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Formation of 2-Substituted 1,3-Diphenylindenes by an *N*-Bromosuccinimide Prompted Dehydrocyclization of 2-Substituted 1,3,3-Triphenyl-1-propenes

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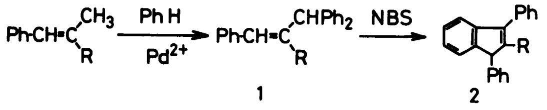
Synopsis. The reactions of a series of 2-substituted 1,3,3-triphenyl-1-propenes with *N*-bromosuccinimide (NBS) afforded the corresponding 2-substituted 1,3-diphenylindenes in moderate yields. A reaction mechanism involving a novel free-radical intramolecular ring-closure reaction is suggested.

N-Bromosuccinimide (NBS) has been extensively used both in the bromination of the allylic and benzylic positions and in the oxidation of many classes of organic compounds.[1] This article details an NBS-prompted conversion of a series of 2-substituted 1,3,3,-triphenyl-1-propene derivatives (**1**) to the 2-substituted 1,3-diphenylindenes (**2**) by means of a novel free-radical intramolecular ring-closure reaction. The starting 2-substituted 1,3,3-triphenyl-1-propenes (**1**) were readily obtainable by the phenylation of the corresponding 2-substituted 1-phenyl-1-propenes using palladium(II) salts as previously reported.[2]

The reactions of **1** with NBS in the presence of benzoyl peroxide unexpectedly gave 2-substituted 1,3-diphenylindenes(**2**); no corresponding benzylic bromination product was detected. The results are shown in Table 1. Thus, ethyl (*E*)-α-(diphenylmethyl)cinnamate ((*E*)-**1a**) reacted with NBS in refluxing benzene or carbon tetrachloride to give 2-ethoxycarbonyl-1,3-diphenylindene (**2a**) as the sole crystalline product in 66—69% yields (Runs 1 and 2). Similar reactions of (*E*)-**1a** by the use of *N*-bromocaprolactam or *N*-bromoacetamide also yielded **2a**, though the yields were somewhat unsatisfactory. In these reactions some of the starting (*E*)-**1a** was recovered together with its isomer ((*Z*)-**1a**). The (*Z*)-isomer ((*Z*)-**1a**) also underwent a similar reaction with NBS to afford **2a** in 63% yield (Run 3). In the same manner, α-(diphenylmethyl)cinnamic acid (**1b**), α-(diphenylmethyl)chalcone (**1c**), 1,2,3,3-tetraphenyl-1-propene (**1d**) and 2-(*p*-methoxyphenyl)-1,3,3-triphenyl-1-propene (**1e**) reacted with NBS to produce the corresponding 2-substituted 1,3-diphenylindene derivatives, **2b—d**, and **2e**, respectively (Run 4—10). The structures of **2a—e** were determined by spectroscopic and elemental analyses. Compound **2d** was identified by a comparison of its melting point and NMR spectrum with those reported in the literature.[3] Furthermore, the hydrogenation of **2d** on Pd–C afforded known *r*-1, *c*-2, *c*-3-triphenylindan, whose structure was identified by comparing its physical data with that from the literature.[4]

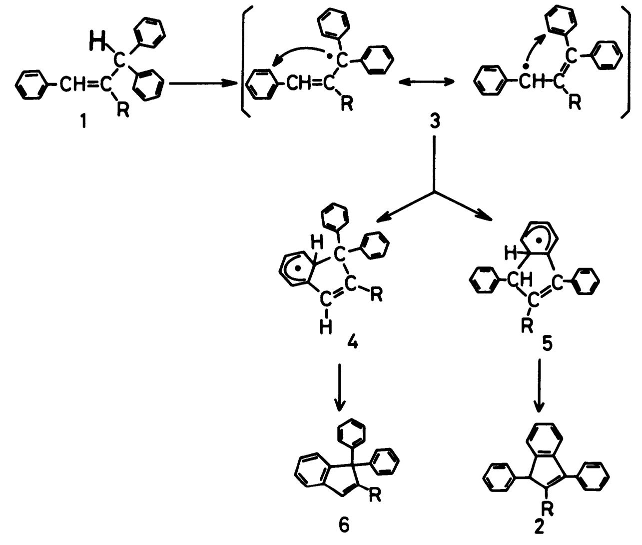


However, an attempted conversion of the nitro derivative (**1f**) into 2-nitro-1,3-diphenylindene (**2f**) was unsuccessful. The starting material was recovered unchanged (Run 11). The reaction, under forced conditions, gave an intractable product mixture.

Table 1. Dehydrocyclization of **1** with NBS

	R	**1**	Solvent	Reaction Time/h	Product	Yield[a] %
1	CO_2Me	(*E*)-**1a**	C_6H_6	6	**2a**	66
2		(*E*)-**1a**	CCl_4	6	**2a**	68
3		(*Z*)-**1a**	C_6H_6	4	**2a**	63
4	CO_2H	(*E*)-**1b**	C_6H_6	5	**2b**	51
5		(*Z*)-**1b**	C_6H_6	5	**2b**	53
6	COC_6H_5	(*E*)-**1c**	C_6H_6	4	**2c**	60
7	C_6H_5	(*E*)-**1d**	C_6H_6	6	**2d**	11
8		(*E*)-**1d**	CCl_4	4	**2d**	42
9		(*Z*)-**1d**	CCl_4	4	**2d**	40
10	C_6H_4-OMe(*p*)	(*E*)-**1e**	CCl_4	4	**2e**	40
11	NO_2	(*E*)-**1f**	CCl_4	8	—[b]	
12	H	(*Z*)-**1g**	C_6H_6	6	**7**[c]	56

a) Isolated yields of the pure products. b) Recovered unchanged. c) The formation of **2g** was not detected.

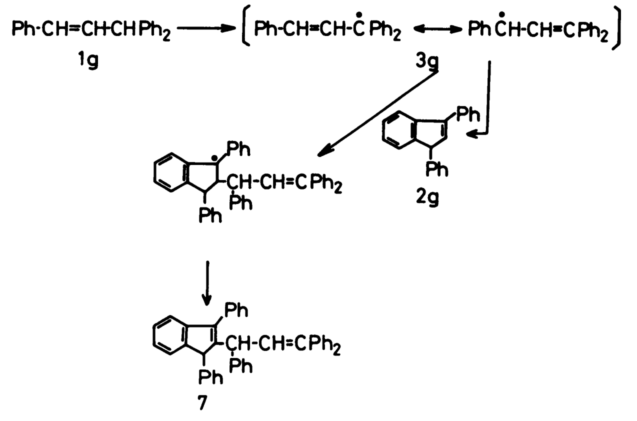


Scheme 1.

The formation of **2** can best be rationalized by the mechanism given in Scheme 1. The boldfaced hydrogen atom in **1**, being both allylic and benzylic, is readily abstracted by NBS to give a resonance-stabilized substituted cinnamyl radical (**3**). In general a cinnamyl radical generated in solutions tends to give products which result from an intramolecular attack; thus, indene was produced.[5,6] The formation of indene was observed solely during the gas-phase pyrolysis of cinnamyl ester.[7] A kinetic isotope effect suggested an intervention of a reversible process of the cinnamyl radical to a cyclic radical intermediate (Ar_2-5 mechanism) and a following rate-determining aromatization step.[7] These results are in contrast to the present observation where the indene derivatives were produced from 1,2,3-trisubstituted cinnamyl radicals. The radical could cyclize either through a cyclized radical (**4**) to give 1,1-diphenylindene derivative (**6**), or through another cyclized radical (**5**) to **2**, or could couple to give a dimer. The absence of the coupling process is best rationalized by taking account of steric hindrance near the reaction sites. The same steric factor also gives an explanation for the failure of a cyclization of the radical to the intermediate radical (**4**).

As mentioned before, the nitro derivative (**1f**) did not afford the corresponding indene (**2f**) (Run 11). The presence of the nitro group on the carbon atom next to the benzylic carbon atom is responsible for the innertness of **1f** under the present reaction conditions.[1c] By the same token, 1,1-diphenyl-2-nitroethane, which has a similar structural feature, also resisted hydrogen abstraction by NBS.

The reaction of 1,3,3-triphenyl-1-propene (**1g**)[8] with NBS did not afford the expected product, 1,3-diphenylindene (**2g**). Instead, a dimeric product, 1,3-diphenyl-2-(1,3,3-triphenyl-2-propenyl)indene (**7**),[9] was obtained (Run 12). This observation suggests that the initially formed **2g** is capable of being attacked by an intermediate 1,3,3-triphenyl-2-propenyl radical (**3g**) at the unsubstituted 2-position of **2g** (Scheme 2).



Scheme 2.

Indene itself was, in fact, supposed to be added by radicals to yield unidentified polymeric materials.[6] However, similar attacks by rather bulky 2-substituted 1,3,3-triphenyl-2-propenyl radicals were highly restricted in the reactions of **1a**—**e**; hence, 1,2,3-trisubstituted indenes survived under the present reaction conditions.

In summary, although NBS has been known to be an effective reagent for the dehydrogenation of allylic and benzylic positions, such an intramolecular dehydrocyclization between allyl and phenyl groups is almost unprecedented. Also, the diphenylation of the 2-substituted 1-phenyl-1-propenes and subsequent cyclization reaction may serve as a synthetic route to a series of 2-substituted 1,3-diphenylindene derivatives.

Experimental

All melting points were uncorrected. ^{1}H NMR spectra were determined with a Hitachi R-24A spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference.

General Procedure for the Dehydrocyclization of 1,3,3-Triphenyl-1-propenes (1). A mixture of the 2-substituted 1,3,3-triphenyl-1-propene (1 mmol), *N*-bromosuccinimide (1.2 mmol) and a catalytic amount of benzoyl peroxide in 30 ml of benzene or carbon tetrachloride was refluxed with stirring for the stated period of time, cooled, and partitioned between benzene and water. The benzene extracts were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) and recrystallization to give **2**. The physical properties of **2** are given below.

2a: Colorless prisms, mp 75 °C, ^{1}H NMR δ=7.36 (s, 4H, phenyl), 7.16 (s, 5H, phenyl), 7.09 (s, 5H, phenyl), 4.96 (s, 1H, methine), 3.43 (s, 3H, methyl), Found: C, 84.36, H, 5.51%. Calcd for $C_{23}H_{18}O_2$: C, 84.64, H, 5.56%.

2b: Colorless microcrystals, mp 194 °C, ^{1}H NMR δ=7.38 (s, 4H, phenyl), 7.28 (s, 5H, phenyl), 7.11 (s, 5H, phenyl), 4.96 (s, 1H, methine), 3.43 (s, 3H, methyl), Found: C, 84.69, H, 5.10%. Calcd for $C_{22}H_{16}O_2$: C, 84.59, H, 5.16%.

2c: Colorless prisms, mp 154 °C, ^{1}H NMR δ=7.50—6.90 (m, 19H, phenyl), 7.28 (s, 5H, phenyl), 7.11 (s, 5H, phenyl), 4.94 (s, 1H, methine), Found: C, 90.42, H, 5.70%. Calcd for $C_{28}H_{20}O$: C, 90.29, H, 5.41%.

2d: Colorless needles, mp 136 °C, ^{1}H NMR δ=7.30 (s, 4H, phenyl), 7.25 (s, 4H, phenyl), 7.05 (s, 5H, phenyl), 6.98 (s, 5H, phenyl), 5.03 (s, 1H, methine), Found: C, 94.02, H, 5.99%. Calcd for $C_{27}H_{20}$: C, 94.15, H, 5.85%.

2e: Colorless needles, mp 95 °C, ^{1}H NMR δ=7.29 (s, 4H, phenyl), 7.10—6.40 (m, 14H, phenyl), 4.96 (s, 1H, methine), 3.56 (s, 3H, methyl), Found: C, 89.99, H, 5.84%. Calcd for $C_{28}H_{22}O$: C, 89.81, H, 5.92%.

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