Tetrahedron Letters,Vol.25,No.32,pp 3461-3462,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

RETRODIENIC REACTIONS XVII [+] - A GENERAL ROUTE TO ALLENES GEM-DIACTIVATED BY ELECTROATTRACTING GROUPS [++] .

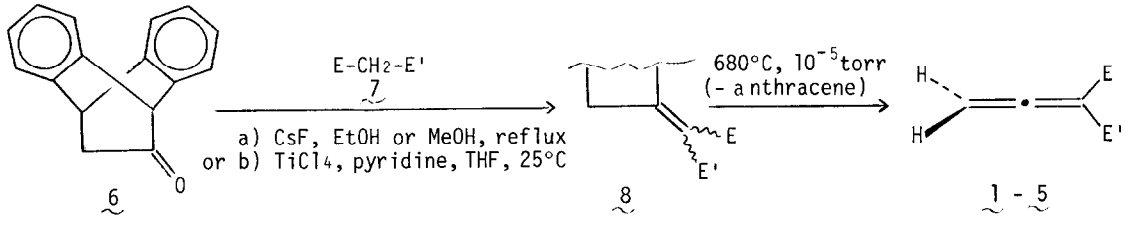
Abdelhak Hakiki, Zoubida Jabry, Jean-Louis Ripoll * and André Thuillier.
Laboratoire de Chimie des Composés Thioorganiques (Equipe de Recherche Associée au CNRS N° 391),
Université de Caen, 14032 Caen, France.

Abstract : Ketone 6 undergoes Knoevenagel condensation with five malonic derivatives 7, yielding, after flash-thermolysis, the gem-diactivated allenes 1-5 in 20-50 % yields.

The synthetic utility and ketene equivalence of allenes gem-disubstituted by electroattracting groups, in nucleophilic additions and ($2\pi + 2\pi$) or dipolar cycloadditions, has been demonstrated [1] ; on the other hand, very few reports are dealing with the synthesis of these compounds : 1,1-bis(ethoxycarbonyl) and (methoxycarbonyl)-3,3-diphenylpropadienes are stable and prepared by Wittig reaction [2] , 1,1-dicyanopropadiene 1 has been identified as its anthracene adduct in the thermolysis of dicyanomethylenecyclooctatriene [3] and 1-cyano-1-ethoxycarbonylpropadiene 2 characterized by low temperature nmr in the photolysis of a diazo-compound [1] . A more general method, involving dehydrohalogenation of α-chloroethylidenemalonates or cyanacetates with triethylamine, conducts to 2, 1-cyano-1-methoxycarbonylpropadiene 3 and 1,1-bis (ethoxycarbonyl)propadiene 4, however, these compounds cannot be isolated and are directly reacted with nucleophiles, imines or diazoalkanes [1].

As part of our work on functionalized allenes (see preceeding paper) we present here the flash-thermolytic retro-Diels-Alder synthesis and isolation of compounds 1 - 4 and of 1,1-bis(methoxycarbonyl)propadiene 5.

Selected conditions of reaction allow the Knoevenagel condensation of ketone 6 [4] with various malonic derivatives 7, leading to compounds 8 in about 80 % yield in each case. Cesium fluoride catalysis [5] (conditions a) is to be preferred for 7, E=CN, E'= CN, CO_2Et, CO_2Me; on the other hand, the use of $TiCl_4$-pyridine complex [6] (conditions b) allows best results in the case of 7, E= E'= CO_2Et or CO_2Me.

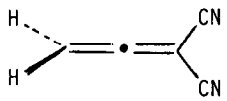
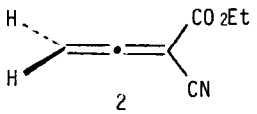
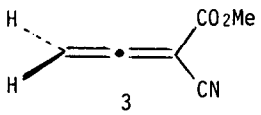
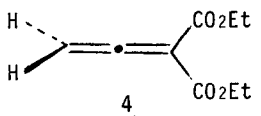
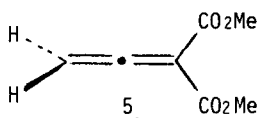


6 8 1 - 5

8 E, E'	mp (°C)	ir (cm^{-1})	
CN, CN	192	2230	
CN, CO_2Et	167	2220	1720
CN, CO_2Me	156	2220	1730
CO_2Et, CO_2Et	105		1720
CO_2Me, CO_2Me	115		1730

Flash thermolysis of compounds 8 leads to allenes 1, 3 and 5 obtained practically pure in 50 % yield ; partial loss of ethylene and decarboxylation, unavoidable in the case of allenes containing ethoxycarbonyl groups, give impure products and lower yield (20 %) for 2 and 4. Relative stabilities of allenes 1 - 5 follow the order 1 (polymerizing rapidly at 0°C) < 2 ~ 3 < 4 ~ 5 (stable several days at room temp.) ; ir and nmr spectra of allenes 1 - 5 are reported in the following table :

Table. ^{1}H nmr and ir spectra of allenes 1 - 5.

allene 1 - 5	^{1}H nmr (δ ppm, $CDCl_3$) at -50°C (1 - 3) or +25°C (4, 5)	ir (solid film, -196°C) C≡N	C=C=C	C=O
 1	6,02 (s)	2240	1965	
 2	5,95 (s, 2H) - 4,41 (q, 2H) - 1,38 (t, 3H) (in agreement with [1])	2220	1960	1720
 3	5,95 (s, 2H) - 3,92 (s, 3H)	2230	1960	1735
 4	5,56 (s, 2H) - 4,23 (q, 4H) - ~1,3 (shaded by impurities)		1965	1725
 5	5,55 (s, 2H) - 3,81 (s, 6H)		1965	1730

$M^{+\cdot}$ are in accord with given structures for allenes 1, 3 and 5. Further work on the subject, full experimental details and description of compounds 8 will be published later.

References

+ - Part XVI : A. Hakiki, J.L. Ripoll and A. Thuillier, preceeding paper.
++ - This work is part of the thesis of A. Hakiki.
1 - C. Guiborel, Thesis, Rennes (1981) ; R. Danion-Bougot, D. Danion and R. Carrié, to be published.
2 - R. Gompper and U. Wolf, *Ann.Chem.*, 1388 and 1406 (1979).
3 - T. Mukai and K. Tomisawa, *Sci.Rep.Tohoku Univ.*(I), 53, 81 (1970) [Chem.Abstr.74, 63756z].
4 - S. Wawzonek and J.V. Hallum, *J.Org.Chem.*, 18, 288 (1953).
5 - L. Rand, J.V. Swisher and C.J. Cronin, *J.Org.Chem.*, 27, 3505 (1962).
6 - W. Lehnert, *Tetrahedron*, 29, 635 (1973).

(Received in France 17 April 1984)