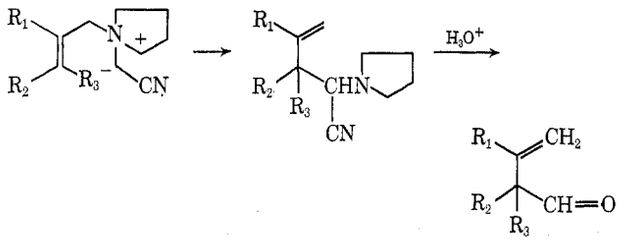
See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

The Synthesis of β,γ-Unsaturated Aldehydes by the [2,3]-Sigmatropic Rearrangement of Allylic Ammonium Ylides

Summary: The [2,3]-sigmatropic rearrangement of ylides derived from allylic *N*-cyanomethylpyrrolidinium salts followed by hydrolysis of the products affords β,γ-unsaturated aldehydes in >90% overall yields.

Sir: The utility of the [2,3]-sigmatropic rearrangements of allylic sulfonium ylides for the preparation of β,γ-unsaturated carbonyl compounds has been demonstrated in several elegant procedures.[1] We have found that analogous sequences based on tetraalkylammonium ylides[2] offer significant advantages in terms of flexibility and high overall yields. A generalized procedure is indicated in Scheme I. The ylide precursors are

SCHEME I

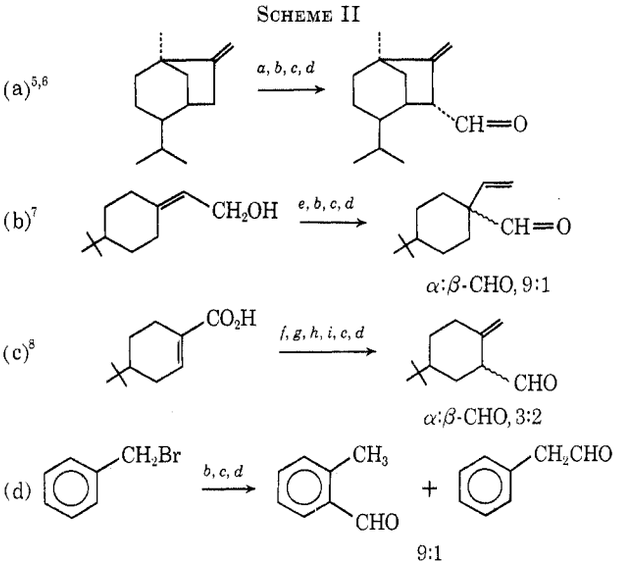


readily constructed either by alkylation of *N*-cyanomethylpyrrolidine (NCMP)[3] with allylic halides or from *N*-allylpyrrolidines and chloroacetonitrile. The alkylations are conveniently carried out in dimethyl sulfoxide (DMSO) and the ammonium salts are not normally isolated, but either tetrahydrofuran (THF) or liquid ammonia is added followed by potassium *tert*-butoxide. Ylide formation and concomitant rearrangement proceed slowly at −78° but rapidly at −33° in the latter solvent; somewhat higher temperatures are required in THF because of solubility problems.

The choice of a pyrrolidine derivative is optional, but was made so as to increase the nucleophilicity of the amine and to facilitate the removal of cyanide ion from the product.[4] The function of the nitrile group is to localize carbanion formation and, subsequently, to act as a leaving group to generate a carbonyl function in the final product. The properties of the nitrile group in such a role are probably difficult to duplicate.

The general utility of the procedure is indicated (Scheme II) by the array of substrates whose structural

SCHEME II



[a]−[i] Reagents: *a*, *N*-bromosuccinimide; *b*, NCMP–DMSO; *c*, KO-*t*-Bu–THF; *d*, aqueous oxalic acid–THF; *e*, PBr_3, pyridine, and ether; *f*, oxalyl chloride and pyridine; *g*, pyrrolidine; *h*, AlH_3; *i*, $ClCH_2CN$.

and functional diversity illustrate the flexibility of this approach. Isolated yields of aldehydes were consistently between 90 and 95% from allylic halides. Formation of α,β-unsaturated aldehydes (where this was possible) accounted for ~15% of the products and occurred, apparently, through equilibration of the intermediate imminium salts with their conjugate dieneamines, since the β,γ-unsaturated aldehydes themselves were stable to the hydrolytic conditions. Stereoselectivity was total in the bicyclooctene example a,[5,6] but diminished as the alternative stereochemical pathways became more equivocal. Undoubtedly this trend could be opposed by the introduction of bulkier substituents, especially onto the cyanomethyl moiety. Marginal improvements in stereoselectivity were obtained in example b,[7] at lower temperatures (85–90%). Example c,[8] which indicated the preferential

(1) (a) J. E. Baldwin and J. A. Walker, *Chem. Commun.*, 354 (1972); (b) E. Hunt and B. Lythgoe, *ibid.*, 757 (1972); (c) E. J. Corey and S. W. Walinsky, *J. Amer. Chem. Soc.*, **94**, 8932 (1972); (d) G. Andrews and D. A. Evans, *Tetrahedron Lett.*, 5121 (1972).

(2) (a) G. V. Kaiser, C. W. Ashbrook, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **93**, 2342 (1971); (b) R. W. Jemison and W. D. Ollis, *Chem. Commun.*, 294 (1969).

(3) A. Lespagnol, E. Cuingnet, and M. Debaert, *Bull. Soc. Chim. Fr.*, 383 (1960).

(4) P. Y. Sollenberger and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 4261 (1970); *cf.* ref 13.

(5) Correct analytical figures were obtained for all new compounds; spectra were consistent with structural assignments. Isomer ratios were determined by glpc and by nmr spectroscopy.

(6) The preparation of the methylene bicyclooctane will be reported elsewhere. Bromination gave a 3.5:1 mixture of secondary and primary bromides which, however, gave only the primary ammonium salt. The preparation of the aldehyde, semicarbazone mp 177–179°, serves as a useful model for the elaboration of prehelminthosporal and similar compounds; *cf.* F. Dorn and D. Arigoni, *Chem. Commun.*, 1342 (1972), and P. de Mayo, R. E. Williams, and Y. E. Spencer, *Can. J. Chem.*, **43**, 1357 (1965).

(7) The alcohol was prepared by AlH_3 reduction of ethyl 4-*tert*-butylcyclohexylideneacetate [H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966)]. Dr. D. A. Evans (*cf.* ref 1d) generously provided spectra and samples for direct comparison with the vinylcarbinols derived from our aldehyde products.

(8) 4-*tert*-Butyl-1-cyclohexenecarboxylic acid [L. Munday, *J. Chem. Soc.*, 1413 (1964)] was prepared by a modification of the method of F. Camps, J. Coll, and J. Pascual, *J. Org. Chem.*, **32**, 2563 (1967). The mixture of aldehydes was characterized by base-catalyzed isomerization to the α,β-unsaturated isomer, semicarbazone mp 204–207°.

formation of axial product, suggested a stereoelectronic requirement for the rearrangement.[9,10] Only in example d was a product arising from a [1,2] shift detected.[11]

We envisage extension of the above methodology by utilization of the metalated *N*-cyanoalkyl function as an acyl carbanion equivalent[12] and work is in progress; *e.g.*, example d simply carried out in DMSO-d_6 afforded α-[^{2}H]tolualdehyde [deuterium enrichment >95%; ν_{max} 2050, 1675 cm^{-1} (-C^{2}H=O)].[13]

Preparation of Pyrrolidinium Salts.—(a) Allylic bromide (10^{-3} mol) was added dropwise to a stirred solution of *N*-cyanomethylpyrrolidine (1.07×10^{-3} mol) in DMSO (3 ml) at ambient temperature under an atmosphere of nitrogen. Completion of salt formation (from 1.0 hr at 20° to 18 hr at 45°) was monitored by nmr spectroscopy. (b) Allylic amine (10^{-3} mol) in DMSO (3 ml) was treated with chloracetonitrile (1.01×10^{-3} mol) under a nitrogen atmosphere and the mixture stirred at 45° for 18 hr.

Ylide Formation and Rearrangement.—A solution of the salt (10^{-3} mol) in DMSO (3 ml) was diluted with dry THF (15 ml) cooled to −10° and treated with solid KO-*t*-Bu (1.25×10^{-3} mol). The reaction mixture was stirred for 3 hr, diluted with hexane (40 ml), washed with brine and water, and dried (Na_2SO_4). Removal of solvent gave rearranged amine.

Hydrolysis of α-Pyrrolidinonitriles.—The nitrile (10^{-3} mol) in THF (8 ml) was treated with a warm solution of oxalic acid (30% w:v, 8 ml); the two-phase mixture was heated under reflux for 0.25 hr, cooled, and extracted with hexane (40 ml). The hexane solution was washed with brine and water, dried (Na_2SO_4), and reduced to dryness to afford a mixture of aldehydes.

Acknowledgment.—J. V. T. gratefully acknowledges the award of an Australian Commonwealth Postgraduate Scholarship.

(9) The Claisen rearrangement of 4-*tert*-butyl-1-cyclohexenylmethyl vinyl ether affords only the axial product: Professor R. E. Ireland, personal communication. Presumably, the transition state for the Claisen rearrangement, with its higher activation energy, is structured more like product; *cf.* R. F. Church, R. E. Ireland, and J. A. Marshall, *J. Org. Chem.*, **27**, 1118 (1962).

(10) S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Commun.*, 1494 (1971).

(11) S. H. Pine, *Org. React.*, **18**, 403 (1970).

(12) (a) D. Seebach, *Angew. Chem, Int. Ed. Engl.*, **8**, 639 (1969); (b) G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, **93**, 5286 (1971).

(13) D. J. Bennett, G. W. Kirby, and V. A. Moss, *Chem. Commun.*, 218 (1967).

DEPARTMENT OF ORGANIC CHEMISTRY
UNIVERSITY OF ADELAIDE
ADELAIDE, SOUTH AUSTRALIA 5000
AUSTRALIA

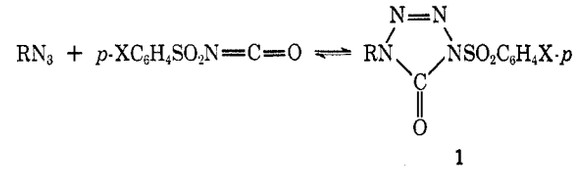
LEWIS N. MANDER*
JOHN V. TURNER

RECEIVED JUNE 8, 1973

1,3-Dipolar Cycloadditions of Alkyl Azides with Sulfonyl Isothiocyanates. A Synthetic Method for 1,2,3,4-Thiatriazolines

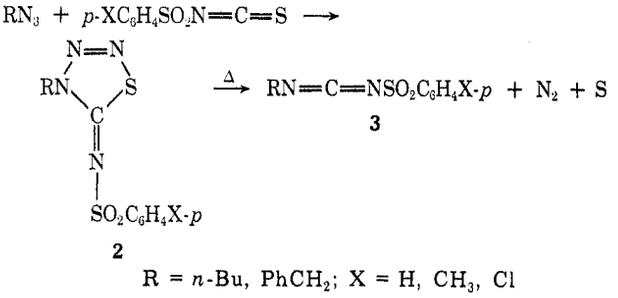
Summary: 4-Alkyl-5-sulfonylimino-Δ^2-1,2,3,4-thiatriazolines (**2**) are readily prepared from alkyl azides and sulfonyl isothiocyanates. Upon thermolysis, they give rise to a novel type of external stabilized 1,3 dipole (**6**) which undergoes cycloaddition with enamines and ynamines.

Sir: We recently reported[1] that alkyl azides and aryl azides reacted with sulfonyl isocyanates to give 1-alkyl- (or aryl-) 4-sulfonyl-Δ^2-tetrazolin-5-ones (**1**).



1

These compounds underwent cycloreversion on thermolysis. Extension of this study to isothiocyanates has led to the observation of a different behavior which we report briefly at this time. *n*-Butyl azide or benzyl azide reacted readily with equimolar amounts of sulfonyl isothiocyanates[2] at room temperature to yield 1:1 adducts in 50–75% yield which were characterized as 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (**2**).

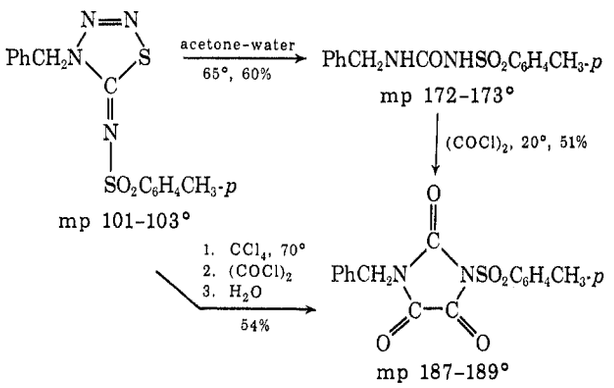


2

R = *n*-Bu, $PhCH_2$; X = H, CH_3, Cl

The structures **2** are consistent with analysis, nmr, ir (C=N at 1510–1535 cm^{-1}),[3] mass spectra (M·$^+$, M·$^+$ − N_2, M·$^+$ − N_2 − S), and degradation experiments. Thus, thermal decomposition of **2** at a moderate temperature (45–80°) furnished the carbodiimides **3** which exhibited a characteristic ir absorption band[4] at 2160 cm^{-1}. The latter were also trapped by typical reagents[5] as illustrated in Scheme I. That

SCHEME I



the isolated products **2** could not be formulated as the C=N adducts (*i.e.*, **5**) is clear from this chemical evidence. Indeed, the isomeric compounds **5**, prepared in 50–80% yield by sulfonation of 1-benzyl- (or butyl-)

(1) J.-M. Vandensavel, G. Smets, and G. L'abbé, *J. Org. Chem.*, **38**, 675 (1973).

(2) K. Hartke, *Arch. Pharm. (Weinheim)*, **299**, 174 (1966).

(3) J. Goerdeler and U. Krone, *Chem. Ber.*, **102**, 2273 (1969).

(4) R. Neidlein and E. Heukelbach, *Arch. Pharm. (Weinheim)*, **299**, 944 (1966); H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, **22**, 1565 (1966).

(5) H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953); F. Kurzer and K. D. Zadeh, *ibid.*, **67**, 107 (1967).