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CONJUGATED HETEROCUMULENES. SYNTHESIS OF C=C-CONJUGATED CARBODIIMIDES BY A WITTIG-TYPE REACTION OF IMINOPHOSPHORANES WITH ISOCYANATES AND THEIR CYCLOADDITIONS[1)]

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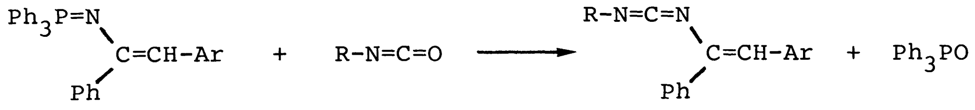
A Wittig-type reaction of N-(1,2-diarylethenyl)iminophosphoranes with isocyanates gave C=C-conjugated carbodiimides, which were utilized in the synthesis of heterocycles.

In recent years some synthetic applications of α,β-unsaturated heterocumulenes in the field of heterocyclic chemistry have been reported.[2)] Especially, cycloaddition reactions of such unsaturated heterocumulenic systems, e.g. ketenes, isocyanates, and ketenimines, provide an attractive entry to a variety of heterocycles. Moreover, an adjacent double bond in conjugation with the cumulated moiety introduces the interesting problem of site selectivity.[2,3)] In this context the chemistry of conjugated carbodiimides has received limited attention,[4)] only the preparation of vinylcarbodiimide and some reactions of acylcarbodiimides have been reported.[5)]

In this communication we wish to describe a useful method for the synthesis of C=C-conjugated carbodiimides by a Wittig-type reaction of iminophosphoranes with isocyanates.[6)] Also some chemical properties, such as inter- and intramolecular cycloaddition reactions will be reported.

N-(1,2-Diarylethenyl)iminophosphoranes[7)] (1, 2.0 mmol) were allowed to react with isocyanates (2, 2.2 mmol) in benzene (20 ml) at room temperature to give N-substituted N'-(1,2-diarylethenyl)carbodiimides 3 and triphenylphosphine oxide (4) in good yields. The carbodiimides could be isolated as a viscous oil (except for 3d, which is a solid, mp 103 °C) by means of short column chromatography (silica gel, benzene-hexane 1:4) though these compounds tend to deteriorate on standing in air.[8)] The spectral data (MS, IR, NMR) of 3 indicate that the carbodiimides obtained are monomeric.[9)]



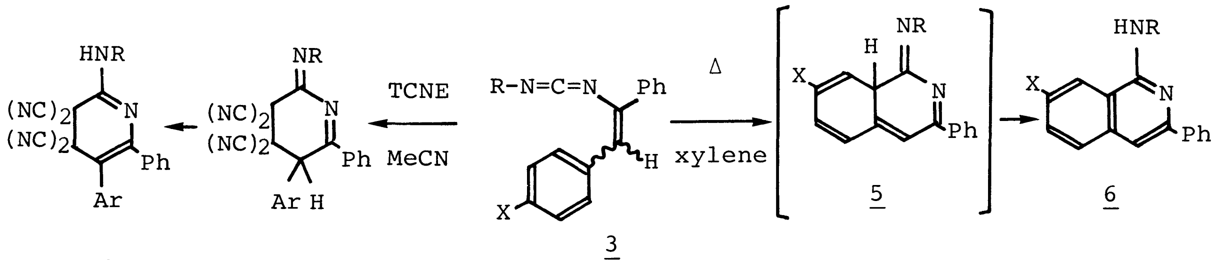
1 2 3 4

Table 1. Conjugated Carbodiimides 3

3[a)]	R	Ar	Yield/% 3	Yield/% 4	IR ν/cm^{-1} N=C=N	^{1}H-NMR δ C=CH
a	C_6H_5	Ph	80	86	2130	6.37
b	p-$CH_3C_6H_4$	Ph	97	99	2130	6.33
c	p-$CH_3OC_6H_4$	Ph	46	54	2130	6.36
d	p-ClC_6H_4	Ph	64	90	2130	6.33
e	c-C_6H_{11}	Ph	86	97	2140	6.12
f	CH_3	Ph	51	65	2130	6.15
g	C_6H_5	p-Tol	90	99	2130	6.33
h	p-$CH_3C_6H_4$	p-Tol	94	96	2120	6.27
i	p-$CH_3OC_6H_4$	p-Tol	75	83	2130	6.25
j	p-ClC_6H_4	p-Tol	70	72	2140	6.37
k	c-C_6H_{11}	p-Tol	94	98	2130	6.07
l	CH_3	p-Tol	70	95	2130	6.12

a) Reaction time: 2 h for R= aryl, 1-2 d for R= alkyl.

Intra and intermolecular cycloaddition reactions of 3 lead to the nitrogen-containing heterocycles (6, 7, and 8) as shown bellow. Upon heating in xylene, 3 underwent an electrocyclic reaction followed by 1,3-proton shift to give 1-(N-substituted)amino-3-phenylisoquinolines (6) (Table 2). Mass spectra of 6 showed molecular ion peaks and the IR spectra exhibited ν N-H absorption bands at 3420-3475 cm^{-1}. The ^{1}H-NMR spectra suggested the exocyclic N-H of 6; e.g. for 6e,k the N-H signal was observed as a doublet (J= 4 Hz), coupled with the methine hydrogen of the cyclohexyl group, and a methyl(R) signal of 6f,l was also split



a-f: X=H, g-l: X=CH$_3$

Table 2. Intra- and Intermolecular Cycloaddition Reactions of 3

Starting diimide	Product 6[a)] Yield/%[d)]	Product 6[a)] Mp θ_m/°C	Product 7 [8][b)] Yield/%[d)]	Product 7 [8][b)] Mp θ_m/°C	>CH-Ar δ ^{1}H-NMR	>CH-Ar δ ^{13}C-NMR
3a	50	104-105	25 [41]	162 [183]	4.18 s	28.5 d
b	40	112-115	71	198	4.76 s	28.4 d
c	53	152	43	202	4.87 s	28.4 d
d	86	153	54	190	4.96 s	28.6 d
e	57	116	54	200	5.18 s	29.0 d
f	40	105-106	69	187	4.54 s	30.5 d
g	73	118	62	135	5.18 s	28.5 d
h	41	112-114	60	163-166	4.78 s	28.5 d
i	73	107	60	163	4.82 s	28.4 d
j	12	150	c)	c)	c)	c)
k	67	120-123	0 [67]	[97-99]	------	------
l	64	70-71	67	174-176	4.38 s	29.7 d

a) Reaction time: 2 h for R= aryl, 7-10 h for R= alkyl.

b) Reaction conditions: 1-11 d at room temp. c) No reaction

d) Isolated total yield from 1, not optimized.

into a doublet. The reaction with a strongly electrophilic dienophile, TCNE, gave [4+2]cycloadducts, 7, which showed characteristic IR absorption peaks of ν C≡N at 2240 cm^{-1} and of ν C=N at 1545 cm^{-1}. The adducts 8, which were formed in cases of 3a and 3k by 1,5-H migration from 7,[10)] displayed a νN-H band at 3430-3250 cm^{-1} and a ν C≡N at 2230-2200 cm^{-1}. The MS, ^{1}H- and ^{13}C-NMR spectra also support the structures of 6, 7, and 8.

The preliminary results show that the carbodiimides 3 containing the conjugated C=C-moiety indeed can be used in the synthesis of heterocyclic systems.

Further work on these heterocyclic synthesis is in progress.

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8) In acetonitrile solution the carbodiimides 3 are relatively stable, but distillation at reduced pressure was unsuccessful.

9) Although we could not determine E- or Z-geometry with respect to the olefinic bond of 3, the obtained carbodiimides (3) seem to be single isomers because of their spectral features.

10) The adduct 8a was formed during purification operations. The adduct 8k was obtained exclusively even after the careful operation. Conversion of 7 into 8 by the action of a base (Et_3N) or an acid (silica gel) was unsuccessful.

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