165. Cycloaddition of Carbodiimides and Triphenylketen-imine to Allenic Acids

Preliminary Communication

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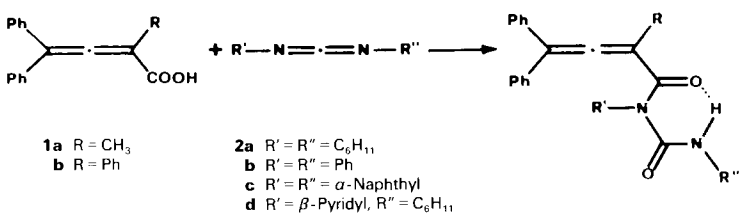
Allenic acids are found to add to dicyclohexylcarbodiimide affording, in the presence of secondary amines, the 1,3-oxazine-4-ones **5**. Under neutral conditions, they add to diaryl- or aryl(cyclohexyl)carbodiimides and triphenylketen-imine to give the corresponding tricyclo[5.2.2.0^{1,5}]undecatriene-3-ones **7**–**9** and **12**.

In the course of our studies on allenic-acid derivatives [1], the attempts to synthesise some allenic-acid amides applying the carbodiimide method led unexpectedly to the formation of addition products with the carbodiimides. Here, we report the structure elucidation of these products and also some chemical transformations conducted with them.

The allenic acids **1a** [2] and **1b**[1]), on treatment with dicyclohexylcarbodiimide (**2a**) in dry THF at room temperature, afforded the allenic acyl ureas **3a** (73%) and **3b** (87%), respectively *(Scheme 1)*. The latter compounds were found to be stable in solution under

Scheme 1



1a R = CH_3
b R = Ph

2a R' = R'' = C_6H_{11}
b R' = R'' = Ph
c R' = R'' = α-Naphthyl
d R' = β-Pyridyl, R'' = C_6H_{11}

3	R	R'	R''
a	CH_3	C_6H_{11}	C_6H_{11}
b	Ph	C_6H_{11}	C_6H_{11}
c[a])	CH_3	Ph	Ph
d[a])	Ph	Ph	Ph
e[a])	CH_3	α-Naphthyl	α-Naphthyl
f[a])	CH_3	β-Pyridyl	C_6H_{11}

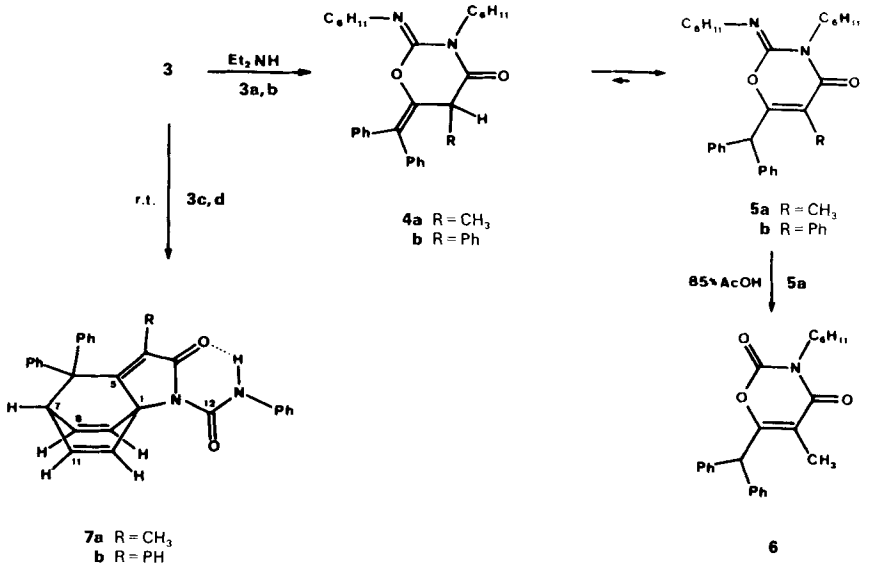
[a]) Intermediate compound.

neutral conditions. In the presence of Et_2NH, however, **3a** and **3b** cyclised to the 2-cyclohexylimino-1,3-oxazine-4-ones **4a**, **b** and **5a**, **b** *(Scheme 2)*. TLC-control revealed that the isomer **4** with an exocyclic double bond was formed first and then isomerised to the more stable **5** with endocyclic double bond. Prep. TLC separation of the reaction mixture at an early stage, *i.e.* at low conversion of **3**, afforded larger amounts of **4**. Under basic conditions, we obtained the same equilibrium mixture when starting from pure **4** or **5**, the latter isomer strongly predominating. Heating of **3a** also produced, in low yields, **4a** and **5a**, the former being predominant.

Structure **5a** was assigned on the basis of spectroscopic data and of the mild hydrolysis to the 1,3-oxazine-2,4-dione **6** (78%, m.p. 119.0–123.0°; *Scheme 2*). This hydrolysis

[1]) Acid **1b** was obtained from the ethyl ester [1] after alkaline hydrolysis, m.p. 175.0–180.0° (dec.).

Scheme 2



corroborates structure **5** and not an alternative uracil structure that would arise when the N-atom acts as donor in the cyclisation of **3a**.

The sequence **1**→**3**→**4**→**5**→**6** represents a new approach for preparing 6-alkyl-1,3-oxazine-2,4-diones *via* an O–C *Michael*-type [1,6]-cyclisation. In this reaction the acylurea portion of **3** is a *Michael* O-donor. To the best of our knowledge, only one precedent of an intramolecular *Michael* reaction with participation of acylureas has been described in the literature [3]. In this case, however, a five-membered ring was closed with the acylurea acting in a thermal reaction as a *Michael* N-donor.

Quite unexpectedly, neither the allene **3c** nor the 1,3-oxazine-4-one **4c** or **5c** were detected when **1a** was reacted with diphenylcarbodiimide (**2b**) at room temperature. In this case, the azatricyclo[5.2.2.$0^{1,5}$]undecatrienone **7a** was isolated in 85% yield *(Scheme 2)*. When using the allenic acid **1b** and diimide **2b**, a mixture of allenic acylurea **3d** (65%) and the tricyclic compound **7b** (25%) was obtained. This is the second observed case of an intramolecular *Diels-Alder* reaction proceeding under surprisingly mild conditions in-spite of the loss of aromaticity [4][2]).

Further, the α-naphthyl-substituted carbodiimide **2c**, when reacted with the allenic acid **1a** at r.t., afforded directly (*via* **3e**) the tetracyclic compound **8** (63%, m.p. 227.0–229.0°; *Scheme 3*).

In the case of the β-pyridyl-substituted carbodiimide **2d**, the 2,8-diazatricyclo[5.2.2.$0^{1,5}$]undecatrienone **9** was obtained from **1a** *via* **3f** under the same mild conditions (72%, m.p. 199.0–204.5°; *Scheme 3*). The latter case represents the first example of an intramolecular cycloaddition reaction with the participation of a pyridine ring as a heterodiene [5].

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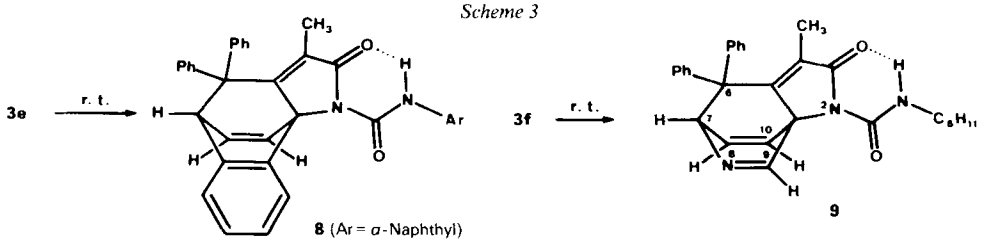
[2]) *Note Added in Proof.* – In the mean-time, some further examples of this reaction type have been published: L. Henn, G. Himbert, K. Diehl, M. Kaftory, *Chem. Ber.* **1986,** *119*, 1953; see also G. Himbert, D. Fink, *Tetrahedron Lett.* **1985,** *26*, 4363.

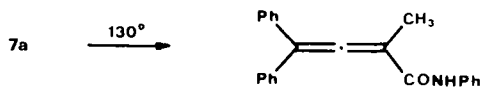
Scheme 3



The structures of the compounds **7a,b**, **8**, and **9** were established on the basis of spectral-data analyses [4]. Especially diagnostically useful were the ^{1}H-NMR signals of H–C(7), H–C(8)/H–C(11) and H–C(9)/H–C(10) and the ^{13}C-NMR signals of C(1), C(6) and C(7)[3]).

On heating in boiling xylene, the acylurea **7a**, not unexpectedly, did not rearrange into the tricyclo[6.2.1.0^{1,5}] system [4]. Instead, a loss of PhNCO and *retro-Diels-Alder* reaction afforded the allenic carboxanilide **10** (84%, m.p. 154.0–155.0°; *Scheme 4*) [6].

Scheme 4



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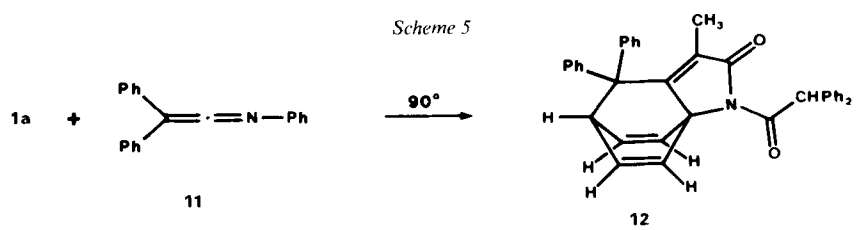
The triphenylketen-imine **11** was shown to react with the allenic acid **1a** only on heating, giving the azatricyclo[5.2.2.0^{1,5}]undecatrienone **12**.

Scheme 5



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[3]) **7a**: ^{1}H-NMR ($CDCl_3$): 10.75 (*s*, NH); 7.64 (*d*, *J* = 8.0 Hz, 2 *o*-H of Ph–N); 7.35 (*t*, *J* = 8.0 Hz, 2 *m*-H of Ph–N); 7.30–7.15 (*m*, 2 Ph–C(6)); 7.10 (*t*, *J* = 8.0 Hz, *p*-H of Ph–N); 6.52 (*dd*, *J* = 6.9, 1.3 Hz, H–C(9), H–C(10)); 6.31 (*t*, *J* = 6.9 Hz, H–C(8), H–C(11)); 4.57 (*t*, *J* = 7.0 Hz, H–C(7)); 1.67 (*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 174.4 (*s*, C(3)); 161.2 (*s*, C(12)); 149.3 (*s*, C(5)); 143.5 (*s*, *C*(arom.)–C(6)); 137.7 (*s*, *C*(arom.)–N); 134.2, 132.2 (2 *d*, C(8), C(9), C(10), C(11)); 129.1, 128.7, 128.2, 126.9, 124.0, 120.0 (6 *d*, CH(arom.)); 126.1 (*s*, C(4)); 72.9 (*s*, C(1)); 58.9 (*s*, C(6)); 52.6 (*d*, C(7)); 11.6 (*q*, CH_3).