Me_2SO to give Hg^0 and a modest yield of 2,3-dinitro-2,3-dimethylbutane. The pre-equilibrium in Scheme 5 must lie far to the

SCHEME 5



left since R_2Hg formation is observed only after sunlamp irradiation and not immediately upon mixing the mercurial with a solution containing the nitronate ion**.

Attempts to couple anions other than nitronates with alkylmercury halides failed (Table 2), although with some anions ($(\text{EtO})_2\text{PO}^-$, NO_2^- , $p\text{-MePh}_2\text{SO}_2^-$) benzylmercury chloride underwent an unusual reductive photodimerization reaction (reaction 4). The photodimerization was observed only with benzylmercury chloride. Simple alkylmercury halides were essentially unreactive



towards diethyl phosphite ion (Table 2) and irradiation afforded none of the dialkylmercury. 2-Chloromercurycyclohexanone was photoreduced by diethyl phosphite ion to mercury metal and (following protic workup) cyclohexanone.

The residues resulting from oxidation of A^- in reaction 4 were not investigated. While the mechanism of bibenzyl formation is not known in detail, benzyl radicals have been established as intermediates. Thus the reaction with $\text{A}^- = (\text{EtO})_2\text{PO}^-$ performed in oxygen-saturated DMSO afforded benzyl alcohol, benzaldehyde, benzoic acid, and only a trace (1.8% yield) of bibenzyl. Oxygen did not appreciably slow the rate of disappearance of the starting materials. Although the reaction did not demonstrate chain character, the yield of bibenzyl was stoichiometrically reduced by the presence of di-*t*-butyl nitroxide. Bibenzyl may either result from the simple dimerization of benzyl radicals or

* The *o*-allyloxyphenyl radical undergoes a very rapid cyclization of the Δ^5 -hexenyl type [17].

** Arylmercury halides are known to be especially sensitive toward symmetrization by ligands which serve to complex mercury(II) halides [18].

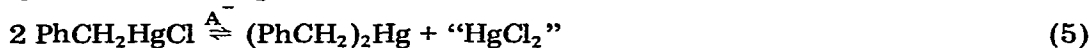
TABLE 2

PHOTOCHEMICAL COUPLING OF RHgCl IN THE PRESENCE OF VARIOUS ANIONS IN Me_2SO SOLUTION ^a

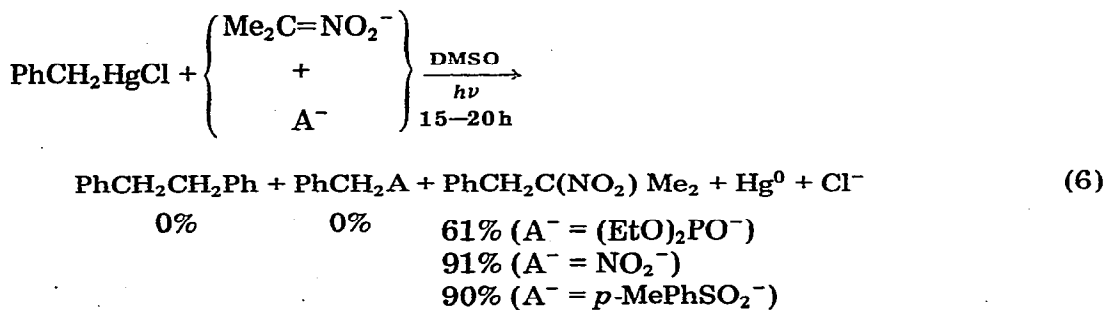
R	Added salt	Time (h)	% R-R
PhCH_2	KOP(OBu)Ph ^b	29	88
PhCH_2	KOP(OEt)_2 ^b	40	84
PhCH_2	$\text{NaO}_2\text{SPhMe-}p$	18	18
PhCH_2	NaN_3 ^c	21	42
PhCH_2	$\text{KOC(Me)}_2\text{Ph}$ ^b	19	0 ^d
PhCH_2	NaNO_2	19	36
$\text{cyclo-C}_6\text{H}_{11}$	KOP(OEt)_2 ^b	70	0 ^d
$n\text{-C}_6\text{H}_{13}$	KOP(OEt)_2 ^b	40	0
$\text{CH}_2\text{-(CH}_2\text{)}_3\text{-C(=O)CH}_3$	KOP(OEt)_2 ^b	9	0 ^e

^a Irradiation of a 1 : 1 ratio of RHgCl and added salt ($\sim 0.1 M$) with a 275 W sunlamp in Pyrex under nitrogen at 30°C . ^b Generated by the action of potassium *t*-butoxide on the conjugate acid. ^c $\text{Me}_2\text{SO}/\text{H}_2\text{O}$ solvent mixture employed. ^d No mercury metal was observed. ^e Cyclohexanone (44% yield) was isolated by an aqueous workup.

may involve the attack of a benzyl radical on a benzylmercurial. For $\text{A}^- = (\text{EtO})_2\text{PO}^-$ the predominant mercury species in solution is bis(benzyl)mercury due to a non-reductive symmetrization (eq. 5) detected by ^1H NMR and isolation experiments (see Experimental section). For $\text{A}^- = \text{NO}_2^-$, however, the symmetrization equilibrium lies to the left.

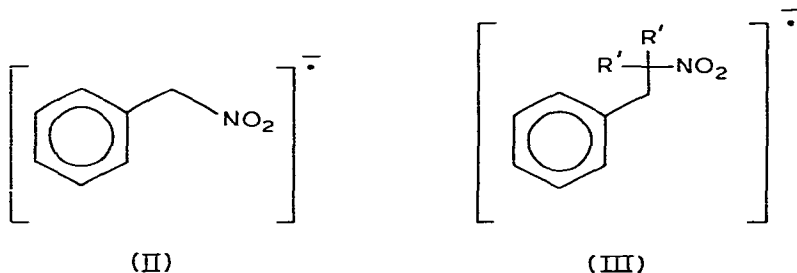


Although anions other than nitronates react with benzylmercury chloride to afford bibenzyl derived from benzyl radicals, competitive reactions of benzylmercury chloride with the anion of 2-nitropropane and a second anion should result only in the S_{RN}^1 coupling product derived from the nitronate ion. Thus selective reaction of benzyl radicals with nitronate ions was observed (eq. 6). Under conditions in which the benzyl radical can be scavenged by a nitronate ion, no bibenzyl is formed.



Reactions 4 and 6 underscore the failure of a series of anions other than nitronates to participate in an S_{RN}^1 process with simple alkyl-type radicals. In most, but not all, cases this failure can be rationalized in terms of the instability of RA^\cdot (Scheme 1). The adduct of a benzyl radical with nitrite ion (II) however, should possess much the same stability as that with a nitronate ion

(III). The observed result is consistent with the observation that the reaction of a radical with an anion often occurs in a contra-thermodynamic fashion, whose rate is controlled mainly by the basicity of the anion [19].



The possibility exists that steps 1 and 3 of Scheme 4 can occur in a concerted manner. The inability of mercurials with $R = \text{vinyl}$ or aryl to participate in Scheme 4 is consistent with the requirement that step 1 is a discrete process. However, at the present time no direct experimental evidence can be presented for the intervention of alkyl-Hg^\cdot in the radical chain substitution reactions observed with nitronate anions.

Experimental

Materials

Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride and was stored under nitrogen with 4A molecular sieves. Dimethyl sulfoxide (Me_2SO) and dimethylformamide (DMF) were used as received or were distilled from calcium hydride at reduced pressure and stored under nitrogen with 4A molecular sieves. Purification of DMF and Me_2SO for reactions of nitronate salts with organomercurials was found to be unnecessary since the qualitative reaction rates and yields were insensitive to the solvent history.

The lithium salts of 2-nitropropane, nitrocyclohexane, and nitroethane were prepared by the procedure of Kornblum [20].

2-Iodomercurycyclohexanone [21], 2-bromomercurycyclohexanone [22], and 2-chloromercurycyclohexanone [23] were prepared by the method of House [21]. Literature methods were also employed for the preparations of benzylmercury chloride [24], 2-chloromercury-1-methoxycyclohexane [25], methylmercury chloride [26], allylmercury chloride [27], neopentylmercury chloride [28], *t*-butylmercury chloride [29], (*E*)-3,3-dimethyl-1-butenylmercury chloride [30], cyclopentylmethylmercury chloride [31], 6-chloromercury-1-hexene [31], 2-chloromercurypropane [32], and *n*-hexylmercury chloride [33]. Bis[benzyl]mercury [34] was prepared by the action of 0.5 equivalents of mercuric chloride on benzylmagnesium chloride in ethyl ether.

Bis[*o*-allyloxyphenyl]mercury was prepared by the slow addition of mercuric chloride (44 mmol) in 40 ml THF to *o*-allyloxyphenyl magnesium bromide (94 mmol) in 60 ml THF under nitrogen, followed by 12 h at reflux. The resulting solution was poured into 1500 ml of 5% aqueous NH_4Cl and the solid product recrystallized from ethanol/water to afford 16 g (73% yield) of the mercurial, m.p. 69.5–70.5°C. Anal. Found: C, 46.32; H, 3.96. $\text{C}_{18}\text{H}_{18}\text{HgO}$ calcd.: C, 46.30; H, 3.89%.

o-Allyloxyphenylmercury chloride was prepared by addition of mercuric chloride (4.4 mmol) in 10 ml THF to bis[*o*-allyloxyphenyl]mercury (4.3 mmol) in 25 ml THF. The solution was warmed to reflux for 30 m, then poured into 250 ml of 2% aqueous NaCl. The crude product was dissolved in 125 ml of chloroform and insoluble inorganic salts were removed by filtration. Removal of the chloroform under vacuum afforded 2.5 g (79% yield) of the pure mercurial, m.p. 93.5–95°C. Anal. Found: C, 29.30; H, 2.44. C₉H₉ClHgO calcd.: C, 29.28; H, 2.46%.

Bis[(*E*)-3,3-dimethyl-1-butenyl]mercury was prepared by the addition of solid (*E*)-3,3-dimethyl-1-butenylmercury chloride (3.1 mmol) to a solution containing potassium *t*-butoxide (5.4 mmol) and diethyl phosphite (7.8 mmol) in 25 ml dry Me₂SO under nitrogen. The solution was stirred for 5 min at room temperature and poured into brine. The product was extracted with ether and the extract washed with distilled water, brine, dried over MgSO₄, and concentrated to afford 0.6 g (100% yield) of the mercurial which was purified by a Kugelrohr distillation at 75°C (0.1 Torr). Anal. Found: C, 39.40; H, 6.12. C₁₂H₂₂Hg calcd.: C, 39.28; H, 6.04.

Phenylmercury chloride was used as received from Aldrich. Samples of cyclohexylmercury chloride [35], *n*-hexylmercury bromide [33], and *n*-hexylmercury iodide [33] were kindly provided by Professor R.C. Larock.

Reaction of benzylmercury chloride with nitronate salts

The following procedure serves as a model for the reactions of nitronate salts with alkylmercury halides.

Benzylmercury chloride (3.0 mmol) was added with magnetic stirring to a solution containing the lithium salt of 2-nitropropane (3.7 mmol) in 50 ml of nitrogen-purged Me₂SO. The solution was irradiated with a 275 W sunlamp positioned approximately 8" from the Pyrex reaction vessel and which maintained the reaction temperature at 35–40°C. Mercury metal precipitated from solution after an induction period of 2 to 3 min and the reaction appeared complete after 120 min. The Me₂SO solution was decanted from the mercury metal into brine (workup of some other reaction mixtures required filtration through a Celite cake) and the product was extracted from the resulting emulsion with ether. The ethereal extract was washed with aqueous sodium thiosulfate (to remove any unreacted mercurial) followed by brine, dried over MgSO₄ and concentrated under vacuum to afford 0.44 g (100% yield) of 2-methyl-2-nitro-1-phenylpropane as a pale green liquid. An analytical sample was obtained by crystallization from ethanol/water, m.p. 25°C. ¹H NMR (ppm, CDCl₃) δ 6.9–7.3 (5H, m); 3.1 (2H, s), 1.5 (6H, s). IR (neat) 3040w, 1540vs, 1495m, 1450w, 1350m, 740s, 720s, 695s cm⁻¹. Anal. Found: C, 67.21; H, 7.43, N, 7.61, MW, 179.09415 (MS, 20 eV). C₁₀H₁₃NO₂ calcd.: 67.02; H, 7.31; N, 7.82%, MW, 179.09463.

Benzylmercury chloride (12 mmol) and the lithium salt of nitrocyclohexane (13 mmol) were irradiated for 2 h in 160 ml Me₂SO to afford 2.4 g (87%) of 1-benzyl-1-nitrocyclohexane. Recrystallization from pentane afforded long white needles of m.p. 68.5–69°C. ¹H NMR (ppm, CDCl₃) δ 6.9–7.3 (5H, m), 3.07 (2H, s), 2.25–2.60 (2H, m), 1.2–1.8 (8H, m), IR (neat, molten) 3030w, 2940s, 2860m, 1585vs, 1500m, 1450s, 1350m, 715s, 695s cm⁻¹. Anal. Found:

C, 71.02; H, 7.90; N, 6.31; *m/e*, 172.12503. Calcd. for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39%, MW - NO_2 , 172.12520.

Benzylmercury chloride (3 mmol) and the lithium salt of nitroethane (6 mmol) were irradiated for 2 h in 75 ml Me_2SO to afford 0.45 g of a liquid found to be a mixture of at least 4 volatile components by GLC (5% SE-30; 90°C). GC-MS analysis revealed a minor component (~5% overall yield) to be 2-nitro-1-phenylpropane, while the major component (~40% overall yield) was the doubly-benzylated product, 2-methyl-2-nitro-1,3-diphenylpropane.

Benzylmercury chloride and the lithium salt of 2-nitropropane when irradiated for 2 h in oxygen-saturated Me_2SO (760 Torr) gave no precipitate of Hg and 90% of the starting mercurial was recovered. Likewise, only a trace of mercury metal precipitated when benzylmercury chloride and the nitronate salt were irradiated for 1 h in Me_2SO containing a trace of di-*t*-butyl nitroxide (5 mole percent). No coupled product was observed and 95% of the starting mercurial was recovered, whereas in the absence of the nitroxide a 60% yield of 2-methyl-2-nitro-1-phenylpropane was found in 1 h.

When benzylmercury chloride and the lithium salt of 2-nitropropane were stirred for 1 h in 75 ml of nitrogen-purged Me_2SO in a flask darkened by tightly wrapped aluminum foil, no mercury metal was formed and the starting mercurial was recovered in 95% yield.

To test for the formation of $PhCH_2Hg(O_2N=CMe_2)$ the reaction between $PhCH_2HgCl$ and the nitronate was performed in Me_2SO-d_6 and followed by 1H NMR. When monitored at several stages of partial reaction the solution only exhibited the spectra of benzylmercury chloride (δ 7.0–7.2 (5H); 2.97 ppm (2H)), lithium 2-nitropropanate (δ 1.85 ppm), and 2-methyl-2-nitro-1-phenylpropane. No intermediate species were detected. This experiment complements the observation that benzylmercury chloride is recovered intact from inhibited reactions.

Reaction of 2-halomercurycyclohexanones with nitronate salts

2-Chloromercurycyclohexanone (1.5 mmol) and the lithium salt of 2-nitropropane were irradiated for 1 h in 30 ml of Me_2SO to afford 170 mg (56% yield) of 2-(α -nitroisopropyl)cyclohexanone as a crystalline solid (m.p. 44–50°C). 1H NMR (ppm, $CDCl_3$) δ 3.5 (1H, m), 1.8–3.7 (9H, m), 1.7 (3H, s), 1.6 (3H, s). IR (neat, molten) 1705s, 1585vs, 1340s cm^{-1} . This β -nitro ketone, which readily lost the elements of HNO_2 , was conveniently characterized as the 2,4-dinitrophenylhydrazone of α -isopropylidene cyclohexanone (m.p. 172–174°C, lit. [36] 181.5–182.5°C). Anal. Found: C, 56.75; H, 5.83; N, 17.78; MW, 318.13279 (MS). $C_{15}H_{18}N_4O_4$ calcd.: C, 56.60; H, 5.70; N, 17.60%, MW, 318.13281.

The lithium salt of nitrocyclohexane (3 mmol) and 2-chloromercurycyclohexanone (2.25 mmol) was irradiated in 30 ml of Me_2SO for 2 h to afford a 60% yield of 2-(α -nitrocyclohexyl)-cyclohexanone. An analytical sample was obtained by recrystallization from pentane (m.p. 66–68°C). 1H NMR (ppm, $CDCl_3$) δ 4.4 (1H, m), 1.0–3.3 (18H, m). IR (neat, molten) 2940s, 1715s, 1540s, 1450m, 1350m, 850m cm^{-1} . MW, 179.14305; $C_{12}H_{18}O$ (MW - NO_2) calcd. 179.14359.

The reaction of 2-chloromercurycyclohexanone with the anion of 2-nitro-

propane was found not to proceed in the presence of 3 mole percent di-*t*-butyl nitroxide or in absolute darkness. A 30 min reaction period was employed for these diagnostic tests. The 30 min control reaction afforded a 41% yield of β -nitro ketone under the standard reaction conditions.

Reaction of n-hexylmercury halides with the lithium salt of 2-nitropropane

n-Hexylmercury chloride (0.6 mmol) and lithium 2-nitropropanate (3.1 mmol) were irradiated in 20 ml of Me₂SO for 37 h. Workup afforded 0.1 g of an oil found to contain a 90% yield of 2-methyl-2-nitrooctane by quantitative ¹H NMR. An analytical sample was obtained by preparative GLC (20% DEGS; 140°C). ¹H NMR (ppm, CDCl₃) δ 1.57 (6H, s), 0.85–2.1 (13H, m). IR (neat) 2920s, 1540s, 1470m, 1395m, 1370w, 850m cm⁻¹. Anal. Found: C, 62.42; H, 10.91; N, 8.18; MW, 127.14035. C₉H₁₉NO₂ calcd.: C, 62.39; H, 11.05; N, 8.08%, MW – NO₂, 127.14067.

Reaction of cyclohexylmercury chloride with lithium and potassium nitronates

Cyclohexylmercury chloride (3.0 mmol) and the lithium salt of 2-nitropropane (8.0 mmol) were irradiated in 30 ml of Me₂SO for 34 h. Workup afforded 0.45 g of an oil found to contain a 76% yield of 2-cyclohexyl-2-nitropropane by quantitative ¹H NMR. Analytically pure samples were obtained by either preparative GLC (20% DEGS; 180°C) or by a Kugelrohr distillation followed by recrystallization from pentane to give material of m.p. 46–47°C. ¹H NMR (ppm, CDCl₃) δ 1.55 (6H, s), 0.6–2.4 (11H, m). IR (KBr) 2920s, 2840m, 1535s, 1450m, 1400m, 1375m, 1350m, 1340m, 840m cm⁻¹. Anal. Found: C, 62.85; H, 9.71; N, 8.08; MW, 125.13251. C₉H₁₇NO₂ calcd.: C, 63.13; H, 10.01; N, 8.18%; MW – NO₂, 125.13303.

Cyclohexylmercury chloride (0.8 mmol) and the lithium salt of nitrocyclohexane (4 mmol) were reacted in 60 ml of Me₂SO employing a 60 h irradiation period to afford 0.2 g of an oil. Quantitative GLC using diphenyl methane as an internal standard (molar response of product/standard = 0.89; 5% SE-30; 170°C) determined the yield of 1-cyclohexyl-1-nitrocyclohexane to be 84%. Attempts to scale up this reaction resulted in drastically reduced yields and complex product mixtures. Improved results were obtained with the potassium salt of nitrocyclohexane (from equivalent amounts of potassium *t*-butoxide and nitrocyclohexane in Me₂SO). Thus reaction of the mercurial (3 mmol) and the potassium nitronate (8 mmol) in 30 ml of Me₂SO employing a 100 h irradiation period afforded 1.2 g of crude oil which was purified by a Kugelrohr distillation at 90°C (0.4 Torr) to afford 0.5 g of white solid (38% yield). For analysis a sample was recrystallized from pentane to give material with m.p. 56–57°C. ¹H NMR (ppm, CDCl₃) δ 2.2–2.6 (3H, m), 0.85–2.0 (18H, m). IR (Nujol), 1538vs, 1345m cm⁻¹. Anal. Found: C, 67.97; H, 10.17. C₁₂H₂₁NO₂ calcd.: C, 68.21; H, 10.02%. MW (MS) found: 164.15568. C₁₂H₂₀ calcd.: 164.15591.

Reaction of 2-chloromercurypropane with the lithium salt of 2-nitropropane

The mercurial (7.0 mmol) and nitronate salt (10 mmol) in 40 ml of Me₂SO were irradiated for 17 h to afford 0.59 g (63% yield) of 2,3-dimethyl-2-nitrobutane [37]. ¹H NMR (ppm, CDCl₃) 2.36 (1H, heptet, *J* = 7 Hz), 1.51 (6H, s), 0.93 (6H, d, *J* = 7 Hz). IR (neat), 2980m, 1540s, 1460m, 1400m, 1390m,

1375m, 1350m, 1150w, 1080w, 855m cm^{-1} . MW (MS) found: 84.09375, calcd for C_6H_{12} (MW - HNO_2): 84.09389.

When the reaction was performed under the same conditions except for the introduction of 0.36 mmol of $(t\text{-Bu})_2\text{NO}^+$, a 17 h irradiation period afforded an 8% yield of 2,3-dimethyl-2-nitrobutane. The determination was made by quantitative PMR.

Reaction of allylmercury chloride with the lithium salt of 2-nitropropane

Allylmercury chloride (7 mmol) and the nitronate salt (21 mmol) were irradiated 24 h in 60 ml of Me_2SO . The usual workup afforded resinous material, which was discarded, and 0.46 g (50% yield) of 4-methyl-4-nitro-1-pentene. An analytical sample was obtained by preparative GLC (20% DEGS; 120°C). ^1H NMR (ppm, CDCl_3) δ 4.6–6.2 (3H, m), 2.68 (2H, d, $J = 6$ Hz), 1.62 (6H, s). IR (neat), 3100w, 3000m, 2960w, 1650w, 1550vs, 1475m, 1400m, 1380m, 1350s, 1000m, 930m, 860m cm^{-1} . Anal. Found: C, 55.56, H, 8.71; N, 10.65, MW, 83.0859. $\text{C}_6\text{H}_{11}\text{NO}_2$ calcd.: C, 55.80; H, 8.58; N, 10.84%, MW - NO_2 , 83.0861.

Reaction of trans-1-chloromercury-2-methoxycyclohexane with the lithium salt of 2-nitropropane

The mercurial (3.0 mmol) and the lithium salt of 2-nitropropane (5.0 mmol) in 50 ml of Me_2SO were irradiated for 47 h. The usual workup afforded 0.13 g of crude material found to contain 14.5% of 2-methoxy-1-(α -nitroisopropyl)-cyclohexane by quantitative ^1H NMR. The GLC chromatogram (20% Carbowax 6000; 150°C) exhibited numerous impurities as well as two components (8 : 1 ratio) exhibiting nearly identical GC-MS fragmentation patterns with $m/e = 155$ (loss of NO_2) as the highest mass. The earlier eluting and major isomer was isolated by preparative GLC (20% DEGS; 180°C). ^1H NMR (ppm, CDCl_3) δ 3.3 (3H, s), 2.8–3.15 (1H, m), 2.4–2.7 (1H, m), 1.5–2.3 (4H, m), 1.1–1.4 (4H, m), 1.6 (3H, s), 1.5 (3H, s). The 100 MHz PMR spectrum permitted the *trans* stereochemistry to be assigned: the complex multiplet corresponding to the α -methoxy proton (δ 1.5–2.3 ppm) was reduced to a 1 : 2 : 1 triplet ($J = 6$ Hz) by decoupling at δ 2.15 ppm. The coupling constant indicates two adjacent *trans* protons. IR (CHCl_3) 2940s, 2820s, 1540s, 1455m, 1380m, 1350m, 1115s, 1095s, 980m, 870m, 860m cm^{-1} . MW(MS), Found: 155.14371; $\text{C}_{10}\text{H}_{14}\text{O}$ (loss of NO_2) calcd.: 155.14359.

Reaction of 6-chloromercury-1-hexene with the lithium and potassium salts of 2-nitropropane

The mercurial (3.0 mmol) and the lithium salt of 2-nitropropane (5.0 mmol) in 30 ml of Me_2SO were irradiated for 48 h to afford 0.2 g of an oil determined by quantitative ^1H NMR to contain a 35% yield of 1-cyclopentyl-2-methyl-2-nitropropane. No olefinic protons were observed in the NMR spectrum. GLC and GC-MS analysis (20% DEGS; 140°C) revealed a 1.4% yield of 2-cyclohexyl-2-nitropropane, identified by comparison with the authentic compound prepared from cyclohexylmercury chloride. The cyclopentylcarbiny product (structure verified by independent synthesis from cyclopentylmethylmercury chloride) was purified for analysis by preparative GLC. ^1H NMR (ppm, CDCl_3)

δ 1.59 (6H, s), 0.68–2.18 (11H, m). IR (neat) 2960s, 2880m, 1540s, 1475w, 1410w, 1400m, 1378m, 1352m, 860w cm^{-1} . Anal. Found: C, 63.39; H, 10.16; N, 8.16. $\text{C}_9\text{H}_{17}\text{NO}_2$ calcd.: C, 63.13, H, 10.01; N, 8.18%.

The yield of 1-cyclopentyl-2-methyl-2-nitropropane was improved to 48% by the use of potassium nitronate (prepared by dissolving equivalent amounts of 2-nitropropane and potassium *t*-butoxide in Me_2SO).

Reaction of cyclopentylmethylmercury chloride with the lithium and potassium salts of 2-nitropropane

The mercurial (3.0 mmol) and lithium nitronate (5.0 mmol) in 30 ml Me_2SO were irradiated for 41 h to afford 0.2 g of crude product found to contain a 35% yield of 1-cyclopentyl-2-methyl-2-nitropropane. The product exhibited the same PMR, IR, and mass spectral features as the cyclopentyl product derived from 6-chloromercury-1-hexene. The yield of 1-cyclopentyl-2-methyl-2-nitropropane was improved to 47% by the use of potassium 2-nitropropanate.

Reaction of benzylmercury chloride with anions other than nitronates

Benzylmercury chloride (3.0 mmol) was added to a stirred solution containing potassium *t*-butoxide (3.6 mmol) and diethyl phosphite (4.0 mmol) in 30 ml of nitrogen-purged Me_2SO . Mercury metal slowly precipitated during the 39.5 h irradiation period. The usual workup afforded 0.23 g (84% yield) of bibenzyl.

The same reaction in the absence of light did not yield metallic mercury and bis[benzyl]mercury was isolated in 100% yield after 5 min and 51% yield after 39.5 h. When bis[benzyl]mercury and diethyl phosphite ion were irradiated in Me_2SO , mercury metal precipitated, but no bibenzyl was formed.

When the reaction was carried out with sunlamp irradiation in oxygen-saturated Me_2SO (760 Torr), metallic mercury appeared to precipitate at a rate comparable to the reaction under nitrogen. Workup afforded a complex mixture containing benzoic acid, benzaldehyde, benzyl alcohol, and a 1.7% yield of bibenzyl.

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