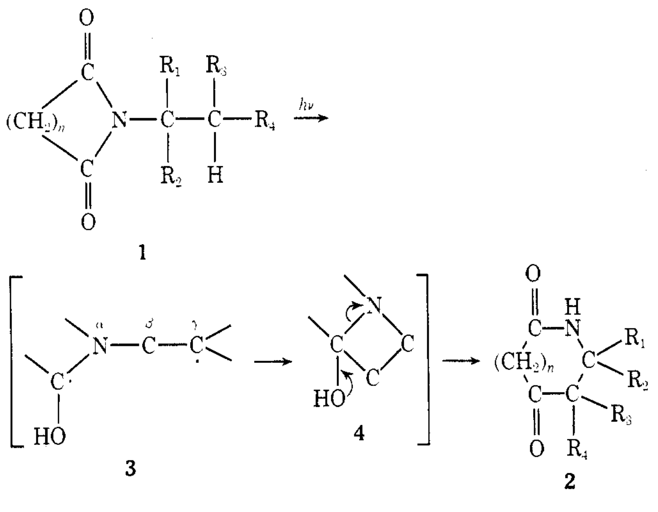
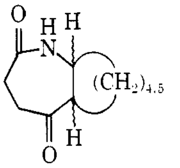
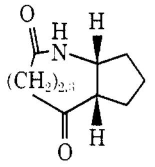
Scheme I



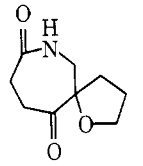
Variation of the N substituents (including heteroatoms and cyclic systems) may lead to a wide variety of products. For example, N-tetrayydrofurfurylsuccinimide gave the expected spiro azepinone **5** (mp 96–98°, 27%). In view of their multifunctionality, these photoproducts will further be used as synthetic intermediates. By activation due to introduction of heteroatoms into the side chain, extensive type II processes seem possible involving δ (or other) hydrogen abstraction.[9] The ring size of the imides (n) could be increased beyond three. In addition, the ring may carry substituents as desired. For example, 1-ethyl-4,4-dimethylglutarimide readily produced **6** (mp 173–174°, 27%).



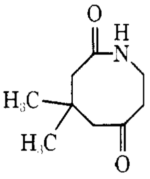
2h.i



2g.m



5



6

Piperylene quenches the formation of **2a** from **1a** indicative of a triplet intermediate. A Stern–Volmer plot in acetonitrile (up to 1 mM) is linear with a slope $k_q\tau$ = 670 M^{-1}.[12] As a plausible mechanism the biradical intermediate **3** is postulated (Scheme I) which is generally accepted in the type II processes of ketones as summarized by Wagner.[13] Such a biradical would either lead to elimination or undergo cyclization to form **4** followed by retrotransannular ring opening[14] giving rise to the ring-enlarged products **2**. Since these cyclic imides are starting materials which can be relatively easily prepared, this method may provide a novel versatile synthetic entry to otherwise rather unaccessible type of compounds including medium-sized and other various heterocyclic systems. Further synthetic scope and the mechanism of the photochemistry of the imide system are under investigation.

References and Notes

(1) Photochemistry of the Imide System. I.

(2) Photoinduced Reactions. XXIV Part XXIII: Y. Kanaoka, K. Sakai, R. Murata, and Y. Hatanaka, *Heterocycles*, **3**, 719 (1975).

(3) Y. Kanaoka and Y. Migita, *Tetrahedron Lett.*, 3693 (1974), and earlier papers cited therein.

(4) To our knowledge very few photochemical studies of aliphatic imides previously reported include vapor-phase photolysis of succinimide,[5] which is, however, of little interest from the synteetic point of view. Examination as well as the literature survey[5,6] of the uv spectra of aliphatic imides revealed that 2537-Å light of a low pressure mercury lamp is convenient for exciting the aliphatic imide carbonyl. Tests on the wavelength dependency of the formation of **2** indeed showed that only the range 230–270 nm is effective with the maximum around 240 nm in accord with the uv of **1a**.

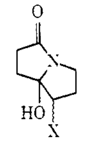
(5) G. Choudhary, A. M. Cameron, and R. A. Back, *J. Phys. Chem.*, **72**, 2289 (1968).

(6) O. H. Wheeler and O. Rosando in "The Chemistry of Amides," J. Zabicky, Ed., Interscience-Wiley, New York, N.Y., 1970, p 358.

(7) Formation of **2a** (degassed acetonitrile solution, 10 mM) was monitored by gas chromatography, and the quantum yield was determined by potassium ferrioxalate actinometry using 2537-Å light on a merry-go-round.

(8) Quantum yield of photocyclization of N-(o-tolyl)phthalimide is on the order of 0.01: Y. Kanaoka, K. Koyama and Y. Hatanaka, unpublished data.

(9) For example, photolysis of succinimides with ether and sulfide moieties in the alkyl chains gave i,[10] which are the products from δ-hydrogen abstraction. Maruyama and Kubo have independently reported some related results.[11]



i, X = OCH$_3$, SCH$_3$

(10) Y. Kanaoka, Y. Hatanaka, H. Nakai, Y. Sato, and T. Mizoguchi, in preparation.

(11) K. Maruyama and Y. Kubo, 33rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1975, Abstracts of Papers, III, p 1176.

(12) The quenching study was performed in degassed acetonitrile solution (10 mM) with 2537-Å light on a merry-go-round. From this, approximate order of τ was estimated to be 10^{-7}–10^{-8} sec.

(13) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

(14) This cyclization–ring opening has been proposed in the phthalimide system; cf. Y. Kanaoka, Y. Migita, K. Koyama, Y. Sato, H. Nakai, and T. Mizoguchi, *Tetrahedron Lett.*, 1193 (1973).

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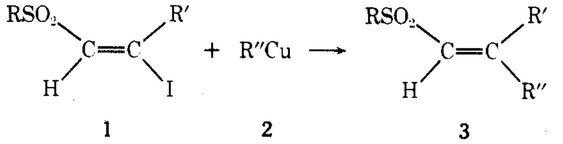
Organocopper Chemistry. The Coupling of (*E*)-2-Iodo-1-alkenyl Sulfones with Monocopper(I) Reagents

Summary: Monocopper(I) reagents (**2**) couple stereospecifically with (E)-2-iodo-1-alkenyl sulfones (**1**) to form β-alkylated 2-alkyl-1-alkenyl sulfones (**3**) with retained configuration.

Sir: The preparation and some of the reactions of 2-iodo- and 2-bromo-1-alkenyl sulfones has been the subject of several recent investigations.[1,2] The stereospecific organocopper coupling of vinyl iodides with organocopper reagents[3,4] has recently been reported as a method for the synthesis of alkenes of known configuration. This work prompts us to report on our preliminary results concerning the stereospecific coupling of a variety of (E)-2-iodo-1-alkenyl sulfones with a variety of monocopper(I) reagents.

Monoalkyl and monoarylcopper(I) reagents couple in good to excellent yields (Table I) with (E)-2-iodo-1-alkenyl sulfones and with complete retention of configuration. The presence of a single isomer is verified by a single set of proton absorptions in the ^{1}H NMR and the absence of absorptions for the isomeric structures. The assignment of configuration is based upon ^{1}H NMR chemical shift data and alternate synthesis.[5]



$$\underset{\mathbf{1}}{RSO_2CH{=}CR'I} + \underset{\mathbf{2}}{R''Cu} \longrightarrow \underset{\mathbf{3}}{RSO_2CH{=}CR'R''}$$

Table I[a]
2-Alkyl-1-alkenyl Sulfones[b]

3	R	R′	R″	% yield
a	CH_3CH_2	n-C_4H_9	CH_3	96
b	CH_3CH_2	n-C_4H_9	n-C_4H_9	93
c	CH_3CH_2	n-C_4H_9	C_6H_5	55
d	CH_3CH_2	C_6H_5	CH_3	80
e	CH_3CH_2	C_6H_5	n-C_4H_9	90
f	CH_3CH_2	t-C_4H_9	CH_3	47
g	p-$CH_3C_6H_4$	n-C_4H_9	CH_3	64
h	p-$CH_3C_6H_4$	n-C_4H_9	n-C_4H_9	99
i	C_6H_5	C_6H_5	C_6H_5	50

[a] All reactions are carried out in THF as solvent. [b] Characterized by ir, ^{1}H NMR, and elemental analysis.

Table II[a]
Yne Ene Sulfones[b]

3	R	R′	% yield	Temp, °C	Time, hr	Mp, °C
j	p-$CH_3C_6H_4$	H	75.5	RT	24	121–122.5
k	p-$CH_3C_6H_4$	CH_3	75.3	RT	48	103–104.5
l	p-$CH_3C_6H_4$	C_6H_5	58.3	130	23	81.0–82.5
m	p-$CH_3C_6H_4$	n-C_4H_9	71.9	RT	72	Oil[c]
n	p-$CH_3C_6H_4$	n-C_6H_{13}	59.7	RT	72	Oil[c]
o	C_6H_5	H	63.0	RT	24	72–74
p	C_6H_5	CH_3	62.3	RT	72	71–73
q	C_6H_5	C_6H_5	67.7	69	22	85.5–87.5
r	CH_3CH_2	CH_3	~50.0	RT	48	Oil[c]
s	CH_3CH_2	C_6H_5	76.3	100	19	76.5–77.5
t	CH_3	CH_3	53.0	RT	72	43–44
u	CH_3	C_6H_5	67.5	60	16	67.5–69.5

[a] In all examples R″ is $C_6H_5C{\equiv}C-$. [b] All compounds were purified by column chromatography; characterized by ir, ^{1}H NMR, and elemental analysis. [c] No boiling point was obtained.

Unlike other substitutions on vinyl halides, which usually require the use of lithium diaryl- or lithium dialkylcuprates, low temperatures (between −20 and −78°C), and long periods of time, substitutions involving (E)-2-iodo-1-alkenyl sulfones proceed rapidly, <30 min at 0°C being sufficient for completion. Also, under these reaction conditions, the presence of a complexing agent, e.g., diisopropyl sulfide, is not required.[5]

In contrast to the alkyl- and arylcopper species, the less reactive cuprous phenylacetylide[6] requires more vigorous reaction conditions to achieve coupling. Cuprous phenylacetylide in pyridine, at room temperature or on heating, reacts with the (E)-2-iodo-1-alkenyl sulfones to yield the coupled products with high stereospecificity and in fair to good yields for the examples studied, as shown in Table II.

The compounds in Table II were characterized in detail by ir, ^{1}H NMR, and elemental analysis. In all cases the couplings proceeded stereospecifically with retention of configuration to yield the (E)-yne ene sulfones. In the crude ^{1}H NMR, traces of the isomeric products were observed in some cases; however, the yields listed in Table II represent yields of the purified (E)-yne ene sulfones.

The assignment of stereochemistry is based upon ^{1}H NMR coupling constants and chemical shift arguments as well as supporting ir absorption data. An in depth description of the stereochemical arguments will be presented at a later date upon conclusion of another study which involves the preparation of the isomeric (Z)-yne ene sulfones. The following procedures are representative.

(Z)-1-Ethanesulfonyl-2-phenyl-1-hexene (3e). Into an oven-dried and nitrogen-flushed, 100-ml flask, equipped with a stoppled side arm, an adapter tube with stopcock connected to a mercury bubbler, and a magnetic stirring bar, was placed 2.44 g (12.52 mmol) of cuprous iodide and 60 ml of dry THF. This suspension was cooled to 0°, when 6.5 ml of 1.94 M n-butyllithium (12.44 mmol) in hexane was added. This was followed by 2.0 g (6.22 mmol) of (E)-1-ethanesulfonyl-2-iodo-2-phenylethylene in 30 ml of THF. After 10 min at 0°C, the reaction mixture was poured into a saturated NH_4Cl solution, extracted with ether, and dried over $MgSO_4$, and solvent was removed in vacuo to yield an oil. Short-path distillation at 140°C and 0.2 mm Hg afforded 1.20 g (90%) of (E)-1-ethanesulfonyl-2-phenyl-1-hexene.

(E)-1-Ethanesulfonyl-2,4-diphenylbut-1-en-3-yne (3s). Into a 200-ml, three-neck, round-bottom flask, fitted with a nitrogen inlet and outlet tube, reflux condenser, magnetic stirrer and stirring bar, oil bath, and paraffin oil bubbler, previously flame dried and purged with nitrogen, was placed 3.29 g (20 mmol) of cuprous phenylacetylide. Dry pyridine, 50 ml, was added to serve as solvent. Then 6.44 g (20 mmol) of (E)-2-iodo-1-ethanesulfonyl-2-phenylethene dissolved in 50 ml of dry pyridine was added. The mixture was heated to 100°C for 11 hr, then poured into 500 ml of H_2O, and extracted with four 200-ml portions of Et_2O. The other extracts were extracted successively with three 100-ml portions of H_2O, three 100-ml portions of 10% HCl, three 100-ml portions of H_2O, and one 100-ml portion of saturated aqueous NaCl. The ether extracts were dried over $MgSO_4$ and decolorized with activated carbon for 2 hr and vacuum filtered, and the ether was removed in vacuo to yield a solid material. The solid was purified by column chromatography on silica gel with benzene as eluent, then recrystallized from 95% EtOH to yield 4.52 g of material melting at 76.5–77.5°C for a 76.3% yield.

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