A Useful Method for Storage and Regeneration of Unstable 1,2-Diarylcyclopropenes

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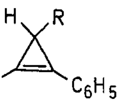
In the course of our studies of arylcyclopropenes[3] moderate quantities of 1,2-diphenyl-(**1**)[4] and 1,2-diphenyl-3-methylcyclopropene (**2**) were repeatedly required. Previously unknown **2** has been prepared in 96% yield from the reaction of methylmagnesium iodide with diphenylcyclopropenyl fluoroborate in diethyl ether at −78° [5].

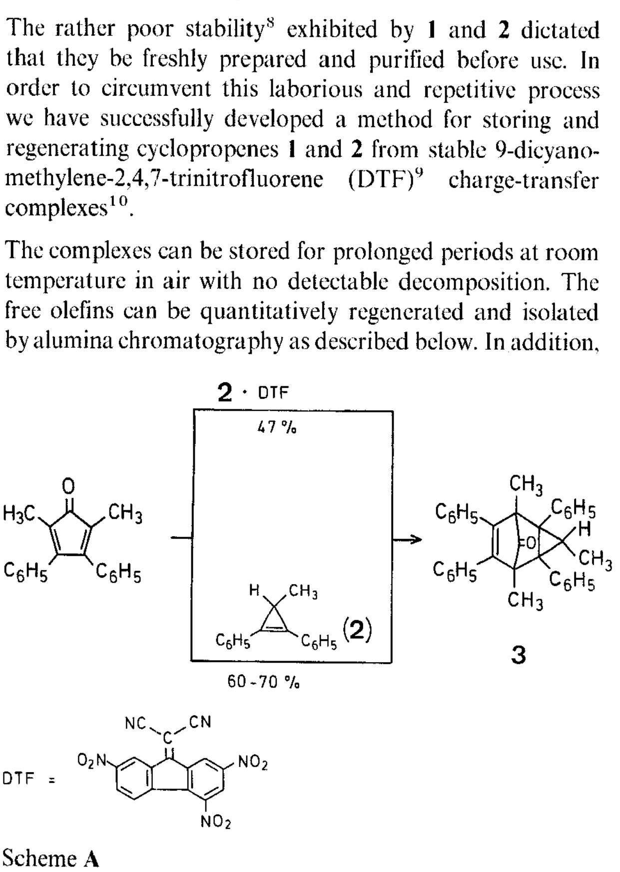


1 R = H
2 R = CH3

On standing in air (10–20 h) a purified sample of **1** turns yellow and can be shown[5] to contain moderate amounts of 1,2-diphenyl-2-propen-1-one[6]. After standing in air for only 2–3 h, a purified sample of **2** is found[5] to contain 2–5% of 1,2-diphenyl-2-buten-1-one[7] in addition to other unidentified oxidation products.

The rather poor stability[8] exhibited by **1** and **2** dictated that they be freshly prepared and purified before use. In order to circumvent this laborious and repetitive process we have successfully developed a method for storing and regenerating cyclopropenes **1** and **2** from stable 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF)[9] charge-transfer complexes[10].

The complexes can be stored for prolonged periods at room temperature in air with no detectable decomposition. The free olefins can be quantitatively regenerated and isolated by alumina chromatography as described below. In addition, the charge-transfer complexes can be used in certain reactions as an *in situ* source of the cyclopropene (Scheme **A**). The yields for this method are comparable to those obtained when free olefin is used.



Scheme **A**

Thus, a single large scale preparation and purification of the diarylcyclopropene with the subsequent preparation of the DTF charge-transfer complex affords a shelf-stable, readily transformable cyclopropene source. It should also be noted that the product mixture isolated after cyclopropene preparation can be treated with DTF to form a crude mixture of charge-transfer complexes. Decomposition on alumina regenerates the original mixture which can be further purified to give pure cyclopropene.

A thorough discussion of the U.V.-visible spectral data for these and other charge-transfer complexes will be presented elsewhere.

Preparation of Charge-Transfer Complexes:

A sample of purified olefin (**1** or **2**, 2–3 mmol) in dichloromethane (5 ml) was added to an equimolar amount of 9-dicyanomethylene-2,4,7-trinitrofluorene in dichloromethane (10 ml). Concentration of the resulting deep green solution on a rotory evaporator, followed by recrystallization of the greenish black solids from dichloromethane gave analytical samples of the 1:1 charge-transfer complexes.

1·DTF Complex: m.p. 175–176°.

$C_{31}H_{17}N_5O_6$	calc.	C 67.03	H 3.08	N 12.61
(555.52)	found	66.88	3.11	12.54

U.V.-Visible (CH_2Cl_2): $\lambda_{max} = 587$ nm.

2·DTF Complex: m.p. 169.5–170.0°.

$C_{32}H_{19}N_5O_6$	calc.	C 67.49	H 3.36	N 12.30
(569.55)	found	67.35	3.42	12.30

U.V.-Visible (CH_2Cl_2): $\lambda_{max} = 585$ nm.

Regeneration of Olefins:

A portion of alumina (2.0 g, Act. II, Matheson, Coleman, and Bell) was added to a solution of charge-transfer complex (0.05 mol) in dichloromethane (5 ml). The slurry was then warmed (30–40°) until a purple color resulted (2–3 min). The solvent was removed on a rotory evaporator and the solid placed on a column (∅ = 1.0 cm) of alumina (5 g). The column was then eluted with pentane (150 ml). Concentration of the entire fraction followed by ultraviolet spectral analysis of the material present indicated quantitative recovery of olefins **1** or **2** (based on the amount of 1:1 complex used).

Preparation of 1,3,5-Trimethyl-2,4,6,7-tetraphenyltricyclo-[3.2.1.0^{2,4}]-oct-6-en-8-one (3):

A solution of **2**·DTF charge-transfer complex (165 mg, 0.3 mmol) and the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone[11] (78 mg, 0.15 mmol) in chloroform (8 ml) was heated to reflux for 48 h under nitrogen. The resulting solution was concentrated on a rotory evaporator and the residue was chromatographed on a thick layer plate (10 cm × 20 cm × 2.0 mm) of silica gel (Merck HF-254) which was eluted with chloroform/pentane (1:4). Extraction of the material in the leading band with chloroform gave the desired product **3**; yield: 65 mg (47%); m.p. 205–206.5°. I.R. ($CHCl_3$): $\nu = 1760$ cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$): $\delta = 7.50$–7.00 (m, 20H$_{arom}$), 1.79 (q, 1H, $J = 5.9$ Hz), 1.12 (d, 3H, $J = 6$ Hz), 0.90 ppm (s, 6H).

Mass spectrum (70 eV): *exact mass* 466.2321 (*calc.* 466.2296).

When the reaction was repeated with the substitution of pure olefin for the charge-transfer complex 60–70% yields of **3** were obtained. The stereochemistry of adduct **3** is currently under investigation.

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