ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 132 (2000) 167–173

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Multiplicity and selectivity of cyclopent[a]acenaphthylenylidene

Heinz Durr [a], Aboel-Magd A. Abdel-Wahab [b],*, Mohamed T. Ismail [b], Omima S. Mohamed [b]

[a] University of Saarbruecken, Fb. 11.2, Saarbruecken, Germany

[b] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

Received 22 June 1999; received in revised form 3 January 2000; accepted 10 January 2000

Abstract

Cyclopent[a]acenaphthylenylidene 1 has been generated by photolysis from its precursor, the diazocompound 1a. Carbene 1could be trapped in olefinic substrates to afford the spirocyclopropanes 8–12. In addition triplet products of 1 such as 13 and dimer 14 were isolated. With *trans*-β-methylstyrene 1 undergoes a stereospecific addition. 2,3-Dimethylbutadiene and 1 reacted to the vinylspirocyclopropane 16 and 17. Competition experiments of 1 with styrenes give a linear Hammett correlation with a ρ=0.38. Therefore, 1 is regarded as a nucleophilic singlet carbene in its additions to styrenes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Diazocompounds; Cyclopent[a]acenaphthylenspiro-cyclopropanes

1. Introduction

A principal aim in the photochemistry of diazo compounds is to correlate the observed chemistry with the multiplicity, singlet or triplet spin state, and selectivity of the carbene formed. The present work includes studies of carbene 1 on which the carbene carbon is incorporated into a polynuclear condensed ring system. It was reported that tetraphenyldiazocyclopentadiene and other related diazo compounds photochemically produce the corresponding carbenes [1] (Scheme 1). Durr et al. [2,3] reported that tetraphenyldiazocyclopentadiene was recovered unchanged when refluxed in benzene.

On heating with high boiling solvents like mesitylene it gave tetraphenylcyclopentadiene and CH insertion products [2–4]. In contrast, Balasubramanian and Narasimhan found that the related 8-diazo-7,9-diphenylcyclopent[a]acenaphthylene 1a undergoes thermal decomposition in benzene affording products involving the intermediacy of the corresponding carbene [5]. In continuation to our interest in the carbene chemistry [6–8], carbene 1 was the subject of the present study to shed more light on its spin states and chemical reactivity since no detailed mechanistic study has been reported with regard to 1. (Scheme 2)

2. Results and discussion

The diazoprecursor 1a of 7,9-diphenylcyclo-8H-pent[a] acenaphthyleny-lidene (1) was prepared through five reaction steps starting from dibenzyl ketone and acenaphthenequinone [9,10].

Irradiation of 1a and trapping the carbene 1 in different quenchers such as styrene (2), styrene derivatives (*p*-methyl styrene (3), *p*-methoxystyrene (4), *p*-chlorostyrene (5) and *trans*-β-methylstyrene (6)), 2,3-dimethyl-1,3-butadiene (7) gave the products indicated in Scheme 2 and Table 1.

The photolysis of 1a was controlled by TLC technique, the products were separated by column chromatography and the results are summarized in Table 1.

Table 1 shows that irradiation of 1a in styrenes 2–6 gave the corresponding spirocyclopropane derivatives 8–12 as major products, in addition to 7,9-diphenyl-8H-cyclopent[a] acenaphthylene (13) and the dimer 14 in trace amounts. The structures of 8–13 were confirmed by elemental analysis, mass spectrometric analysis, ^{1}H NMR and ^{13}C NMR spectra (Section 3) Table 2.

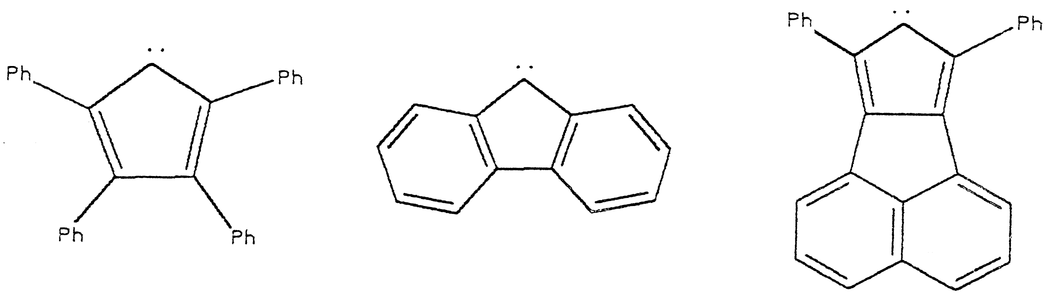
The ^{1}H NMR spectra of compounds 9–11 as well as the ^{13}C NMR and mass spectra were consistent with a spirocyclopropane structure.

The formation of the cyclopropane adducts 8–12 in addition to the 7,9-diphenyl-8H-cyclopent[a]acenaphthylene 13 and the dimer 14 indicates that both singlet and triplet spin states are reactive under these conditions.

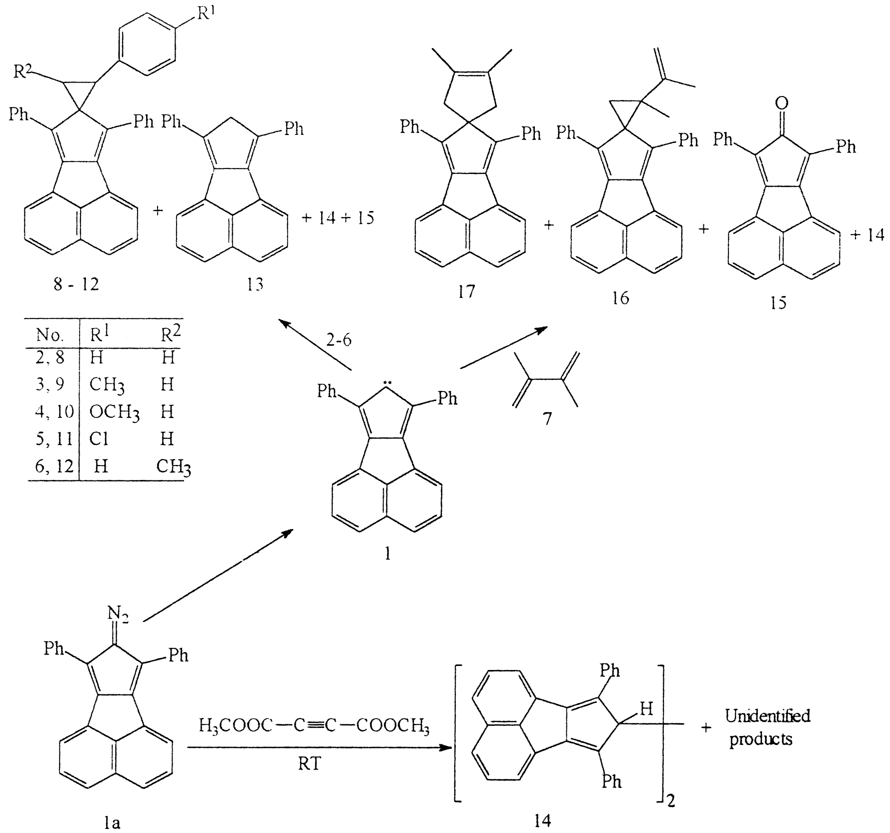
---

* Corresponding author. Fax: +20-88-312564.
E-mail address: aawahab@aun.eun.eg (A.-M.A. Abdel-Wahab)

1010-6030/00/$ – see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S1010-6030(00)00210-0



Scheme 1.



No.	R1	R2
2, 8	H	H
3, 9	CH_3	H
4, 10	OCH_3	H
5, 11	Cl	H
6, 12	H	CH_3

Scheme 2. Photolysis and thermolysis of 1a in different trapping agents.

2.1. *Multiplicity of* 1

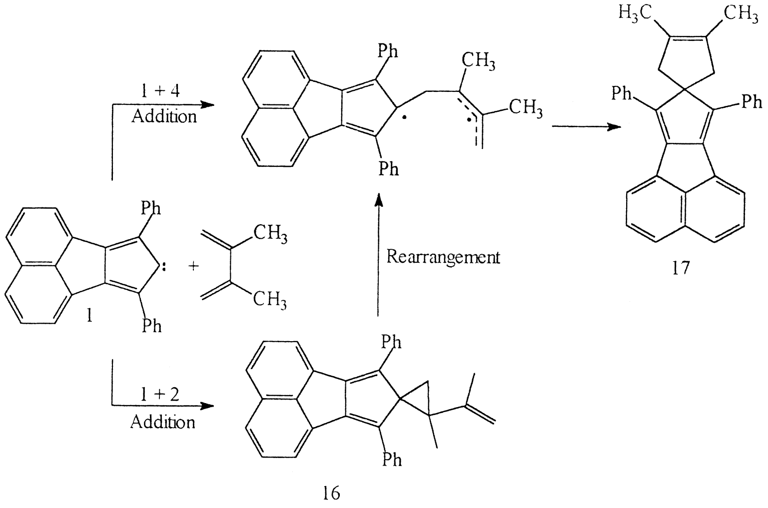
Irradiation of 1a in 2,3-dimethyl-1,3-butadiene as triplet trapping agent gave the corresponding spirocyclopropane adduct 16 in 47% yield. The ^{1}H NMR spectrum of this adduct showed peaks at δ=1.59 ppm (s, 3H, CH_3 at C-6′), 1.61 ppm Is (s, 3H, CH_3 at C-7′), 2.48 (d, 1H, H_A, J_{BA}=16.95 Hz), 2.82 (d, 1H, H_C, J_{DC}=19.62 Hz), 3.11 (d, 1H, H_D, J_{CD}=19.62 Hz) and 3.28 ppm (d, 1H, H_B, J_{AB}=16.95 Hz).

Table 1
Photolysis of 1a in different trapping agents

Trapping agent	Time (h)	Products (yield %)
Styrene	2.5	8 (31), 13 (6), 14 (3)
p-Methylstyrene	3.0	9 (19), 13 (4), 14 (6)
p-Methoxystyrene	2.5	10 (16), 13 (5), 14 (4)
p-Chlorostyrene	2.5	11 (31.9), 13 (4), 14(trace)
Trans-β-methylstyrene	3.5	12 (28), 13 (28), 15 (4)
2,3-Dimethyl-1,3-butadiene	2.5	16 (47), 17 (14), 14 (5) 15 (4)

The ^{13}C NMR spectrum revealed two peaks at δ=18.92 ppm and 19.10 ppm for two methyl groups (C-6′and C-7′). Also, two methylene groups appeared at δ=32.60 ppm and 41.38 ppm for C-3′and C-5′. In addition, ^{13}C-DEPT technique was applied to confirm the origin of these peaks [11].

Interestingly, another compound 17 was separated by column chromatography from the photolysate and identified as a 1,4-adduct. Mass spectrum of this compound 17 gave a molecular ion peak at *m*/*z*=422, also representing the base peak.



Scheme 3.

Significantly, the ^{13}C NMR spectrum of this product showed three types of aliphatic carbons at δ=13.7 ppm (C-6′, C-7′, 2CH$_3$), 46.68 ppm (C-2′, C-5′, 2CH$_2$) and at 68.00 ppm (C-I′). Also, ^{13}C-DEPT technique was used to support the hypothesis connecting the type and position of the aliphatic carbons C-1′, C-2′, C-5′, C-6′ and C-7′. Accordingly, compound 17 could be identified as a 1,4-addition product of the carbene 1 with 2,3-dimethyl-1,3-butadiene. This 1,4-addition can occur either from the triplet state or via formation of 17 by a thermal rearrangement of 16 (Scheme 3) [12,13].

In addition to the investigation of the multiplicity of 7,9-diphenyl-8H-cyclopent[a]acenaphthylenylidene (1) via interaction with the triplet scavenger 2,3-dimethyl-1,3-butadiene, the stereospecificity of the addition of 1 to *trans*-β-methylstyrene has been checked. On irradiation of 1a in pure *trans*-β-methylstyrene and separation of the photolysis mixture by column chromatography the spirocyclopropane adduct 12 (13%) was obtained.

The ^{1}H NMR spectrum of 12 revealed aliphatic protons at δ=1.87 ppm (d, 3H, CH$_3$, J_{AB}=4.98 Hz), 3.08 ppm (m, 1H, H$_A$) and 3.69 ppm (d, 1H, H$_C$, J_{AC}=8.50 Hz). Also, 7,9-diphenyl-8H-cyclopent[a]acenaphthylene 13 (28%) was separated and identified using NMR, TLC with an authentic sample and elemental analysis. The third product was the ketone 15 (4%). It could be formed by oxygen trapping.

Table 2
Competition experiments: photolysis of 1a in equimolar mixtures of styrene (2) and *p*-substituted styrenes (3–5)

R	k_{rel}	log k_{rel}	σ_P	σ_p^+
p-OCH$_3$	0.53	−0.27	−0.27	−0.78
p-CH$_3$	0.62	−0.21	−0.17	−0.31
H	1.00	0.00	0.00	0.00
p-CI	1.09	0.04	0.24	0.11

In conclusion, the formation of 7,9-diphenyl-8H-cyclopent[a]acenaphthylene 13 and the dimer 14 during the reaction of 1 with styrenes and the formation of the 1,4-addition product 17 with 2,3-dimethyl-1,3-butadiene indicates that carbene 1 reacts as a diradical through hydrogen abstraction or dimerization. The separation of only the *trans*-spirocyclopropane adduct 12, and the absence of *cis*-adduct indicates that the reactive spin state of carbene 1 with styrenes is the singlet one [14–20].Therefore, carbene 1 is an example for the existence of singlet–triplet equilibrium in aryl carbenes.

2.2. Selectivity of 1

As pointed out before, photolysis or thermolysis of the diazo compound 1a generates the corresponding carbene 1. In carbenes, the carbon atom has two high-lying orbitals. The addition of a carbene to an olefin could be represented by (a) and (b), for electrophilic and nucleophilic carbenes, respectively. So, the electrophilic carbene adds through p orbital (LUMO),and the nucleophilic carbene through σ orbital (HOMO) [21]. Electron-donating substituents on the carbene raise the LUMO energy, stabilize the carbene and increase the carbene selectivity, whereas electron withdrawing groups lower the LUMO energy and decrease selectivity.

As discussed before, carbene 1 has been added to styrenes 2–5 and gave cyclopropane products 8–11. Therefore, the selectivity of this carbene has been tested by determining the k_{rel} of the substituted spirocyclopropane with respect to the parent compound, obtained via irradiation of the diazo precursor in styrene and substituted styrenes (Fig. 1).

The k_{rel} values were plotted versus the Hammett constants [22] (σ_p or σ_p^+) using the simple equation:

$$\log\ k_{rel} = \rho\,\sigma$$

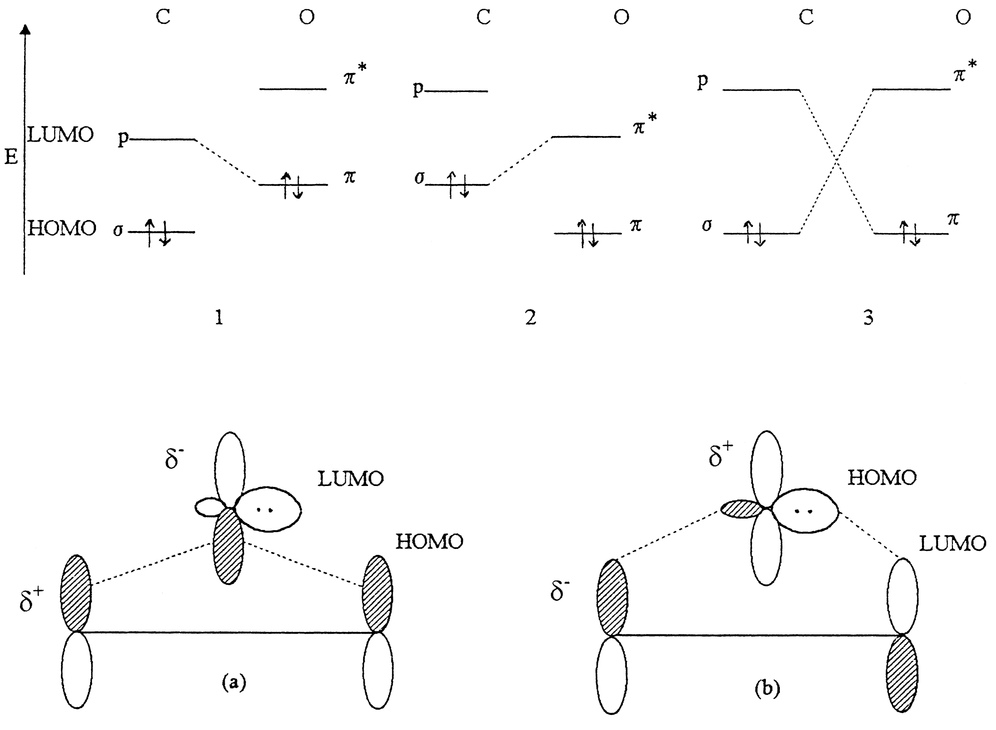


Fig. 1. Orbital interaction between carbene (C) and olefin (O).

Fig. 2 showed a linear correlation between k_{rel} and σ_{p} or σ_{p}^{+}. The reaction constant has a positive value (ρ=0.38) which indicated that carbene 1 reacts with styrenes as nucleophilic carbene and according to FMO theory [21], i.e. the interaction between carbene 1 and styrene (olefin) occurred by HOMO_{C}-LUMO_{O} interaction.

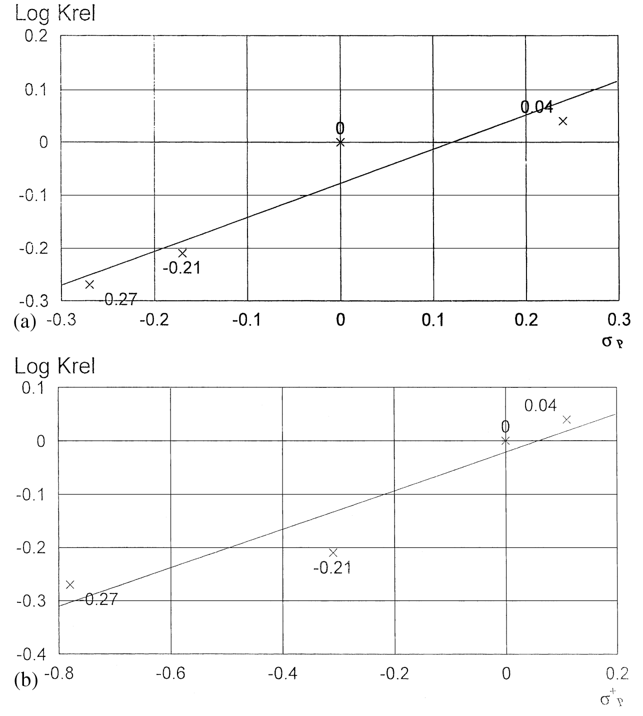


Fig. 2. Hammett correlation for the addition of carbene 1 to styrenes. (a): Relationship between $\log k_{\text{rel}}$ and σ_{p}; (b): relationship between $\log k_{\text{rel}}$ and σ_{p}^{+}.

3. Experimental

3.1. Instruments

3.1.1. Mass spectra (MS)

These analysis were carried out on Mass Spectrometer MAT-311(Varian) with electron energy 70 eV.

3.1.2. ^{1}H Nuclear magnetic resonance spectra (^{1}H NMR)

^{1}H NMR spectra were recorded on 400 Aspect 3000, Bruker (400 MHz) in the suitable deuteriated solvent using TMS as internal standard.

3.1.3. ^{13}C Nuclear magnetic resonance spectra (^{13}C NMR)

Were recorded also on 400 Aspect 3000, Bruker (400 MHz).

3.1.4. Ultraviolet spectra (UV)

UV analyses were effected on a Shimadzu double-beam Spectrophotometer UV-200 S.

3.1.5. Elemental analysis

These were carried out by Ultramikroschnell-method using Walisch Elemental Analyser Model 1106 Carlo Erba Strumentatione.

3.1.6. Photolysis systems

All the photolytic reactions were carried out in a 20 ml pyrex glass cell fitted with a side arm and an internal cooling tube and externally irradiated with a Hanovia high pressure mercury lamp (450 W) using pyrex filter and the whole system was contained in an aluminum container which serves as a light reflector.

3.1.7. Materials used

Dibenzyl ketone, acenaphthenequinone, styrene 2, *p*-methylstyrene 3, *p*-methoxystyrene 4, *trans*-β-methylstyrene 6 and 2,3-dimethyl-1,3-butadiene 7 were purchased from Aldrich. *p*-Chlorostyrene 5 was prepared as described in the literature [23].

3.2. Reaction of 7,9-diphenylcyclopent[a]acenaphthylenylidene 1 in different quenchers

A weighed amount of 8-diazo-7,9-diphenylcyclopent[a] acenaphthylene 1a was suspended in a certain volume of the quencher and placed in the photolysis cell. The mixture was photolyzed, using the Hanovia high pressure mercury lamp (450 W), while continuous magnetic stirring. The reaction was monitored with TLC technique.

At the end of photolysis, the contents of the cell were quantitatively transferred into a distillation flask. The excess quencher was distilled under vacuum and the residue was separated by column chromatography on silica gel. The products were identified using IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis techniques. Results are tabulated in Table 1.

4. Photolysis of 1a styrene

A suspension of 0.40 g (1.086×10^{-3} mole) of 1a in 20 ml styrene was irradiated for 2.5 h and was monitored with TLC. The excess of styrene was distilled under vacuum and the residue was separated by column chromatography on silica gel and petroleum ether (40–60°C) as eluent. The first fraction was 7,9-diphenyl-8H cyclopent[a]acenaphthylene 13, 0.02 g, 6%; mp: 222°C [7] mp 220–221°C, identified by comparison with an authentic sample using TLC technique.

The second fraction was 7,9-diphenylcyclopent[a]acenaphthylene-8-spiro-1′-(2′-phenyl)cyclopropane 8, 0.15 g, 31%; mp: 200°C; IR (KBr): 3060 cm^{-1} (CH of cyclopropane ring), 3040 cm^{-1} (CH aromatic), 1600 cm^{-1} (C=C aromatic); ^{1}H NMR ($CDC1_3$): δ (ppm)=2.36 (d, d, 1H, H_A, J_{BA}=8.4, J_{CA}=9.2 Hz), 2.75 (d, d, 1H, H_B, J_{AB}=8.4, $J_{CB=}$8.8 Hz), 3.01 (t, 1H, H_C, J_{BC}=8.8, J_{AC}=9.2 Hz), 6.74–7.61 (m, 21H, aromatic). Elemental analysis for $C_{35}H_{24}$ (444): calcd.: C 94.59; H 5.4; found: C 94.22; H 5.38.

The third fraction was the dimer 14 of yellow fluorescent colour (0.023 g, 3%), mp: >295°C (decomp.); ^{1}H NMR ($CDCI_3$): δ (ppm)=5.73 (d, 2H, 2CH, J=7.43 Hz), 7.00–7.50 (m, 23H, aromatic); MS: *m*/*z*: 682 [$(M)^{+\bullet}$, 22.2%], 680 [$(M-H_2)^+$, 100%].

5. Photolysis of 1a in *p*-methylstyrene

In 20 ml of *p*-methylstyrene, 0.30 g (8.15×10^{-4} mole) of 1a was suspended and irradiated for 3 h. The reaction mixture was treated as before. The first product 13 was eluted with petroleum ether (40–60°C) (0.01 g, 4%); mp: 223°C [7] mp 220–221°C). The second product was 7,9-diphenylcyclopent[a]acenaphylene-8H-spiro-1′-[2′-(*p*-methylphenyl)]cyclopropane (9, 0.07 g, 19%); mp: 173–175°C; IR (KBr): 3070 cm^{-1} (CH of cyclopropane ring), 3040 cm^{-1} (CH aromatic), 1600 cm^{-1} (C=C aromatic); ^{1}H NMR ($CDCI_3$): δ (ppm)=2.16 (s, 3H, CH_3), 2.34–2.38 (d, d, 1H H_A, J_{BA}=8.40, J_{CA}=9.12 Hz), 2.75 (d, d, 1H, H_B, J_{AB}=8.40, J_{CB}=8.77 Hz), 2.99 (t, 1H, H_C, J_{AC}=9.12, J_{BC}=8.77 Hz), 6.09–7.63 (m, 20H, aromatic). Elemental analysis for $C_{36}H_{26}$ (458): calcd.: C 94.3; H 5.68; found: C 93.8; H 5.65.

The third fraction was the dimer (14, 0.03 g, 6%) mp: >297°C (decomp.).

6. Photolysis of 1a in *p*-methoxystyrene

As in the case of *p*-methylstyrene, 0.30 g (8.15×l0^{-4} mole) of 1a was suspended in 20 ml *p*-methoxystyrene and irradiated as in the general procedure.

The first separated product was 13 (0.0l 5 g, 5%) and the second product was 7,9-diphenylcyclopent[a]acenaphthylene-8H-spiro-1′[2′(*p*-methoxy-phenyl)]cyclopropane (10, 0.06 g, 16%) eluted with petroleum ether (40–60°C)/benzene mixture (20:1); mp: 175°C; IR (KBr): 3070 cm^{-1} (CH of cyclopropane ring), 3030 cm^{-1} (CH aromatic), 1600 cm^{-1} (C=C aromatic); ^{1}H NMR ($CDCI_3$): δ (ppm)=2.35 (d, d, 1H, H_A, J_{BA}=8, J_{CA}=9 Hz), 3.74 (s, 3H, OCH_3), 6.6–7.7 (m, 20H, aromatic); MS: *m*/*z*=474 [$(M)^{+\bullet}$, 100%], 366 [$(M-C_7H_7O)^{+\bullet}$, 57.7%]. Elemental analysis for $C_{36}H_{26}O$ (473): calcd.: C 91.10; H 5.48; C 91.50; H 5.21.

Finally, the dimer 14 was also eluted with petroleum ether/benzene mixture (10:1) and identified (0.02 g, 4%).

7. Photolysis of 1a in *p*-chlorostyrene

A suspension of 0.30 g (8.15×10^{-4} mole) of 1a in 20 ml of *p*-chlorostyrene was irradiated for 2.75 h and monitored with TLC. The excess *p*-chlorostyrene was distilled and the residue was separated on silica gel column chromatography. The first separated product 13 was eluted with petroleum ether (40–60°C)/benzene mixture (25:1), (0.0l g, 4%). The second product 7,9-diphenylcyclopent[a]acenaphthylene-8H-spiro-1′-[2′-(*p*-chlorophenyl)]cyclopropane 11 was eluted with petroleum ether/benzene mixture (25:2), (0.124 g, 31.9%); mp: 120°C and was identified by ^{1}H NMR ($CDCI_3$): δ (ppm)=2.38 (m, 1H, H_A), 2.74 (m, 1H, H_B), 2.94 (t, 1H, H_C), 6.7–7.8 (m, 20H, aromatic). the dimer 14 was separated in trace amount.

8. Photolysis of 1a in trans -β-methylstyrene

In 20 ml *trans*-β-methylstyrene, 0.25 g (6.8×l0^{-4} mole) of 1a was suspended and the mixture was irradiated 3.5 h and the reaction was controlled by TLC. The reaction mixture was treated as described before. The hydrocarbon 13 was the first eluted product with petroleum ether (40–60°C) yield (0.08 g, 28%); mp: 224°C ([9] mp; 228°C); ^{1}H NMR ($CDCI_3$): δ (ppm): 4.41 (s, 2H, CH_2), 7.11–8.05 1m, 16H, aromatic). Elemental analysis for $C_{27}H_{11}$ (342): calcd.: C 94.70; H 5.26; found; C 93.96; H 5.52.

Also, from petroleum ether (40–60°C), 7,9-diphenylcyclopent[a]acenaphthylene-8H-spiro-1′-(*trans*-2′-methyl-3′-phenyl)cyclopropane 12 was separated (0.04 g, 13%) ^{1}H NMR ($CDCI_3$): δ (ppm)=1.17 (d, 3H, CH_3, J_{AC}=4.98 Hz), 3.08 (m, 1H, H_A), 3.69 (d, 1H H_C, J_{AC}=8.5 Hz), 6.10–7.87 (m, 21H, aromatic). The third product was the ketone 15, identified using authentic sample (0.0l g, 4%).

9. Photolysis of 1a in 2,3-dimethyl-1,3-butadiene

A 0.20 g (6.79×10^{-4} mole) of 1a was suspended in 20 ml 2,3-dimethyl-1,3-butadiene and photolyzed for 2 h and 30 min. The photolysate was treated as before to give 7,9-diphenylcyclopent[a]acenaphthylene-8H-spiro-1′-(3′,4′-dimethylcyclopent-3′-ene) 17, eluted with petroleum ether (40–60°C), (0.04 g 14%); mp: 222°C; ^{1}H NMR ($CDCI_3$): δ (ppm)=1.64 (s, 6H, $2CH_3$), 2.94 (s, 4H, $2CH_2$), 7.24–7.82 (m, 16H, aromatic);^{13}C NMR ($CDCI_3$): δ (ppm)=13.7 (C-6′, C-7′, $2CH_3$), 46.68 (C-2′, C-5′, $2CH_2$), 68.0 (C-8,1′), 118.9–146.26 (26C, aromatics); MS: *m*/*z*=422 [(M)$^{+\bullet}$, 100%], 407 [(M−CH_3)$^{+\bullet}$, 28%], 392 [(M−CH_3)$^{\bullet}$, 7.22%]. The second product was 7,9-diphenylcyclopent[a]acenaphthylene-8H-spiro-1′-(2′-methyl-2′-propen)cyclopropane (16, 0.13 g, 47%), mp: 125°C; IR (KBr); 3070 cm^{-1} (CH of cyclopropane ring), 3040 cm^{-1} (CH aromatic), 2940, 2860, 2880 cm^{-1} (CH_2, CH_3), 1600 cm^{-1} (C=C aromatic); ^{1}H NMR ($CDCI_3$); δ (ppm)=1.59 (s, 3H, CH_3 at C-6′), 1.61 (s, 3H, CH_3 at C-7′), 2.48 (d, 1H, H_A, J_{AB}=16.95 Hz), 2.82 (d, 1H, H_C, J_{DC}=19.62 Hz), 3.1 (d, 1H, H_D, J_{CD}=19.62 Hz), 3.28 (d, 1H, H_B, J_{AB}=16.95 Hz), 7.14–7.68 (m, 16H, aromatics); ^{13}C NMR ($CDCI_3$); δ (ppm)=18.92 (C-6′), 19.1 (C-7′), 32.6 (C-3′), 41.38 (C-5′), 56.0 (C-8,1′), 120.80–157.57 (26C, aromatic). The dimer 14 was the third product and also eluted with petroleum ether (0.02 g, 5%); mp: >295°C; ^{1}H NMR ($CDCI_3$); δ (ppm)=5.72 (d, 2H, 2CH, *J*=7.43 Hz), 7.07–7.58 (m, 34 H, aromatics); MS: *m*/*z*=682 [(M)$^{+\bullet}$, 22,2%], 680 [(M - 2H)$^{+\bullet}$, 100%]. The last product was the ketone (15, 0.01 g, 4%); mp: 289°C [24] mp: 289–290°C.

10. Reaction of 1a with dimethyl acetylenedicarboxylate

A suspension of 0.20 g (5.43×10^{-4} mole) of 1a in 20 ml ether was placed in a round bottom flask and magnetically stirred. A few drops of dry methylene chloride were added until the diazo compound 1a was dissolved and then 0.15 g (1.05×l0^{-3} mole) of dimethyl acetylenedicarboxylate was added with stirring. The flask was fitted with calcium chloride drying tube and stirred in the dark at room temperature for 2 h and then allowed to stand for 1 week and monitored with TLC technique. Then the excess of solvent was evaporated and the residue was washed with petroleum ether. Only a yellow substance was separated which was identified as the dimer 14 in small amount (0.02 g, 5%); mp: >295°C (decompn.): ^{1}H NMR ($CDC1_3$); δ (ppm)=5.64 (d, 2H, 2CH, *J*=7.43 Hz), 7.00–7.51 (m, 34H, aromatics). TLC analysis of the filtrate indicated the presence of another unidentified products.

Acknowledgements

We thank the Egyptian Government (O.S. Mohamed) and the DAAD Foundation (A.A. Abdel-Wahab) for their generous support. Thanks are also given to P. Schwarz for his help in the NMR spectra.

References

[1] W. Ando, in: Saul Patai (Ed.), The Chemistry of Diazonium and Diazo Groups, Wiley, New York, 1978, p. 342.
[2] H. Durr, G. Scheppers, Liebigs Ann. Chem. 734 (1970) 141.
[3] H. Durr, Houben Weyl, Vol. lV/5b and El 9b, Thieme Verlag, Stuttgart, 1975, p. 1158 and 1989, p. 775.
[4] D. Lloyd, F. Wasson, J. Chem. Soc., 1966, 408.
[5] P. Balasubramanian, K. Narasimhan, Tetrahedron Lett. 22 (1981) 685.
[6] A.A. Abdel-Wahab, S.H. Doss, H. Durr, N.J. Turro, I.R. Gould, J. Org. Chem. 52 (1987) 429.
[7] S.H. Doss, A.A. Abdel-Wahab, E.M. Fruhauf, H. Durr, I.R. Gould, N.J. Turro, J. Org. Chem. 52 (1987) 434.
[8] A.A. Abdel-Wahab, M.T. Ismail, O.S. Mohamed, H. Durr, Y. Ma, Liebigs Ann. Recueil, 1997, 1611, 1618.
[9] Ya.N. Kreitsberga, O.Ya. Neil, Zh. Org. Khim. 14 (1978) 1640.
[10] M. Regitz, A. Liedhegener, Tetrahedron 23 (1967) 2701.
[11] C.H. Hoder, C.D. Schaeffer, Jr., The Introduction to Multinuclear NMR, Theory and Application, The Benjamin/Cummings Publishing Company, Menlo Park, California, 1987.
[12] A. Hackenberger, H. Durr, Chem. Ber. 117 (1984) 2644.
[13] A. Hackenberger, H. Durr, Tetrahedron Lett., 1979, 4541.
[14] H. Durr, Top. Curr. Chem. 40 (1973) 103.
[15] H. Durr, Top. Curr. Chem. 55 (1975) 87.
[16] P.S. Skell, R.C. Woodworth, J. Am. Chem. Soc. 78 (1956) 4496.

[17] P.S. Skell, R.C. Woodworth, J. Am. Chem. Soc. 81 (1959) 3383.
[18] N. Bodor, M.J.S. Dewar, J.S. Wasson, J. Am. Chem. Soc. 94 (1972) 9095.
[19] M.J.S. Dewar, R.C. Haddon, P.K. Weiner, J. Am. Chem. Soc. 96 (1974) 254.
[20] P.P. Gaspar, C.T. Lin, B.L. Whitsel Dunbar, D.P. Mack, P. Balasubramanian, J. Am. Chem. Soc. l06 (1984) 2128.
[21] R.A. Moss, Acc. Chem. Res. 13 (1980) 58.
[22] L.P. Hammett, Physikalische Organische Chemie, Verlag Chemie, Weinheim, 1973.
[23] R. Bross, M. Anteunis, Synthetic Communication 6 (1976) 53.
[24] W. Dilthey, S. Henkels, A. Schfafer, J. Prakt. Chem. 151 (1938) 97.