

A New Synthesis of 1,2-Bisylidenecyclobutanes and their Application to the Construction of Polycyclic Ring Systems *via* Sequential Diels–Alder Reactions

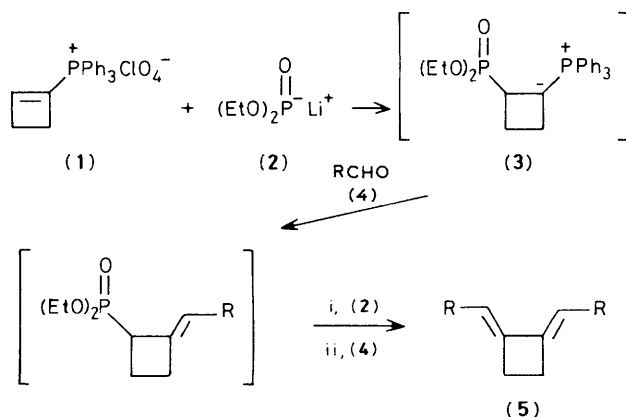
Toru Minami,* Yuki Taniguchi, and Ichiro Hirao

Department of Industrial Chemistry, Kyushu Institute of Technology, Sensuicho, Tobata, Kitakyushu 804, Japan

1,2-Bisarylidenecyclobutanes, conveniently synthesized from the (cyclobut-1-enyl)triphenylphosphonium salt, diethyl lithiophosphonate, and aromatic aldehydes, readily undergo sequential Diels–Alder reactions with dienophiles to give good yields of polycyclic compounds.

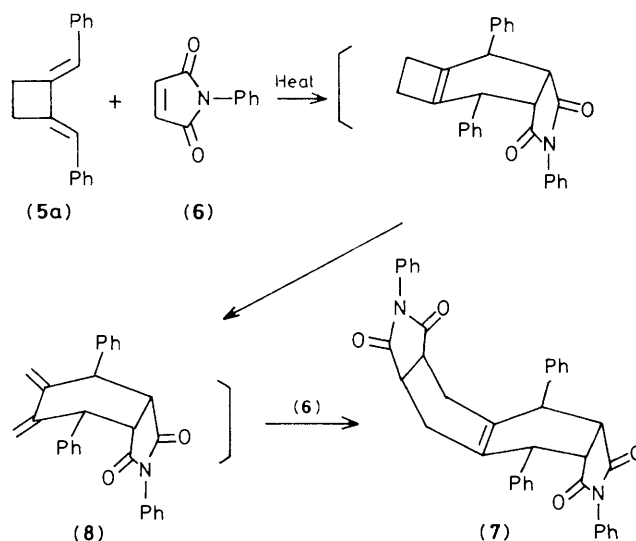
We have recently reported the synthesis of the (cyclobut-1-enyl)triphenylphosphonium salt (1) and its use for the production of cyclobutanes bearing extensive functionality, which are not easily accessible.¹ Although the preparation of 1,2-bismethylenecyclobutane and its synthetic applications have been well studied,² to the best of our knowledge convenient methods for the synthesis of 1,2-bisylidenecyclobutanes have not been reported. We now describe a simple method for the preparation of 1,2-bisylidenecyclobutanes and their application to the construction of polycyclic ring systems *via* sequential Diels–Alder reactions.

The ylide (3), generated *in situ* from the phosphonium salt (1) (5 mmol) and diethyl lithiophosphonate (2) (10 mmol) in



Scheme 1 a; R = Ph
b; R = CH=CHPh

tetrahydrofuran (THF)–dimethylformamide (DMF) (30 ml; 5:1), reacted with benzaldehyde (4a) (10.5 mmol) at room temperature for 24 h to give the *E,E*-bis(benzylidene)cyclobutane (5a)[†] (70%), m.p. 140 °C. Treatment of



Scheme 2

[†] N.m.r. data (CDCl₃): (5a), ¹H δ 3.15 (s, 4H, CH₂), 6.64 (s, 2H, =CH), and 7.31 (br. s, 10H, Ph); ¹³C, δ 30.81, 117.57, 126.66, 127.85, 128.60, 137.52, and 143.80; (5b), ¹H δ 2.83 (s, 4H, CH₂), 6.20–6.90 (m, 6H, =CH), and 7.05–7.55 (m, 10H, Ph); ¹³C, δ 26.29, 119.51, 125.45, 126.37, 127.40, 128.65, 131.80, 137.80, and 144.77.

(3) with cinnamaldehyde (4b) similarly led to the bis-(cinnamylidene)cyclobutane (5b)[†] (43%), m.p. 167–169 °C.

Reaction of the diene (5a) with *N*-phenylmaleimide (6a) in toluene at 150 °C for 30 h in a sealed tube afforded exclusively the bis-imide (7)[‡] (74%), m.p. 160–162 °C; ¹H n.m.r. (CDCl₃) δ 2.47 (br. s, 4H), 3.1–4.2 (m, 6H), 5.95–6.25 (dd, *J* 2.65 and 6.05 Hz, 2H, Ph), and 6.9–7.7 (m, 18H, Ph); ¹³C n.m.r. (CDCl₃) δ 29.89, 40.47, 43.67, 45.27, 126.20, 127.80, 128.37, 128.65, 129.40, 129.97, 132.26, 137.57, 174.44, and 178.55.

As shown in Scheme 2, the formation of (7) can be explained by sequential Diels–Alder reactions of (5a) with (6). In contrast, similar reactions of (5a) with dimethyl or diethyl maleate and diethyl fumarate afforded mixtures of the *syn*- and *anti*-1:2 adducts (*anti*:*syn* respectively 4:1, 7:3, and 1:1 from ¹³C n.m.r.) in 72, 45, and 83% yields, respectively. The reaction of (5a) with dimethyl acetylenedicarboxylate gave

only the dehydrogenated 1:2 adduct tetramethyl 1,4-diphenylnaphthalene-2,3,6,7-tetracarboxylate (45%).[§]

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[‡] Although we cannot exclude the stereoisomeric *syn*-form, we assign the product the *anti*-structure (7) since significant steric repulsion between the *N*-phenylimide ring in the initially formed 1:1 Diels–Alder adduct (8) and a second molecule of (6) would hinder the subsequent Diels–Alder reaction of (8) with (6) from the *syn*-direction.

[§] M.p. 61 °C; ν_{\max} , 1730 cm⁻¹; ¹H n.m.r. (CDCl₃) δ 3.51 (s, 6H, Me), 3.84 (s, 6H, Me), 7.0–7.60 (m, 10H, Ph), and 8.06 (s, 2H, naphthyl); ¹³C n.m.r. (CDCl₃) δ 52.41, 52.81, 128.43, 128.83, 129.11, 129.91, 131.34, 133.0, 136.26, 139.69, 167.52, and 168.04.