

Table I. Results Realized for the Conversion of Representative Olefins into Ethers by the Solvomercuration–Demercuration Procedure Utilizing Mercuric Acetate or Trifluoroacetate and Alcohols

Olefin	Hg(O ₂ CCX ₃) ₂ X	Ether, ROR' R	Yield of ethers, % ^{a-c} for R' =			
			Methoxy	Ethoxy	Isopropoxy	<i>t</i> -Butoxy
1-Hexene	H	2-Hexyl	90	98	91 (20)	27 ^d (480)
	F		100	100	100	100
3,3-Dimethyl-1-butene	H	Pinacolyl	83 ^e	72	12	4 (1400)
	F		100	100	99	85 ^f (1100)
Styrene	H	α -Phenethyl	97			90 (20)
	F					18 (1440)
Cyclohexene	H	Cyclohexyl	100	100	73 (90)	90
	F		100	100	98	90
Norbornene	H	<i>exo</i> -Norbornyl	89	60	15 (30)	1 (1200)
	F		100	100	95	90 (600)
2-Methyl-1-butene	H	<i>t</i> -Amyl	100	100	90	0 (1440)
	F		88	86	58 (1)	0
α -Methylstyrene	H	<i>t</i> -Cumyl	100			

^a Yield by glpc analysis. ^b Reaction time was 10 min unless specified otherwise in parentheses (minutes). ^c All new compounds gave satisfactory elementary analyses and nmr spectra. ^d The product contained 12% of *n*-hexyl *t*-butyl ether. ^e The product contained 2% of 3,3-dimethyl-1-butyl methyl ether. ^f Product contains both the Markovnikov and anti-Markovnikov ethers.

were allowed to proceed for approximately 10 min after the solutions had become homogeneous. Finally, the reactions with mercuric acetate and *t*-butyl alcohol were very slow and the yields of the desired ethers were low.

The use of mercuric trifluoroacetate provides both a fast rate and a high yield of essentially all of the ethers, including the *t*-butyl ether derivatives. Only in the case of 2-methyl-1-butene were we unsuccessful in preparing the *t*-butyl ether. Evidently the formation of the di-*t*-alkyl ether involves such high steric strain⁴ as to provide a major hurdle which the system fails to surmount. The results with mercuric acetate and trifluoroacetate are summarized in Table I.

Mercuric trifluoroacetate was readily prepared in molar quantities by the following simple procedure. One mole of mercuric oxide was dissolved in 300 ml of trifluoroacetic acid. Then 1 mol of trifluoroacetic anhydride was added at a rate sufficient to maintain a gentle reflux. The solvent was removed under vacuum⁵ and 418 g (98% yield) of mercuric trifluoroacetate, mp 164–168°, was obtained (mp 167–169° after two recrystallizations from trifluoroacetic acid⁶). In contrast to mercuric acetate, the salt is easily soluble at 25° in a wide variety of organic solvents such as dimethylformamide, dimethyl sulfoxide, acetone, ethyl acetate, tetrahydrofuran, ethyl ether, and benzene.⁷

Both the high reactivity of the reagent and its high solubility in the alcohols used as reaction media result in very fast reactions. With two exceptions the reactions are essentially complete in 10 min or less to provide excellent yields of the desired ethers. In the case of norbornene⁸ and 3,3-dimethyl-1-butene the initial product in *t*-butyl alcohol is not the *t*-butoxy derivative, but the corresponding trifluoroacetate. Reduction at this stage yields the ester or alcohol. However, on standing at room temperature, the initial products are converted into the *t*-butoxy derivatives and reduction then yields the desired *t*-butyl ethers. This is the reason

(4) E. J. Smutny and A. Bondi, *J. Phys. Chem.*, **65**, 546 (1961).

(5) It is perfectly satisfactory for use in subsequent preparations without further treatment.

(6) D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **33**, 1002 (1955), report mp 165–167°.

(7) This high solubility in inert solvents promises to make this salt highly useful for extending the scope of the solvomercuration–demercuration reaction.

(8) E. Tobler and D. J. Foster, *Helv. Chim. Acta*, **48**, 366 (1965).

for the relatively long reaction times utilized for these derivatives (Table I).

No rearrangements were observed. Even the labile olefin, 3,3-dimethyl-1-butene, was converted into pinacolyl methyl ether without change in the carbon skeleton. In almost all cases the reactions proceeded to give the Markovnikov product essentially exclusively. However, in the reaction of mercuric acetate with 3,3-dimethyl-1-butene and methanol the presence of 2% of the anti-Markovnikov methyl ether was observed in the product. In the related reaction of 1-hexene and *t*-butyl alcohol the product contained 12% of the anti-Markovnikov product, *n*-hexyl *t*-butyl ether. Similar results were observed with mercuric trifluoroacetate.

In conclusion, the present developments make available a new, highly convenient synthetic route for the conversion of olefins into the Markovnikov ethers. Even more exciting is the promise that solvomercuration–demercuration can be developed into a highly versatile, general approach for additions to the double bond in the Markovnikov direction without isomerizations or rearrangements. We are actively exploring this possibility.

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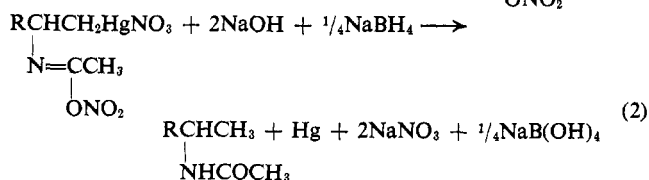
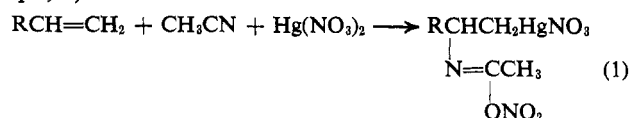
The Solvomercuration–Demercuration of Representative Olefins in the Presence of Acetonitrile. A Convenient Procedure for the Synthesis of Amines

Sir:

The solvomercuration–demercuration of representative olefins in the presence of water provides a convenient procedure for the Markovnikov hydration of the carbon–carbon double bond.¹ Similarly, the solvomercuration–demercuration of olefins in the presence of alcohols provides a highly convenient route

(1) H. C. Brown and P. J. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

to the corresponding ethers.² We now wish to report that the solvomercuration-demercuration of olefins in the presence of acetonitrile provides a convenient technique for the Markovnikov amination of carbon-carbon double bonds. Neither mercuric acetate nor mercuric trifluoroacetate was satisfactory in this reaction. Apparently these anions compete favorably with acetonitrile for the mercuric intermediate. However, mercuric nitrate^{3,4} proved highly satisfactory (eq 1, 2).



Previously, Wright and his coworkers had reported that cyclohexene could be converted to the corresponding β -mercuric amide by treating the olefin with mercuric nitrate in the presence of fuming nitric acid.³ However, Sokolov and Reutov have recently reported that anhydrous mercuric nitrate is satisfactory for this reaction.⁴ Wright and his coworkers isolated the intermediate by adding water and sodium chloride to the initial reaction mixture precipitating the β -acetaminocyclohexylmercuric chloride. They reported that they were unable to remove the mercury by reduction either with hydrazine or with sodium borohydride, apparently forming a bismercurial instead. However, demercuration with sodium amalgam was successful. Sokolov and Reutov made no attempt to reduce the intermediate.

As was pointed out earlier there are major disadvantages to a preparative procedure which requires the isolation and handling of a toxic organomercuric halide for subsequent reduction with sodium amalgam.¹ Accordingly, we undertook to ascertain whether these difficulties could be circumvented. Indeed, we observed that the reaction of olefins with acetonitrile proceeds rapidly at 25°, under the influence of anhydrous mercuric nitrate,⁴ without the necessity of the fuming nitric acid previously employed.³ With the nitric acid absent, we could apply the borohydride reduction directly to the initial adduct, without precipitating it as the chloride. The reduction proceeded cleanly,⁵ yielding the corresponding N-alkylacetamide.

It was convenient to isolate and characterize the products as the N-alkylacetamides. However, it is apparent that the hydrolysis of these intermediates should provide the corresponding amines. Consequently, this amidomercuration-demercuration technique provides a convenient procedure for the amination of double bonds.

(2) H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, **91**, 5646 (1969).

(3) D. Chow, J. H. Robson, and G. F. Wright, *Can. J. Chem.*, **43**, 312 (1965).

(4) V. I. Sokolov and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1) 222 (1968).

(5) The difference in our results with those previously reported³ is puzzling. Possibly the isolation of the mercurial as the chloride is responsible for the difficulty reported for the attempted reduction with sodium borohydride. However, we have been more interested in exploring the scope of this simple *in situ* procedure than in tracing down the cause of the difference in results.

The reaction appears to possess wide applicability. Thus, cyclohexene was readily converted into N-cyclohexylacetamide in a yield of 95%. The ready conversion of terminal olefins into the corresponding Markovnikov derivatives, without rearrangement, is especially promising. Thus 1-hexene was converted into N-2-hexylacetamide in a yield of 92%, and 3,3-dimethyl-1-butene was converted into N-pinacolylacetamide in a yield of 90%. Representative results are presented in Table I.

Table I. Results Realized for the Conversion of Representative Olefins into N-Alkylacetamides by the Solvomercuration-Demercuration Procedure Utilizing Mercuric Nitrate and Acetonitrile

Olefin	Acetamide	Yield, % ^{a,b}
1-Hexene	N-2-Hexyl	92
1-Decene	N-2-Decyl	86
3,3-Dimethyl-1-butene	N-Pinacolyl	90
Styrene	N- α -Phenethyl	50
Cyclopentene	N-Cyclopentyl	70
Cyclohexene	N-Cyclohexyl	95

^a Yield by glpc analysis. ^b The preparations were carried out by the procedure described in the text, but the scale was reduced to 5 mmol.

Preliminary attempts to utilize a tertiary olefin, 2-methyl-1-pentene, failed. However, we are hopeful that a modification of the procedure will make it possible to extend the synthesis to such tertiary olefins.

The simplicity and convenience of this amidomercuration-demercuration procedure are best exemplified by the following synthesis. In a stirred flask was placed 100 ml of acetonitrile and 64.8 g (0.200 mol) of mercuric nitrate. To this mixture, cooled externally, was added 16.8 g (0.200 mol) of 1-hexene, with stirring, at such a rate as to maintain the temperature below 30°. After stirring at room temperature for 1 hr, the mixture was cooled and reduction achieved by adding 200 ml of 3.0 M sodium hydroxide, followed by 200 ml of 0.5 M sodium borohydride in 3.0 M sodium hydroxide. After 1 hr, the water layer was saturated with sodium chloride and the product taken up with ethyl ether. Distillation yielded 20 g of N-2-hexylacetamide, bp 106–111° (1.8 mm), n_D^{20} 1.4431 (lit.⁶ bp 101–105° at 1.5 mm, n_D^{20} 1.4425), a yield of 70%.

The present synthesis is reminiscent of the Ritter amide synthesis.^{7,8} However, it avoids the strong acids required in that synthesis and promises to be relatively free of the kinds of rearrangements caused by strong acids, as indicated by the successful application of the synthesis to 3,3-dimethyl-1-butene (Table I).

This study was restricted to acetonitrile as a convenient route to the N-alkylacetamides for conversion to amines. Consequently, we did not apply the synthesis to other nitriles. However, Sokolov and Reutov have recently reported that cyclohexene can be made to react with other nitriles, such as benzonitrile, benzyl cyanide, and ethyl cyanoacetate, to form the cor-

(6) Y. L. Gol'dfarb, E. A. Krasnyanshaya, and B. P. Fabrichnyi, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1825 (1962).

(7) J. J. Ritter and P. P. Miniere, *J. Amer. Chem. Soc.*, **70**, 4045 (1948).

(8) See also T. L. Cairns, P. J. Graham, P. L. Barrick, and R. S. Schreiber, *J. Org. Chem.*, **17**, 751 (1952).

responding β -amidocyclohexylmercurials.⁴ Consequently, it would appear that the present combined procedure should be widely applicable to the conversion of olefins into the corresponding N-alkylamides.

The present results suggest that the solvomercuration-demercuration reaction may possess wide applicability for making reactions, previously achieved only with strong acids, possible under very mild reaction conditions. We continue to explore this possibility.

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The Structures of Cyclopentadienylmercuric Halides and Dicyclopentadienylmercury

Sir:

We wish to report the first evidence that unequivocally establishes the predominant molecular configuration in solution of the cyclopentadienylmercury compounds CpHgX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{and Cp}$).¹ It has been inferred earlier⁴ from certain similarities that exist between the infrared spectra of these compounds and cyclopentadiene itself, together with the fact that Cp_2Hg forms an adduct with maleic anhydride, that the Cp rings are σ -bonded to the mercury atom. On the other hand, nmr data published to date on these systems^{4b,5-8} cannot be unequivocally interpreted in terms of either σ -Cp, π -allyl, or π -Cp (ferrocenyl) bonding. The debate concerning the relative merits of such forms of bonding can now, however, be resolved by considering the new data communicated here.

We have studied the nmr spectra of the above-mentioned CpHgX compounds in various ethereal solvents over the temperature range -140 to 120° and will illustrate our findings with spectra acquired on $0.03 M$ CpHgCl in perdeuteriotetrahydrofuran ($\text{THF-}d_6$) between -113 and 22° (Figure 1). All the spectra between -113 and -7° are consistent with CpHgCl being a fluxional⁹ molecule with a nuclear configuration

(1) Cp_2Hg was prepared from CpTi and HgCl_2 .² CpHgX compounds ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) were prepared from Cp_2Hg and the corresponding HgX_2 .³ Each compound was analyzed for all the elements C, H, Hg, and halogen. Excellent agreement between the analytical values and theory was obtained in each instance.

(2) A. N. Nesmeyanov, R. B. Materikova, and N. S. Kochetkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1334 (1963).

(3) A. N. Nesmeyanov, G. G. Dvoryantseva, N. S. Kochetkova, R. B. Materikova, and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, 159, 847 (1964).

(4) (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 2, 32 (1956); (b) T. S. Piper and G. Wilkinson, *ibid.*, 3, 104 (1956); (c) H. P. Fritz, *Advan. Organometal. Chem.*, 1, 288 (1964).

(5) W. Strohmeier and R. M. Lemmon, *Z. Naturforsch.*, 14a, 109 (1959).

(6) (a) G. G. Dvoryantseva, K. F. Turchin, R. B. Materikova, Yu. N. Sheinker, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 166, 868 (1966); (b) A. N. Nesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedin, and N. S. Kochetkova, *Tetrahedron Lett.*, 3753 (1968); (c) *Chem. Commun.*, 105 (1969).

(7) E. Maslowsky and K. Nakamoto, *ibid.*, 257 (1968). In this paper, nmr spectra of Cp_2Hg in liquid SO_2 are discussed. Contrary to what is there concluded, we suspect that the observations are influenced by impurities and/or by a reaction of the solute with solvent. Similar conclusions have also recently been independently arrived at by other workers.^{6c}

(8) A. W. Kitching and B. F. Hegarty, *J. Organometal. Chem.*, 16, P39 (1969).

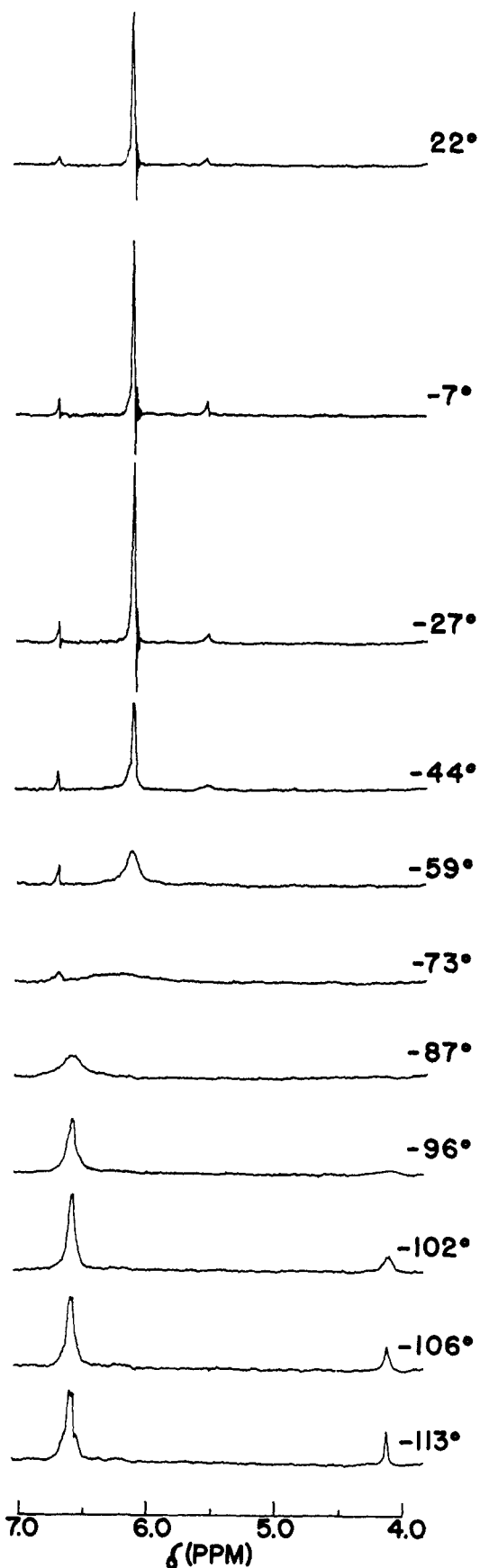


Figure 1. Temperature-dependent 100-MHz nmr spectra of $0.03 M$ CpHgCl in $\text{THF-}d_6$. The abscissa is calibrated in ppm downfield from internal tetramethylsilane.

(9) (a) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 2, 115 (1963); (b) F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).