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QUINTET CARBENES

m-PHENYLENEBIS(PHENYLMETHYLENE) AND *m*-PHENYLENEBIS(METHYLENE)

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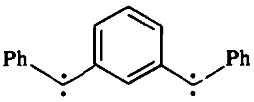
Abstract—Chemical reactivity of quintet carbenes, *m*-phenylenebis(phenylmethylene) (**1**) and *m*-phenylenebis(methylene) (**2**) has been studied. Dicarbene **1** adds to 1,1-diphenylethylene (84%) and strongly abstracts an H atom. Dicarbene **1** has a triplet-like character. Photolysis of 1,3-bis(α-diazomethyl)-benzene (**6**) in *cis*-2-butene results in nearly stereospecific cyclopropanation (98%, *cis–cis* adducts, **20–22**), accompanied by 2% *trans–cis* adducts (**24–25**). Dilution of *cis*-2-butene with cyclohexane affords the *trans–trans* adduct (**23**). The quintet *m*-phenylenebis(methylene) is probably the key intermediate in the nonstereospecific addition in the dilution experiment, the *trans–trans* adducts (**23**) arising *via* the quintet carbene.

INTRODUCTION

A STUDY of singlet or triplet carbenes, reveals that singlet carbenes undergo insertion reactions and stereospecific addition reactions to a C═C double bond, while triplet carbens show abstraction reactions and nonstereospecific addition reactions.[1]

Recently, ESR studies[2,3] revealed that the ground states of *m*-phenylenebis-(phenylmethylene) (**1**) and *m*-phenylenebis(methylene) (**2**) are quintet. We report the chemical reactivity of dicarbenes, **1** and **2**, and that the quintet state of **2** adds to 2-butene in a nonstereospecific manner.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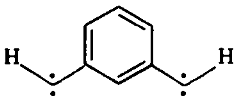
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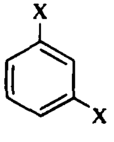
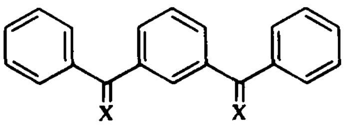
RESULTS

m-*Phenylenebis(phenylmethylene)* (**1**)

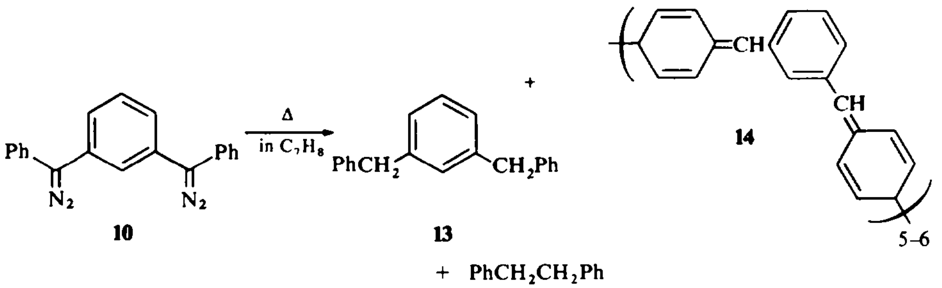
1,3-Dibenzoylbenzene (**8**), prepared from isophthalic acid (**3**) *via* the corresponding acid chloride (**4**), had a m.p. 108–109° and not as reported m.p. 101–102°[4], and it


3: X = —CO_2H
4: X = —COCl
5: X = —CHO
6: X = —CHN_2
7: X = —$CHBr_2$


8: X = O
9: X = NNH_2
10: X = N_2
11: X = H and OH
12: X = H and OAc

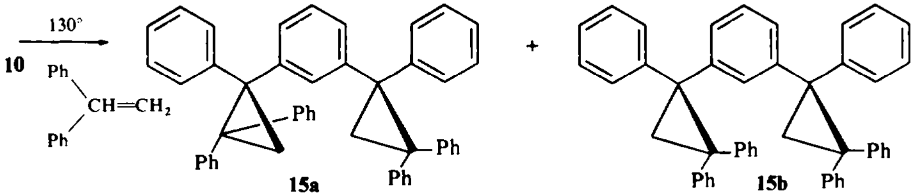
therefore was independently synthesized by oxidation of dialcohol (**11**). Oxidation of the hydrazone **9** of **8** afforded 1,3-bis(α-diazobenzyl)benzene (**10**) in 80% yield.

Pyrolysis of **10** gave 1,3-bis(benzyl)benzene (**13**), oligomer (**14**) and 1,2-diphenylethane. The structure of **13** was confirmed by comparison with an authentic sample. The structure of **14**, shown in Scheme 1, was assigned by its molecular weight (osmotic pressure, ~1420) and elemental analysis (C:H = 5:4). Abstraction of hydrogens from toluene will give rise to **13** and **14**, while coupling of benzyl radical will form 1,2-diphenylethane.



SCHEME 1

Pyrolysis of **10** in 1,1-diphenylethylene followed by chromatography gave adducts, m.p. 181–182° and 144·5–147°, in 84% yield. The structural assignment of racemic (**15a**) and meso (**15b**) isomers was not determined. Photolysis of **10** in the presence of oxygen afforded 1,3-dibenzoylbenzene (**8**) in 100% yield. These results are consistent



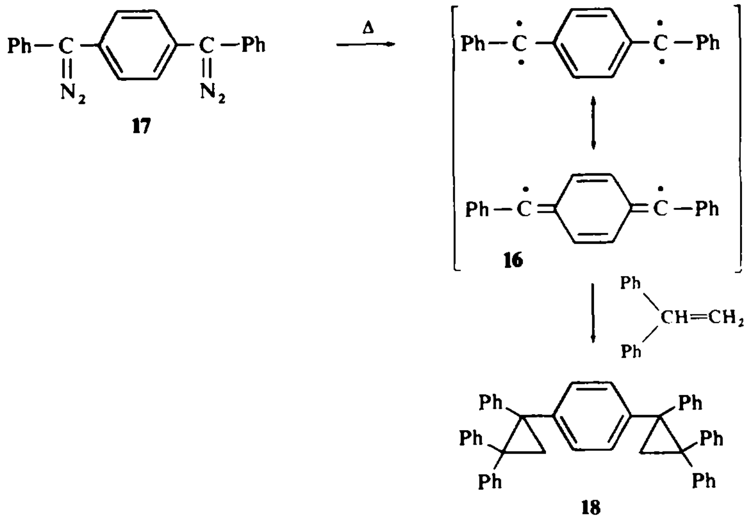
SCHEME 2

with those of *p*-phenylenebis(phenylmethylene) (**16**),[5] the ground state of which is triplet:[6] Pyrolysis of 1,4-bis(α-diazobenzyl)benzene in toluene gave rise to 1,2-diphenylethane and polymer.[5] Reaction of dicarbene **16** with oxygen gave 1,4-dibenzoylbenzene,[5] and addition to 1,1-diphenylethylene afforded the adduct **18** in 63% yield. Although these results suggest that dicarbene **1** has a triplet-state character, the reactivity of **1** cannot with certainty be attributed to the quintet state.

m-*Phenylenebis(methylene)* (**2**)

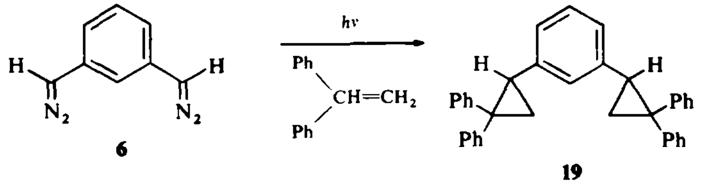
Oxidation of the hydrazone of isophthal aldehyde gave the unstable 1,3-bis(α-diazomethyl)benzene (**6**). The IR spectrum of **6** showed the characteristic absorption of the diazo group at 2080 cm^{-1}. Treatment of **6** with hydrogen bromide gave rise to ω,ω′-dibromo-*m*-xylene.

Photolysis of **6** in 1,1-diphenylethylene led to 1,3-bis(2′,2′-diphenylcyclopropyl)benzene (**19**) in a 87% yield. The NMR spectrum of **19** showed that ABX type



SCHEME 3

absorption in the reagion at δ 1·5–2·0 (the cyclopropyl protons, 4H) and δ 2·5–2·7 (the methine protons, 2H). Thus, the fact that dicarbene **2** added to 1,1-diphenylethylene in a high yield stimulated us to investigate the stereochemistry of the addition reaction with 2-butene. The smaller molecular weight of **2** than **1** permitted the use of VPC for precise analysis of the adducts.



SCHEME 4

Photolysis of **6** in *cis*-2-butene led to the adducts in 17% yield. VPC analysis indicated that three major products (98%) and two minor products (2%). The NMR spectra revealed that the major products were *syn–syn* (**20**), *anti–anti* (**21**) and *syn–anti* (**22**) of 1,3-bis(*cis*-2′,3′-dimethylcyclopropyl)benzene. The ratio was 1·4 : 1·0 : 2·7. It is noteworthy that all three major products maintained the stereochemistry of the Me groups of *cis*-2-butene.[*] The isomers **20**, **21** and **22** gave satisfactory elemental analyses. Their IR spectra agreed with the assigned structures. Analysis of their NMR spectra was focussed on the Me group.[8] *syn–syn* (**20**) and *anti–anti* (**21**) Isomers should show one kind of Me protons. The Me protons (H^a) of **20** are located inside the shielded (+) reagion, while those of **21** (H^b) are somewhat deshielded (−). Upon

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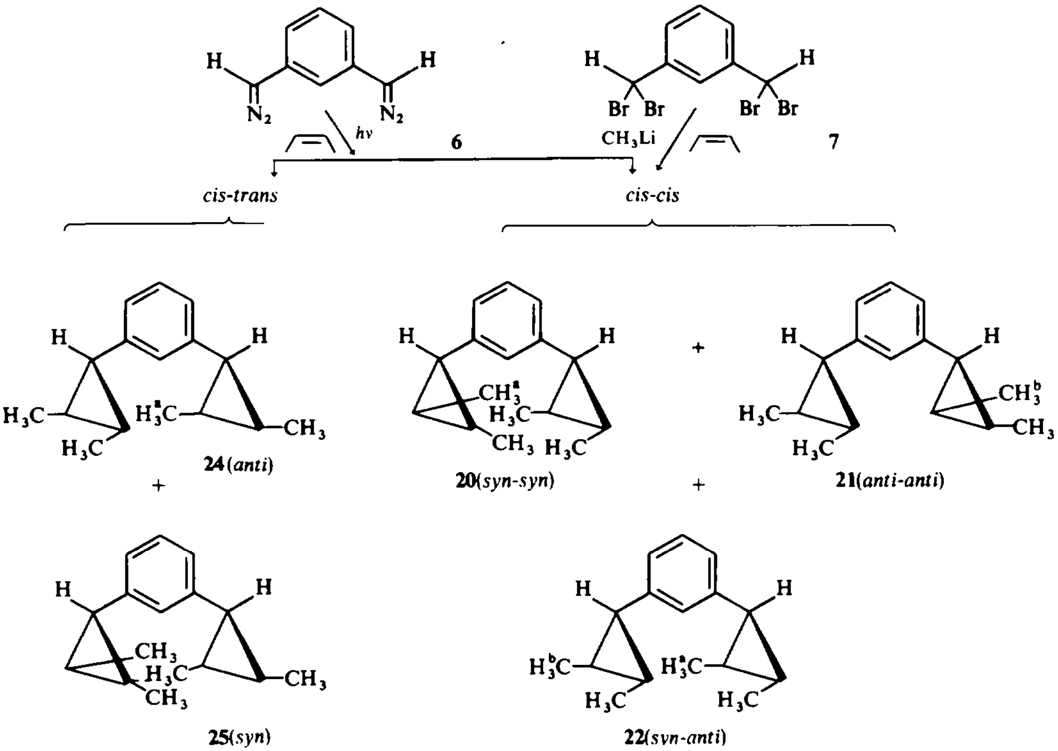
[*] Gutsche reported about 3% nonstereospecificity in the addition reaction of phenylmethylene to *trans*-2-butene and about 2·5% nonstereospecificity in its addition to *cis*-2-butene.[7] Closs reported corresponding values of 0·5–1 and 3–5% for experiments in the pure olefins.[8] Control experiments indicated 0·5% of contaminated stereoisomers could be detected by VPC.

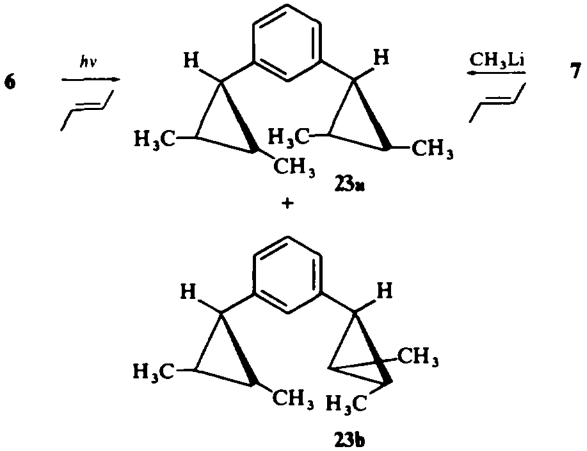
rotation of the phenyl group through 360°, the *cis* protons (H^a) will pass through the shielded area twice, while the *trans* protons (H^b) will remain deshielded in any conformation. Indeed, the NMR spectra of **20** showed the Me protons as doublets at δ 0·87 (12H), while that of **21** showed the Me protons at δ 1·14 (12H). The Me protons of 1,1-dimethylcyclopropane appeared at δ 1·05.[8] On the other hand, the *syn–anti* isomer (**22**) should show two kinds of Me protons; the Me protons of **22** appeared as two doublets centred at δ 0·93 (6H) and 1·14 (6H). For further confirmation of the stereochemistry of the addition reaction, the carbenoid reaction which showed to proceed stereospecifically was carried out.[8] Treatment of $\omega,\omega,\omega',\omega'$-tetrabromo-*m*-xylene (**7**) with methyllithium at −15° in the presence of *cis*-2-butene afforded a mixture of the three isomers, **20**–**22**, in the ratio 7·6: 1·0: 14, respectively. The ratio of *syn*/*anti* of the photolysis of diazo compound **6** in *cis*-2-butene is 1·4, while that of the reaction of tetrabromide **7** with methyllithium in *cis*-2-butene is 7·6. These differences should be attributed to the intermediacy of a free carbene in the photolysis and that of carbenoid molecule which is lower than the triplet-ground state of the carbene.[8] It is of interest that the *syn*/*anti* ratio (1:4) of dicarbene **2** to *cis*-2-butene are larger than that (1·1) of phenylmethylene. This may be due to the fact that the energy of dicarbene **2** is lower than that of phenylmethylene.



SCHEME 5

The structures of the minor product were assigned as *anti* (**24**) and *syn* (**25**) *cis–trans* adducts by the NMR spectra. The Me protons of **24** appeared as two doublets centred at δ 0·78 (3H) and 1·13 (9H), while that of **25** appeared at δ 0·93 (9H) and 1·18 (3H). For further confirmation of structural assignment, *cis–trans* adducts (**24** and **25**) were prepared by the carbenoid reaction of **7** in the mixture of *cis*- and *trans*-2-butenes (1 : 1). The VPC analyses showed that the adducts of the photolysis of **6** in *cis*-2-butene were not contaminated with the *trans–trans* adduct (**23**) (0·5% of **23** was detectable).

Photolysis of **6** in *trans*-2-butene gave rise to 1,3-bis(*trans*-2′,3′-dimethylcyclopropyl)benzene (**23**) in 15% yield. The NMR spectrum of **23** showed the Me protons as two doublets centred at δ 1·18 (6H) and δ 0·78 (6H). The carbenoid reaction of **7** with methyllithium in the presence of *trans*-2-butene led to **23** stereospecifically.



Scheme 6

Six isomers (**20–25**) of the adducts could be completely separated by VPC (microwax, column temp 210°, see Experimental), though **23a** and **23b** could not be separated.

Control experiments showed the cyclopropane derivatives (**20–25**) were not isomerized under the reaction conditions, and further irradiation of **20–25** gave rise to ring cleavage. *cis* and *trans*-2-Butenes were not isomerized during the irradiation.

Nonstereospecific addition (3%) of phenylcarbene to *cis*-2-butene is attributed to the triplet state,[7] and hence nonstereospecificity of the addition reactions of **2**, of which ground state is quintet,[2,3] would be reationalized either as triplet or as quintet state reactions. In order to clarify this interesting point, a hydrogen abstraction reaction which is usually attributed to a triplet state[9a] and a dilution experiment by an intert solvent,[10] was carried out.

In the photolyses of **6** in toluene or ether, hydrogen-abstraction products such as 1,2-diphenylethylene or 1,2-diethoxybutane could not be obtained: therefore, a triplet state probably does not play an important role in this reaction. A typical triplet carbene, *p*-phenylenebis(methylene) abstracts hydrogen strongly; photolysis of 1,4-bis(α-diazomethyl)benzene in THF afforded a polymer and octahydro-2,2′-bifuran (46%), and in ether a polymer and 2,3-diethoxybutane.[11] Photolysis of **6** in the mixture of cyclohexane and *cis*-2-butene was studied, in the hope that the additive would function as an inert diluent, allowing a singlet to undergo enough fruitless collisions, so that an appreciable proportion would cross to the triplet or quintet state, resulting in an enhancement of nonstereospecific addition. The data in Table 1 show that under the conditions where the cyclohexane:*cis*-2-butene was 100:1, 7% of *trans* isomer **23** was obtained.

Table 1. Addition of *m*-phenylenebis(methylene) (**2**) to *cis*-2-butene[b]

Dilution[a]	*cis–cis* Adducts			*cis–trans* Adducts		*trans–trans* Adducts
	20	**21**	**22**	**24**	**25**	**23**
Neat	27	52	19	1·5	0·5	0
		98		2		0
1:10		83		13		4
1:100		68		25		7

[a] Ratio of *cis*-2-butene to cyclohexane.

[b] Relative ratio determined gas chromatographically.

Absorption spectra of dicarbene 1 *and* 2

The ground states of dicarbene **1** and **2** were demonstrated to be quintet by ESR spectra.[2,3] The absorption spectra at the delay time 10^{-6} sec which was obtained from flash photolysis of a solution of **10** (5×10^{-5} mole) in deoxygenated liquid paraffin at room temperature[9a] was consistent with the absorption spectrum obtained in the rigid glass at 77°K.[12] Therefore, the electronic state of carbene **1** would be same either in the rigid glass at 77°K or in liquid paraffin at room temperature. The delay time indicated that the life time of quintet **1** would be 10^{-5} sec. This suggested that the abstraction reaction of **1** would be attributed to the quintet state of **1**, since in photolysis of **10** sufficient of quintet **1** is formed, and its life time is long enough to

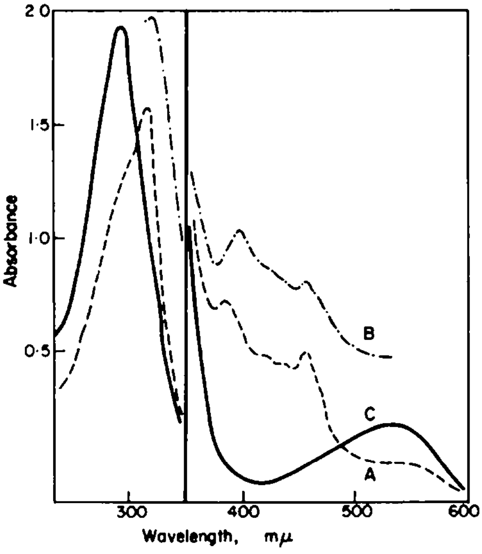
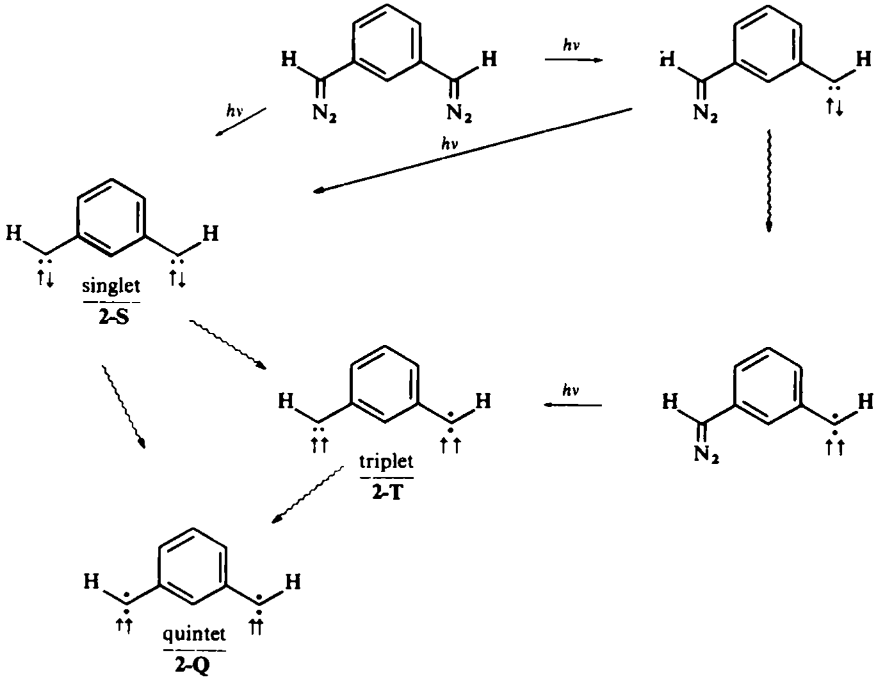


Fig 1. Electronic absorption spectra of *m*-phenylenebis(phenylmethylene) (**1**). A: Absorption spectrum of dicarbene **1** produced by photolysis of 1,3-bis(α-diazobenzyl)-benzene (**10**) at 77°K with Hg-lamp.[12] B: Absorption spectrum of dicarbene **1** by flash photolysis at 20° (relative intensity). C: Absorption spectrum of diazo compound **10**

abstract hydrogen. Although ESR spectrum of quintet **2** was obtained at 4°K, the ESR and absorption spectra of quintet **2** was not obtained at 77°K, since quintet **2** is unstable at 77°K and might proceed to further reactions.

DISCUSSION

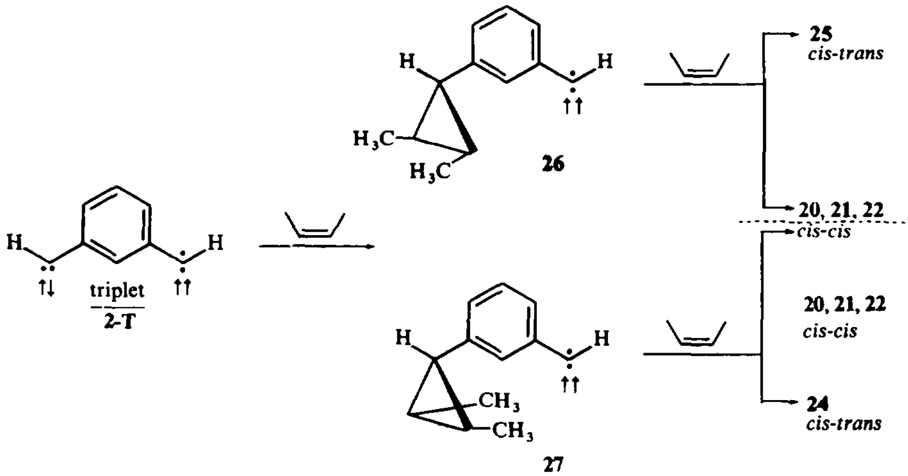
Hydrogen abstraction of dicarbene **1** from toluene, reaction with oxygen and the addition to 1,1-diphenylethylene are consistent with the reactivity of dicarbene **16**. This suggests that dicarbene **1** is similar in character to the triplet **16**. Formation of **20**–**22** and **23** in the photolysis reactions of **6** could be attributed to the singlet state. Stereospecificity (97%) in the reaction of phenylmethylene, whose ground state is triplet, to *cis*-2-butene is attributed to the reaction of the singlet state.[7,8] A detailed UV study showed that formation of **1** from the diazo compound **10** is a one-photon process.[12] The first electronic state of dicarbene **2** would be the singlet state (**2-S**), when **6** was photodecomposed by the one-photon process as in the photodecomposition of **10**.[12] The energy level of **2-S** would be higher than that of the triplet state (**2-T**) and the quintet state (**2-Q**) as shown in Scheme 7.



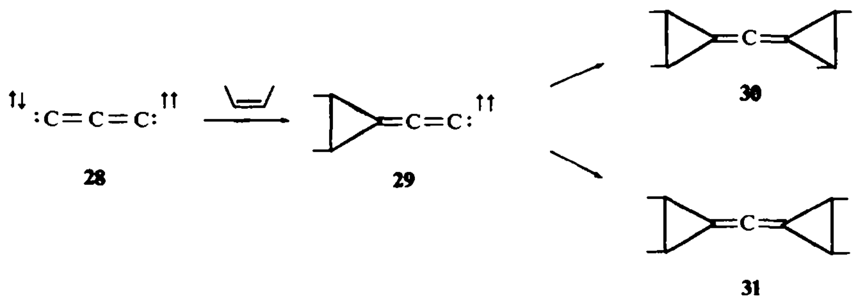
Scheme 7

Jones showed that the dilution of *cis* olefin in hexafluorobenzene lowers the ratio of *cis* to *trans* cyclopropane until the *trans* product predominates, presumably because collisions with the inert solvent molecules can induce intersystem crossing in the initially formed singlet carbene and the triplet carbene so formed is not stereospecific in its addition.[10] Diazo compound **6** was decomposed in the mixture of *cis*-2-butene and cyclohexane. The ratio of *cis*-2-butene to cyclohexane was changed from $\frac{1}{10}$ to

$\frac{1}{100}$. Careful analyses of the products revealed that a considerable amount of the *trans–trans* cyclopropane **23** was formed (Table 1). Consequently, it seems reasonable that the quintet state is responsible for the formation of the *trans–trans* adduct and the triplet state can be excluded. The reaction of the triplet (**2-T**) with *cis*-2-butene will give rise to the *cis–trans* isomers (**24** and **25**) together with *cis–cis* isomers (**20–22**), but will not form the *trans–trans* isomer (**23**), since the reactivity of the singlet state is generally higher than that of the triplet state, and hence the initial intermediate will be the triplet states, **26** and **27**. Skell reported the first addition of C_3 (**28**) as stereospecific, leading to a biradical intermediate (**29**) and the second step as nonstereospecific, leading to triplet biradical intermediates which suffer equilibration by rotation about the single bond prior to ring closure.[13] Furthermore, Moss demonstrated that in phenylmethylene the singlet state adds to 2-butene faster than the triplet state.[14] It should be noted that the *trans–trans* adduct (**23**) was obtained in the dilution experiments of cyclohexane. Formation of the *trans–trans* isomer (**23**) from *cis*-2-butene would be attributed to the reaction of the quintet state (**2-Q**). The first addition is nonstereospecific, leading to triplet states, **32–34**, and then the second

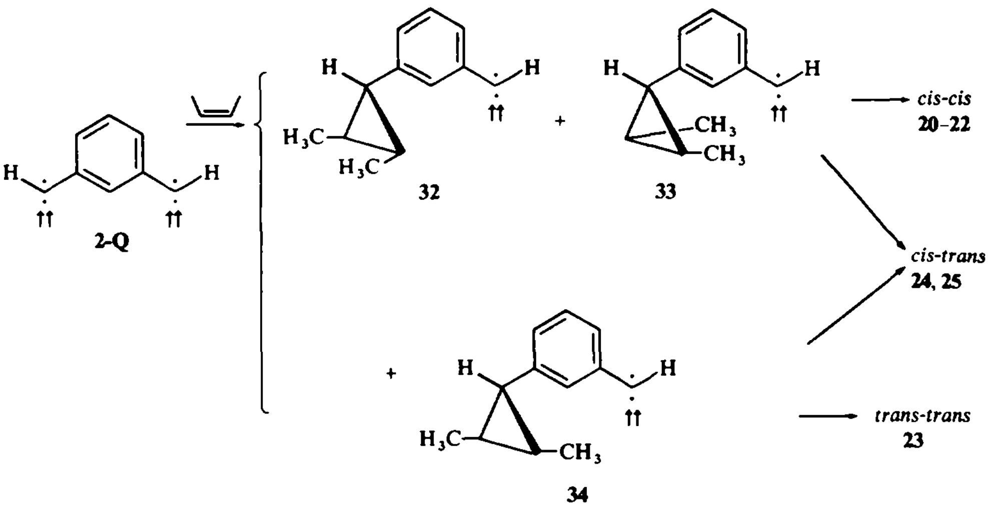


SCHEME 8



SCHEME 9

nonstereospecific addition of **34** forms the *trans-trans* adduct **23** as shown in Scheme 10. Thus, the quintet state of **2** add to 2-butene in a nonstereospecific manner.



Scheme 10

EXPERIMENTAL

All m.ps were uncorrected. IR spectra were determined with a Hitachi-S2 spectrometer. NMR spectra were recorded with a JNM-4H-100 spectrometer against internal TMS. UV spectra were measured on Hitachi-EPS-2 or Cary 14 spectrometers. Flash photolyses were carried out with the procedure described before.[9a] Light petroleum refers to the fraction b.p. 40-70°.

1,3-Dibenzoylbenzene (**8**). A mixture of *m*-phthalic acid (100 g, 0·60 mole) and $SOCl_2$ (250 ml) was heated under reflux for 4 hr. Evaporation of excess $SOCl_2$ followed by distillation gave **4** b.p. 143-144°/13 mm Hg. To a suspension of $AlCl_3$ (200 g, 1·5 mole) in benzene (200 ml) was added a soln of isophthaloyl chloride in benzene (200 ml) with heating under reflux. After standing for 30 min, the mixture was poured into ice-water. The benzene extract was washed with a dil NaOH aq and water. Drying over $CaCl_2$ followed by evaporation of benzene afforded white crystals of **8** (84 g, 50% yield calculated from *m*-phthalic acid), m.p. 109-110° (from EtOH); IR (nujol mull) 1658 cm^{-1} (C=O): UV_{max} (EtOH) 233 nm (log ε 4·51), 252 (4·54). (Found: C, 83·31; H, 4·96. Calc. for $C_{20}H_{14}O_2$: C, 83·93; H, 4·93%). The reported m.p. was 101-102°.[4] Therefore, another method was carried out. To a stirred soln of isophthal aldehyde (4 g, 0·03 mole) in a mixture of dry ether (40 ml) and dry THF (30 ml) PhMgBr was added [prepared from Mg (2·8 g; 0·12 mole) and bromobenzene (17·5 g; 0·10 mole) in ether (50 ml) for 1 hr]. After standing for 8 hr at room temp, the organic layer was separated, washed with water and dried over $MgSO_4$. Evaporation of ether gave white crystals. Recrystallization from benzene gave **11** in 50% yield, m.p. 153-154°; IR (nujol mull) 3350 cm^{-1} (O—H), 1036, 1026 (C—O); UV_{max} (EtOH) 235 nm (4·36), 273 (4·39). (Found: C, 82·85; H, 6·31. Calc. for $C_{24}H_{22}O_4$: C, 82·73; H, 6·25%). To a stirred soln of **11** (1·0 g, 3·5 mmole) in a mixture of benzene (25 ml) and AcOH (25 ml) was slowly added a soln of sodium dichromate (7·5 g, 25 mmole) in AcOH (17·5 ml) at room temp. After further stirring for 1 hr at 50-60°, the mixture was poured into ice-water. The benzene extract was dried over $MgSO_4$, and evaporation of benzene gave **8** (0·70 g, m.p. 108-109°), which was identical with that obtained by the Friedel-Craft reaction.

1,3-Dibenzoylbenzene hydrazone (**9**). A mixture of **8** (50 g, 0·18 mole), hydrazine hydrate (100%, 30 g, 0·60 mole) and conc HCl (10 ml) was heated under reflux for 24 hr. Recrystallization of the ppt from benzene gave pure (22 g, 40%), m.p. 163-164°; IR (nujol mull) 3430, 3325, 3250 cm^{-1}; UV_{max} (EtOH) 235 nm (4·40), 273 (4·43). (Found: C, 76·32; H, 5·77. Calc. for $C_{20}H_{18}N_2$: C, 76·40; H, 5·77%).

1,3-Bis(α-diazobenzyl)benzene (**10**). To a mixture of **9** (1·53 g, 4·88 mmole), yellow mercuric oxide (16 g) and dry ether (100 ml), two drops of a saturated soln of KOH in EtOH was added and the mixture stirred for 2 hr at room temp. Filtration and evaporation of ether *in vacuo* gave a red-coloured crystalline material. Recrystallization from CH_2Cl_2–light petroleum gave **10** (1·21 g, 80%), m.p. 125° (dec); IR (nujol mull) 2060 cm^{-1} (N=N); UV_{max} (EtOH) 224 nm (4·08), 290 (4·35), 525 (2·98). (Found: C, 77·17; H, 4·58. Calc. for $C_{20}H_{14}N_4$: C, 77·40, H, 4·55%). Treatment of **10** with AcOH gave **12**, m.p. 158–161°.

Thermal decomposition of 1,3-*bis*(α-*diazobenzyl*)*benzene* (**10**) *in toluene*. A soln of **10** (1·75 g, 5·65 mmole) in toluene (30 ml) was added dropwise to toluene (10 ml) under reflux. After evolution of N_2 ceased, the toluene was evaporated and the residue submitted to aluminum chromatography. Elution with a mixture of cyclohexane and benzene (2:1) gave 1,2-diphenylethane (m.p. 50–51·5°) (lit.[15] m.p. 52°) and **13**.[16] The latter was synthesized both by the reaction of PhMgBr with ω,ω′-dibromo-*m*-xylene[17] and by reduction of **8** with HI (48%). Further elution with benzene gave **14**, m.p. 113–150°. (Found: C, 93·63; H, 6·34%). The molecular weight (VPO) was 1420; therefore, the structure was the oligmer which has 5–6 components of the biradical formed by abstraction of two H atoms by *m*-phenylenebis(phenylmethylene) (**1**).

Thermal decomposition of 1,3-(α-*diazobenzyl*)*benzene* (**10**) *in* 1,1-*diphenylethylene*. A soln of **10** (6 g) in 1,1-diphenylethylene (160 ml) was heated at 130° for 5 hr. After evaporation of excess 1,1-diphenylethylene *in vacuo*, the residual oil (17 g) was submitted to aluminum chromatography. Elution with cyclohexane and benzene gave **15** (10·3 g, 84%). Careful recrystallization from EtOH gave two isomers, m.p. 181·5–182° and m.p. 144·5–147°. M.p. 181–182°; IR (nujol mull) 1028 cm^{-1}; NMR (CCl_4) δ 2·19 (cyclopropyl H, AB, 4H), 6·50–7·10 (aromatic H, m, 34H); UV_{max} (EtOH) 236, 244, 256, 262, 269, 286 nm. (Found: C, 93·77; H, 6·18. Calc. for $C_{48}H_{38}$: C, 93·77; H, 6·23%), m.p. 144·5–147°; IR (nujol mull) 1028 cm^{-1}; NMR (CCl_4) δ 2·28 (cyclopropyl H, AB, 4H), 6·50–7·15 (aromatic H, m, 34H); UV_{max} (EtOH) 238, 270, 277 nm. (Found: C, 93·54; H, 6·32. Calc. for $C_{48}H_{38}$: C, 93·17; H, 6·32%).

Photolysis of 1,3-(α-*diazobenzyl*)*benzene* (**10**) *in the presence of oxygen*. A soln of **10** (0·37 g, 1·1 mmole) in oxygen-saturated benzene (130 ml) was photolyzed until the colour of **10** disappeared. Benzene was removed, and recrystallization from EtOH gave **8** (10·2 g, 100%), m.p. 108–109°.

Thermolysis of 1,4-*bis*(α-*diazobenzyl*)*benzene* (**17**) *in* 1,1-*diphenylethylene*. Thermal decomposition of a soln of **17** (6 g) in 1,1-diphenylethylene (160 ml) at 130° followed by separation by aluminum chromatography eluted with cyclohexane–benzene gave **18** in 63% yield, m.p. 219–220° (from benzene); IR (nujol mull) 1028 cm^{-1}. (Found: C, 93·83; H, 6·41. Calc. for $C_{36}H_{30}$: C, 93·46; H, 6·54%).

1,3-*Bis*(α-*diazomethyl*)*benzene* (**6**). Isophthal aldehyde (30 g, 0·22 mole) was dissolved in EtOH (150 ml). Anhydrous hydrazine (100%, 384 g) was added, and the mixture was stirred for 24 hr at 60–70°. Concentration of the soln and recrystallization from EtOH gave **6** (18 g, 50%), m.p. 107–108°; IR (nujol mull) 3325, 3150 cm^{-1}. To a suspension of **6** (12 g, 12·3 mmole), yellow HgO (46·8 g, 21·6 mmole), Na_2SO_4 (2 g) in ether (200 ml) two drops of alcoholic KOH was added. The mixture was maintained below 15° in an ice bath and stirred for 2 hr. The resulting red soln was filtered off. Since **6** is unstable, its ether soln was used without further purification. The yield of **6** was determined to be 50–70%. The concentration of **6** in the ether soln was determined by converting **6** to dibenzoate by treatment with benzoic acid. Treatment of **6** with HBr gave rise to ω,ω′-dibromo-*m*-xylene, m.p. 77–78° (Lit. m.p. 77–78°).[17]

Photolysis of 1,3-(α-*diazomethyl*)*benzene* (**6**) *in the presence of* 1,1-*diphenylethylene*. A mixture of an ethereal soln of **6** (25 mmole) and 1,1-diphenylethylene (10 ml) was photolyzed under N_2 until evolution of N_2 ceased. Evaporation of ether gave a residual oil (18·6 g), which was submitted to aluminum chromatography. Elution with CCl_4–benzene (1:1) afforded **19** (9·6 g, 87%); IR (liquid film) 1028 cm^{-1}; NMR (CCl_4) ABX type, δ 1·5–2·0 (4H, cyclopropyl H), δ 2·5–2·75 (2H, methine H), and 6·2–7·3 (m, 24H). (Found: C, 93·29; H, 6·51. Calc. for $C_{36}H_{30}$: C, 93·46; H, 6·54%).

Photolysis of 1,3-*bis*(α-*diazomethyl*)*benzene* (**6**) *in* cis-2-*butene*. Dry *cis*-2-butene (450 ml) was introduced into a cylindrical flask equipped with a high pressure mercury lamp under N_2. An ether soln of **6** (0·06 mmole, 85 ml) was added at 0°. The mixture was photolyzed until the colour of **6** disappeared. The polymer which adhered on the wall of the qualz lamp was mechanically removed to avoid shielding of photons from the soln. After elimination of *cis*-2-butene and ether, distillation of the residual oil gave a colourless liquid (b.p. 110–150°/1 mm Hg, 1·0 g). VPC (microwax 7 m, column temp 210°) indicated that three major products (98%) and two minor products (2%) were obtained. The NMR spectra revealed that the major products were *syn–syn* (**20**), *anti–anti* (**21**) and *syn–anti* (**22**) of 1,3-bis(*cis*-2′,3′-dimethylcyclopropyl)benzene. The ratio was 1·4:1·0:2·7. The isomer **20**: IR (liquid film) 1060 cm^{-1}; NMR (CCl_4) δ 0·87 (d, 12H), 0·80–1·30 (m, 4H), 1·80–2·05 (m, 2H), 6·80–7·15 (m, 4H). (Found: C, 89·56; H, 10·35. Calc. for $C_{16}H_{22}$: C, 89·65; H, 10·35%). The isomer **21**, 1060 cm^{-1}: NMR (CCl_4) δ 1·14 (d, 12H), 0·90–1·40 (m, 4H), 1·80–2·05 (m, 2H), 6·50–7·15 (m, 4H). (Found: C, 89·93; H, 10·38. Calc. for $C_{16}H_{22}$: C, 89·65; H, 10·35%). The isomer **22**: IR 1060 cm^{-1}; NMR (CCl_4) δ 0·93 (d, 6H), 1·14 (d, 6H), 0·95–1·40 (m, 4H), 1·80–2·05 (t, 2H), 6·50–7·14 (m, 4H). The minor products were assigned as *anti* (**24**) and *syn* (**25**) *cis–trans* cyclopropanes by their NMR spectra. The isomer **24**: NMR (CCl_4) δ 0·78 (d, 3H), 1·13 (m, 9H), 0·8–1·3 (m, 4H), 6·5–7·1 (m, 4H). The isomer **25**: NMR (CCl_4) δ 0·93 (m, 9H), 1·18 (d, 3H), 0·9–1·4 (m, 4H), 1·8–2·0 (m, 2H), 6·8–7·1 (m, 4H). For further confirmation of the structural assignment the carbenoid reaction was carried out as follows: To a soln of **7** in a mixture of *cis* and *trans*-2-butenes (1 : 1) was added a soln of MeLi in ether (1 eq) and the products submitted to VPC. Two new peaks were collected. Their spectral data were identical with those obtained from photolysis of **6** in *cis*-2-butene.

Photolysis of 1,3-*bis*(α-*diazomethyl*)*benzene* (**6**) *in* trans-2-*butene*. The reaction was carried out as described for photolysis in *cis*-2-butene. Compound **23** was obtained in 15% yield, NMR (CCl_4) δ 0·78 (d, 6H), 1·18 (d, 6H), 0·75–1·05 (m, 4H), 1·6–1·8 (m, 2H), 6·75–7·15 (m, 4H). (Found: C, 89·90; H, 10·43. Calc. for $C_{16}H_{22}$: C, 89·65; H, 10·35%).

Carbenoid reactions. To a soln of $\mathbf{7}^{18}$ (7·2 g, 17·2 mmole) in *cis*-2-butene (350 ml), a soln of MeLi (34·4 mmole) in ether (140 ml) was added dropwise at −10° with stirring. After additional stirring for 1 hr at room temp, *cis*-2-butene was recovered. The ether soln was poured into ice-water, the ether extract was washed with water and dried over $MgSO_4$. Evaporation of ether followed by distillation gave the adducts, **20**–**22** (b.p. 110–150°/1 mm Hg), which were subjected to VPC. The products were identical with those obtained by photochemical decomposition of **6**. The ratio of **20**:**21**:**22** was 7·6:1:14. The IR and NMR spectra obtained by preparative VPC were identical with those obtained from photolysis of **6**. The carbenoid reaction of **7** in *trans*-2-butene was carried out. The NMR and IR spectra of the adduct were identical with those of the adduct obtained from photolysis of **6** in *trans*-2-butene.

Dilution experiments. In a typical reaction, cyclohexane and *cis*-2-butene were mixed in known proportion with an etheral soln of **6** (7 mmole) in a Pyrex test tube. After photolysis, the samples were concentrated by distillation and analyzed by VPC (Table 1). The retention times of the cyclopropanes (**20**–**25**) were as follows (column temp 210°, microwax 7 m, the flow rate of He, 1·6 kg/cm^2, Yanagimoto-5DH): **23** (46 min), **24** (57), **25** (60), **22** (75), **21** (79) and **20** (86). Photoisomerization of **20** was investigated by preparing a soln of the pure compound (20 μl in 5 ml of ether) and irradiation in a quartz flask, under N_2, with a high-pressure mercury lamp. At intervals, aliquots were removed and analyzed by VPC. Under the usual conditions, *cis*-**20** was not isomerized; however, by further irradiation **20** was slightly isomerized to **24** and **25**, and the cleavage of the cyclopropane ring was observed. Several further control experiments are described in the Results.

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