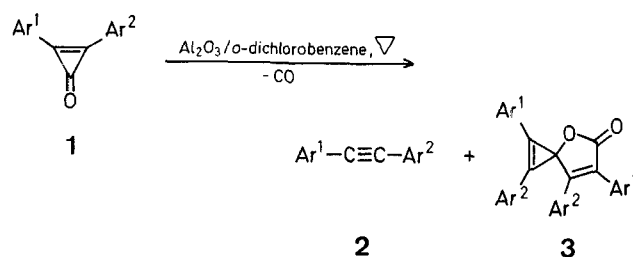


Preparation of Diarylacetylenes via Cyclopropanones

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The photochemical and thermal decarbonylation of cyclopropanones has often been reported as an incidental reaction of this species¹. Only a single detailed study of the thermal reaction as a preparative procedure has been described, however, and this only for diphenylcyclopropanone². We wish to report a general



	Ar ¹	Ar ²		Ar ¹	Ar ²
a			g		
b			h		
c			i		
d			j		
e			k		
f			l		

Table 1. Diarylcyclopropenones (**1**) Prepared and Used for the Synthesis of Diarylacetylenes (**2**) (Yields: 90–100%)

1	m.p. [°C] (solvent)	Molecular formula ^a or reference
a	120° (ethanol/water)	Ref. ⁴
b	122–123° (benzene/cyclohexane)	C ₁₆ H ₁₂ O ₂ (236.3)
c	125° (cyclohexane)	C ₁₇ H ₁₄ O (234.3)
d	121–123° (benzene/cyclohexane)	C ₁₇ H ₁₄ O ₃ (266.3)
e	95° (methanol/water)	C ₁₇ H ₁₄ O ₃ (266.3)
f	130–131° (methanol)	C ₂₀ H ₁₄ O ₂ (286.3) ^b
g	180° (methanol/water)	Ref. ⁶
h	195° (methanol)	Ref. ⁷
i	162° (ethanol/water)	C ₂₅ H ₁₈ O ₃ (366.4)
j	> 300° (1,4-dioxan)	C ₃₁ H ₁₈ O (406.5)
k	180° (2-propanol/water)	C ₁₉ H ₁₈ O ₅ (326.3)
l	179° (ethyl acetate)	Ref. ⁸

^a The microanalyses (except for **1f**) were in satisfactory agreement with the calculated values: C, ± 0.3 ; H, ± 0.3 .

^b Although good analytical data could not be obtained for this sample, the corresponding acetylene was obtained in good yield.

Table 2. Diarylacetylenes (**2**) Prepared from Diarylcyclopropenones (**1**)

2	Reaction time [h]	Yield [%] of crude ^a product	m.p. [°C] of recrystallized product (solvent)	Molecular formula ^b or reference
a	4		60° (cyclohexane)	
b	4	91	57–58° (methanol)	Ref. ⁹
c	4	89	86–87° (methanol/ water)	C ₁₆ H ₁₄ (206.3)
d	4	90	44° (methanol/ water)	C ₁₆ H ₁₄ O ₂ (222.3)
e	4	92	46° (ligroin)	C ₁₆ H ₁₄ O ₂ (222.3)
f	4	91	75–76° (methanol)	C ₁₉ H ₁₄ O (258.3)
g	3	94	144–146° (methanol)	C ₁₆ H ₁₄ O ₂ (222.3)
h	7	95	130–131° (cyclohexane)	Ref. ¹⁰
i	3	87	180° (benzene/ cyclohexane)	C ₂₄ H ₁₈ O ₂ (338.4)
j	4	94	> 315° (1,4-dioxan)	Ref. ¹¹
k	4	93	158–159° (ethanol)	C ₁₈ H ₁₈ O ₄ (298.3)
l^c	2.5	79	177° (acetonitrile)	Ref. ¹²

^a Crude products were > 90% pure according to ¹H-N.M.R. analysis.

^b The microanalyses were in satisfactory agreement with the calculated values: C, ± 0.3 ; H, ± 0.3 .

^c Cyclopropenone precursor prepared according to Ref.⁸.

procedure for the high-yield preparation of a wide variety of diarylacetylenes (**2**) from the corresponding cyclopropenones (**1**) that avoids the formation of the spiro-dimer (**3**) which often accompanies acetylene formation^{2,3}.

In a typical procedure, an *o*-dichlorobenzene solution of an appropriate diarylcyclopropenone (**1**) containing an equal weight of alumina pellets is refluxed until decarbonylation is complete and then stripped to dryness. The residue is recrystallized from a suitable solvent to furnish the corresponding pure diarylacetylene (**2**).

Erratic results were encountered with decane, trichlorobenzene, dodecane, or *o*-dichlorobenzene (without alumina) as solvents. The resulting acetylenes often showing carbonyl-containing contaminants.

In summary, decarbonylation of diarylcyclopropenones in the presence of alumina offers a convenient, versatile method for the preparation of diarylacetylenes and, in fact, is one of the few available methods for the preparation of unsymmetrical diarylacetylenes.

The cyclopropenones **1** were prepared by variations of the following general procedures. Bis[3-nitrophenyl]-cyclopropenone (**1l**) was prepared by the method described in Ref.⁸. Contact of the skin with diarylcyclopropenones should be strictly avoided¹³.

Symmetrical Cyclopropenones; General Procedure:

A suspension of anhydrous aluminum chloride in 1,2-dichloroethane (5 wt%) is stirred with an equimolar amount of tetrachlorocyclopropene. The resulting suspension is cooled to a suitable temperature (–30°C for reactive arenes such as 2-methoxynaphthalene, room temperature for benzene) and treated with the desired aromatic compound (2 molar equivalents). The reaction mixture is slowly heated until reaction is complete (disappearance of the aromatic substrate as determined by G.L.C.). A thorough water washing converts the resulting chlorodiarylcyclopropenium salts to the corresponding cyclopropenones in nearly quantitative yield.

Unsymmetrical Cyclopropenones; General Procedure:

The previous procedure is followed, but with 1 equiv of each aromatic substrate added separately, the least nucleophilic first. Yields are 90–100% for all cyclopropenones.

Diarylacetylenes (**2**); General Procedure:

A 20% solution of a cyclopropenone (**1**) in *o*-dichlorobenzene is stirred with an equal weight of alumina pellets (amount not optimized) and refluxed until an I.R. spectrum of the solution shows disappearance of the cyclopropenone carbonyl (at $\nu = 1800$ – 1850 cm^{–1}). Evaporation of the solvent furnishes product in good purity (>90% yield). The product is recrystallized from an appropriate solvent.

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