

The Reaction of Iodine Azide with Diphenylfulvene

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Fulvenes, structural isomers of benzenoids, have attracted the interest of organic chemists, especially because of the dual characters between conjugated olefins and aromatics. They give Diels-Alder Adducts in their 1,4-positions¹⁾ as well as substitution products with bromine.²⁾ We were interested in the introduction of nitrogen atoms into the fulvene skeleton to examine possible modifications of the original chemical features.

Fulvenes might be converted into azides by Hassner's method using iodine azide.³⁾ Application of this method seems to be of interest since Hassner's documents are limited to mono-olefinic compounds except for 1,3-cyclo-octadiene.³⁾ This paper deals with the elucidation of the structures of the reaction products from diphenylfulvene (**1**) and iodine azide.

The reaction of iodine azide with **1**⁴⁾ gave an oily mixture consisting of two diastereoisomeric diazido racemates, complete purification of which was unsuccessful. Treatment of the mixture with two equivalents of dimethyl acetylenedicarboxylate (DAC) gave two crystalline racemates (**3a—b**). The yields and physical constants of the racemates are summarized in Table 1, and their UV spectra given in Fig. 1. Their IR spectra are quite similar except slight differences in the fingerprint regions. Thus, the spectral similarities confirmed their skeletal and functional identity. Unequivocal assignments of the NMR signals in the region of τ 3.1—3.9 (2 olefinic protons and 2 protons on C₁ and C₂) were impossible due to their ambiguous resolutions.

TABLE 1. YIELDS AND PHYSICAL CONSTANTS OF **3a—b**

	3a	3b
Mp (°C)	165—167	162—164
Yield (%)	40	30
$\nu_{\text{KBr}}^{\text{max}}$ cm ⁻¹	1730	1730
$\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ)	288 (4.25) 224 (4.35)	284 (4.15) 222 (4.26)
NMR (CDCl ₃) τ	2.6—3.1 (10H, Ph) 3.1—3.2 (1H, m) 3.3—3.5 (2H, m) 3.7—3.9 (1H, m)	2.6—3.1 (10H, Ph) 3.1—3.3 (1H, m) 3.3—3.5 (2H, m) 3.5—3.7 (1H, m)
Me=methyl	6.08 (3H, s, Me) 6.15 (3H, s, Me) 6.26 (3H, s, Me) 6.29 (3H, s, Me)	6.1 (3H, s, Me) 6.15 (3H, s, Me) 6.18 (3H, s, Me) 6.23 (3H, s, Me)

1) For a review on fulvenes, see P. Yates, "Advances in Alicyclic Chemistry," Academic Press, New York-London, **2**, 136 (1968).

2) J. H. Day and C. Pidwerbesky, *J. Org. Chem.*, **20**, 89 (1955).

3) A. Hassner, *Accounts Chem. Res.*, **4**, 9 (1971) and the literatures cited therein.

4) J. L. Kice and F. M. Parham, *J. Amer. Chem. Soc.*, **80**, 3792 (1958).

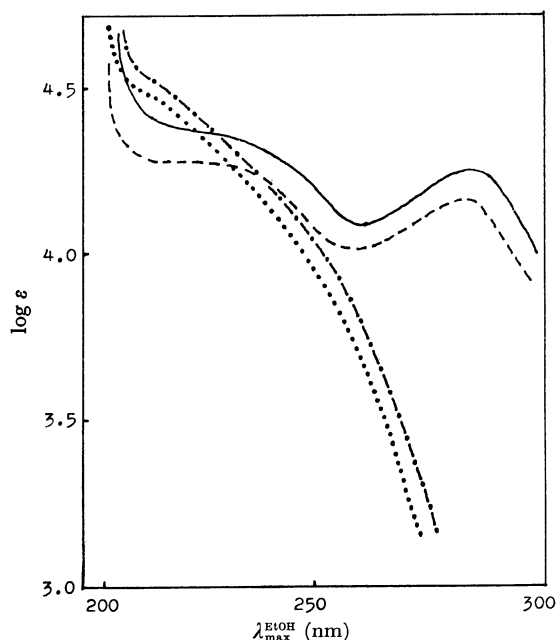
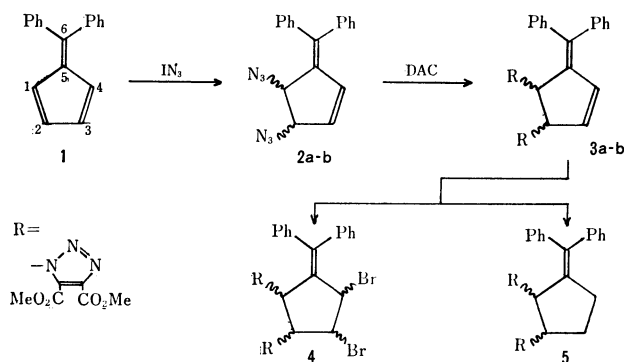
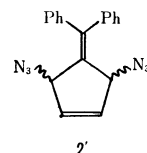


Fig. 1. UV Spectra of **3a** (—), **3b** (---), **4** (-·-·-), and **5** (·····) in EtOH.

Thus, the initial products should be diazido compounds with the same skeleton and π -conjugation system.

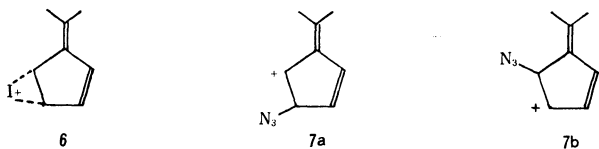


Attempts were made to saturate a double bond in **3a—b** by hydrogenation and bromination for the exclusion of another possible 1,4-adduct (**2'**). Thus, the dibromo compound (**4**) and tetrahydrofulvene (**5**) were obtained from **3b**, whereas the corresponding reaction products from **3a** were intractable. The UV spectra



of **4** and **5** (Fig. 1.) show complete disappearance of the absorption at 288 nm of **3a**, leaving the overlap of absorptions due to the triazole rings and the diphenylethylene group as inflections. It is well-known that 1,1-diphenylethylene absorbs at 250 nm ($\log \epsilon$ 4.0)⁵ and that the extension of a π -conjugation system by a double bond usually causes a bathochromic shift of approximately 30 nm. The absorption at 288 nm coincides with the expected value 280 nm, even assuming some steric restrictions between the diphenylethylene group and one of the triazole rings in **3**. It is anticipated that the saturation of an isolated double bond as in **2** would cause no essential change of a UV spectrum related to a major chromophore as diphenylethylene in **2'**.

It is thus concluded that **3a—b** are *cis* and *trans* racemates of 1,2-bis[4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazolyl]-1,2-dihydro-6,6-diphenylfulvene and **2a—b** should be the corresponding steric isomers of the 1,2-diazido compounds. Configurational ascription for each compound is difficult at the present stage.



Addition of iodine azide to olefins generally results in *trans* addition through the cationic intermediate like **6**.³⁾ The fact that any addition product having both I and N₃ groups, could not be detected under the present reactions would be rationalized by the marked resonance stabilization of the intermediate carbonium ion (**7a** or/and **7b**), formed by elimination of I[−], due to the extended conjugation which would involve the polar azide group itself. Thus, the attack of the nucleophilic azide ion on **7a** or/and **7b**, most probably in an S_N1 manner, would yield only one set of *cis* and *trans* isomers (**2a—b**) in roughly similar yields. This is in good accordance with our results. At present, it is difficult to say which of **7a** and **7b** was actual or major intermediate.

Experimental

All the melting points are uncorrected. The electronic spectra were measured on a JASCO Model ORD/UV-5 spectrophotometer and the infrared spectra on a JASCO Model IR-S spectrophotometer. The NMR spectra were recorded with a JNM C-60HL NMR spectrometer, TMS being used as an internal standard.

1,2-Diazido-1,2-dihydro-6,6-diphenylfulvene (2a—b). To a stirred suspension of sodium azide (3.0 g, 46 mmol) in dry acetonitrile (20 ml) in a methanol-ice bath was slowly added iodine monochloride (3.7 g, 23 mmol) for over 5 min. A solution of diphenylfulvene (**1**) (4.6 g, 20 mmol) in benzene

(10 ml) was added. The mixture was allowed to attain room temperature and was stirred for additional 24 hr. The red-brown slurry was poured into water (50 ml) and the mixture was extracted with ether (3 × 50 ml). The combined ethereal solutions were washed with 5% sodium thiosulfate solution. It turned out that the dark color of the ethereal layer could not be completely removed even by repeated washing. The ethereal layer was then washed with water, dried over magnesium sulfate and evaporated *in vacuo* to a dark-brown paste, which was chromatographed on a silica gel column (40 × 2 cm) using benzene as an eluant. A small amount of the starting material was recovered from the first few fractions. TLC with the use of silica gel and benzene showed one major spot with a couple of slower-moving traces. After removal of the benzene *in vacuo*, the residue gave monoclinic needles on standing at −30°C. The crude yield was 80%. IR(KBr): 2120 cm^{−1} (ν N₃). This product was used as such for the next synthesis to evade possible danger of explosion during the course of recrystallization.

1,2-Bis[4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazolyl]-1,2-dihydro-6,6-diphenylfulvene (3a—b). To a solution of the diazido mixture (**2a—b**) (1 g) in benzene (20 ml) was added DAC (1 g, 7 mmol), and the mixture was heated to reflux overnight. After the solvent was evaporated off, the residual paste was applied on a silica gel column (40 × 2 cm). Elution with benzene removed the excess DAC and unreacted starting material. The column was then eluted with 0.7% ethanol in benzene. The faster-moving fractions gave a pale yellow powder (**3a**) of mp 165—167°C from a mixture of chloroform and methanol. The slower-moving fractions also gave a pale yellow powder of mp 162—164°C from the same solvent.

Found for **3a**: C, 60.32; H, 4.53; N, 13.93%. Found for **3b**: C, 60.12; H, 4.63; N, 13.93%. Calcd for C₃₀H₂₆N₆O₈: C, 60.19; H, 4.38; N, 14.04%.

1,2-Bis[4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazolyl]-1,2-dihydro-3,4-dibromo-6,6-diphenylfulvene (4). To a stirred cold solution of **3a** (0.5 g, 0.84 mmol) in chloroform (8 ml) was added bromine (160 mg, 1 mmol) and the mixture was allowed to stand at room temperature for 2 hr. The dark-brown mixture was evaporated *in vacuo* to give **4** (0.44 g, 70%) as colorless powder, mp 205—207°C (from chloroform-acetone). Beilstein test: positive. IR(KBr): 1720 cm^{−1} (ν C=O). UV spectrum is given in Fig. 1. NMR(CDCl₃) τ : 2.4—3.0 (m, 10H, 2Ph), 3.0—3.3 (m, 2H, 1- and 2-protons), 4.1—4.4 (m, 2H, 3- and 4-protons), 6.05 (s, 3H, Me), 6.1 (s, 3H, Me), 6.25 (s, 3H, Me), and 6.45 (s, 3H, Me).

Found: C, 47.30; H, 3.54; N, 11.11%. Calcd for C₃₀H₂₆N₆O₈Br₂: C, 47.51; H, 3.46; N, 11.08%.

1,2-Bis[4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazolyl]-1,2,3,4-tetrahydro-6,6-diphenylfulvene (5). **3a** (0.5 g, 0.84 mmol) was dissolved in acetone (10 ml) and hydrogenated in the presence of Pd-C at atmospheric pressure for 5 hr. After standing overnight in hydrogen, the mixture was separated from the catalyst and evaporated *in vacuo* to give **5** as colorless granules, mp 165—167°C (from methanol). Yield: 0.33 g (65%). IR(KBr): 1720 cm^{−1} (ν C=O). For the UV spectrum, see Fig. 1. NMR(CDCl₃) τ : 2.7—3.2 (m, 10H, 2Ph), 4.0—4.5 (m, 2H, 1- and 2-protons), 6.0—6.2 (broad singlet, 6H, 2Me), 6.25—6.6 (m, 6H, 2Me), 7.2—7.7 (m, 2H), and 7.8—8.2 (m, 2H).

Found: C, 59.48; H, 4.74; N, 13.83%. Calcd for C₃₀H₂₈N₆O₈: C, 59.99; H, 4.70; N, 13.99%.

5) R. E. Lyle, E. J. DeWitt, and I. C. Pattison, *J. Amer. Chem. Soc.*, **78**, 61 (1956).