# Photochemical Decomposition of Benzocyclobutenone *p*-Toluenesulfonylhydrazone

Aryeh A. Frimer,* Joseph Weiss, and Zilpa Rosental

*The Ethel and David Resnick Chair in Active Oxygen Chemistry, The Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel*

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The photochemical decomposition of benzocyclobutenone *p*-toluenesulfonylhydrazone led to a wide variety of products including the *E*- and *Z*-isomers of 1,1′-bi(benzocyclobutenylidene) **6a**; *cis–trans*-benzocyclobutenylidene trimer **7**; cyclohepatrienes **8–10**; benzocyclobutenone azine in it's *anti–anti* (**11**), *anti–syn* (**12**), and *syn–syn* conformations (**13**); *anti*- and *syn*-benzocyclobutenone *N*-benzocyclobutenyl-*N*-tosylhydrazone (**14** and **15**, respectively); (benzocyclobutenyl)hydrazine (**16**); benzocyclobutenyl *p*-tolyl sulfone (**17**); and benzocyclobutenone **1**. Their isolation, identification and mechanism of formation are discussed. The data indicate that while the addition of arylcarbenes to alkenes results in the preferential formation of the more-hindered *syn* products, arylcarbene **5** adds to aryl olefins (styrenes and dimer **6**) in a stereospecific *anti* orientation to give the less-hindered product. In addition, the minimal steric effects observed in these systems presumably results from the 90° angle of the cyclobutyl ring, which pulls the phenyl ring back and thus minimizes its steric contribution.

## Introduction

As part of our ongoing interest in the photooxidation of ring-strained olefins,[1] we felt it of value to study the oxygenation reactions of alkylidenebenzocyclobutenes in general and 1,1′-bi(benzocyclobutenylidene) [**6a**, *E*- and *Z*-isomers; see Figure 1] in particular.[1i] We needed, however, a convenient approach to such systems. Methylated analogs **6b** and **6c** have been synthesized by the dimerization of the related carbenes (**5**), generated *in situ* in the condensed phase via the photolysis of the corresponding benzocyclobutenone *p*-tosylhydrazone salt (**2**, Figure 1).[2] Interestingly, the photolytic approach generates bi(benzocyclobutenylidenes) in a 32–52% yield, but little information is given about the fate of the remaining 50–70%. Furthermore, there has been no similar photochemical preparation reported for **6a**. We decided, therefore, to explore the UV photolysis of **2a**.[2f] While this indeed proved to be a facile route to **6a** (in a 46% yield),[3] a plethora of interesting side-products corresponding to the remaining 54% were formed as well. Their isolation, identification, and mechanism of formation are discussed below.

## Results and Discussion

**A. Photolysis.** UV photolysis of the sodium salt of benzocyclobutenone *p*-tosylhydrazone[2d] (**2a**) in benzene yielded not only the desired *E*- and *Z*-isomers of 1,1′-bi-(benzocyclobutenylidene) [**6a-*E*** and **6a-*Z***, in a 25 and 20% yield, respectively], but also trimer **7** (20% yield) and eleven other minor products containing one or more benzocyclobutenyl units (see Figure 2). A small amount of *p*-toluenesulfonic acid was also isolated. Of the 14 isolated products, the isomeric bi(benzocyclobutenylidenes) **6a-*E*** and **-*Z***,[2d,3] benzocyclobutenone (**1a**),[2d] cycloheptatrienes **8–10**,[4] and azines **11–13**[2d] are all known compounds. The remaining five, trimer **7**, isomeric tosylhydrazones **14** and **15**, cyclobutylhydrazine **16**, and *p*-tolyl sulfone **17**, were identified by their spectral data, and in the latter cases by independent synthesis. The respective yields were determined from an analysis of the $^1$H NMR spectrum of the crude reaction mixture and are based on the relative number of benzocyclobutene units incorporated into the product.

**B. Bi(benzocyclobutenylidenes) 6a-*E* and -*Z*.** In many of the previous studies on the preparation of bi-(benzocyclobutenylidenes), subdividing the product into its respective *E*- and *Z*-isomers, and distinguishing between them, proved to be far from trivial. Durr and co-workers[2d] report separating **6a-*E*** and **-*Z*** by gas chromatography but could not determine which was which. Barton and Shepherd[3] manually separated the crystals and assigned the *E*-configuration to the higher melting isomer. In our hands, we found that Barton and Shepherd's **6a-*E*** could be conveniently isolated from the reaction mixture by fractional crystallization, while **6a-*Z*** and the remaining aforementioned products could then be separated by column chromatography.

Barton and Shepherd's assignments are consistent with the 300-MHz $^1$H NMR data ($CDCl_3$). Three of the four aromatic hydrogens of the *E*-isomer appear as a multiplet

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(1) (a) Frimer, A. A.; Roth, D.; Sprecher, M. *Tetrahedron Lett.* **1977**, 1927–1930. (b) Frimer, A. A.; Farkash, T.; Sprecher, M. *J. Org. Chem.* **1979**, *44*, 989–995. (c) Frimer, A. A.; Roth, D. *J. Org. Chem.* **1979**, *44*, 3882–3887. (d) Frimer, A. A.; Antebi, A. *J. Org. Chem.* **1980**, *45*, 2334–2340. (e) Frimer, A. A. *Isr. J. Chem.* **1981**, *21*, 194–202. (f) Frimer, A. A. *J. Photochem.* **1984**, *25*, 211–226. (g) Frimer, A. A. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; pp 201–234. (h) Frimer, A. A.; Stephenson, L. M. In *Singlet $O_2$* – Volume II: Reaction Modes and Products – Part I; Frimer, A. A., Ed.; Chemical Rubber Co., Boca Raton, FL, 1985; pp 67–91. (i) Frimer, A. A.; Weiss, J. *J. Org. Chem.* **1993**, *58*, 3660–3667.

(2) (a) Blomquist, A. T.; Heins, C. F. *J. Org. Chem.* **1969**, *34*, 2906–2908. (b) O'Leary, M. A.; Wege, D. *Tetrahedron Lett.* **1978**, 2811–2814. (c) Durr, H.; Nickels, H.; Philippi, W. *Tetrahedron Lett.* **1978**, 4387–4390. (d) Durr, H.; Nickels, H.; Pascala, L. A.; Jones, M., Jr. *J. Org. Chem.* **1980**, *45*, 973–980. (e) O'Leary, M. A.; Wege, D. *Tetrahedron* **1981**, 801–811. (f) Durr and co-workers[2d] report the isolation of **6a** in the flash pyrolysis of **2a**; no yield was given.

(3) A Wittig approach to bi(benzocyclobutenylidenes), including **6a**, has recently been reported: Barton, J. W.; Shepherd, M. K. *J. Chem. Soc. Perkin Trans. 1* **1987**, 1561–1565.

(4) O'Leary, M. A.; Richardson, G. W.; Wege, D. *Tetrahedron* **1981**, 813–823.

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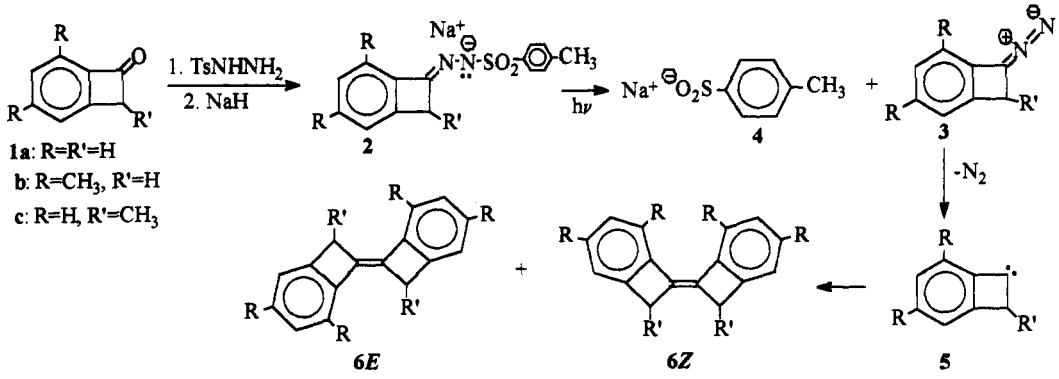



**Figure 1.** Mechanism of formation of **6*E*** and **6*Z***.

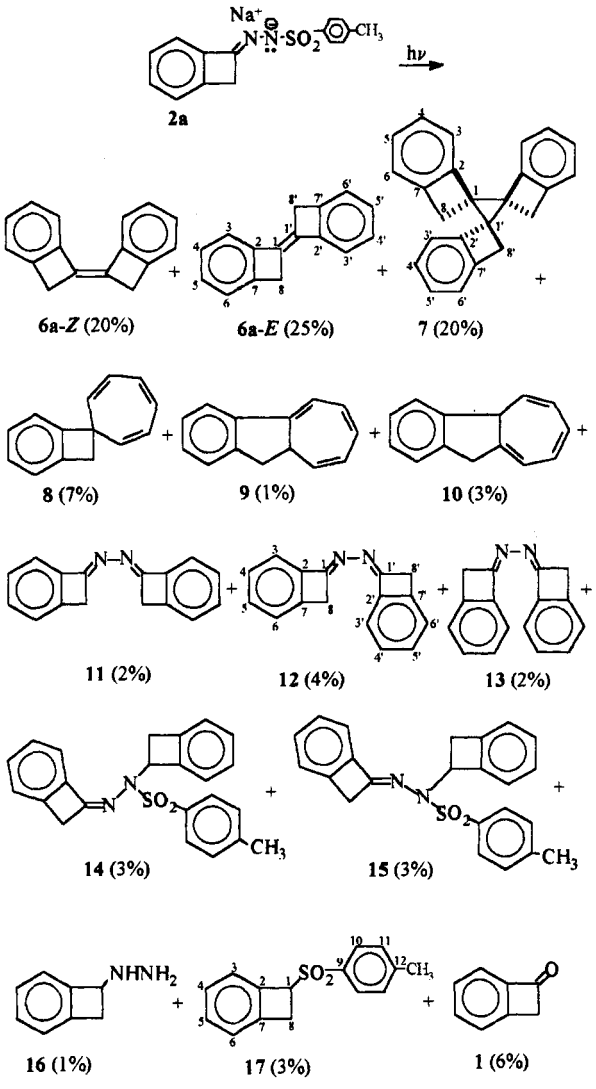
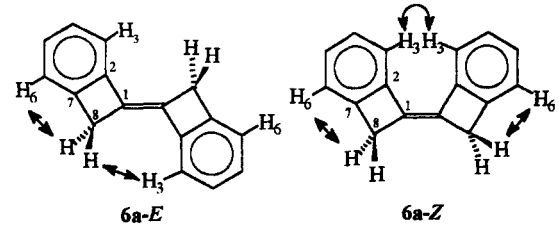



**Figure 2.** Product distribution from the photolysis of tosylhydrazone salt **2a**.

at ca. 7.23 ppm with the remaining hydrogen showing up as a doublet of triplets ($J_{ortho}$ = 7 Hz; $J_{meta}$ = 1 Hz) upfield at 7.13 ppm. By contrast, all four hydrogens in the *Z*-isomer appear relatively downfield as two 2H multiplets centered at approximately 7.30 and 7.22 ppm. This is consistent with the closer proximity of the two aromatic rings in the cis-configuration and the expected diamagnetic deshielding. At the same time, the cyclobutyl methylene hydrogens in the *Z*-isomer are now turned away from the aromatic ring of the neighboring benzocyclobutenylidene moiety and hence appear, as expected, upfield (at 3.712 ppm) from those of the *E*-isomer (3.810 ppm).[5]

Final confirmation of the above identification was based on an NOE experiment on the sample assigned an *E*-configuration by Barton and Shepherd.[3] This experiment first necessitated the assignment of the aromatic protons, which was facilitated by the magnitude of the long-range (benzylic) coupling constants to the cyclobutyl methylene hydrogens (easily identified by decoupling experiments). In the difference NOE experiment,[6] we observed a significant enhancement (ca. 3%) of both aryl hydrogens to the cyclobutane ring, $H_3$ and $H_6$, in eq 1. Only in the *E*-isomer is an enhancement expected not only for the vicinal aryl hydrogen $H_6$, but also across the double bond to the other hydrogen $H_3$. Since the results were essentially identical whether the NOE experiment was performed in $CDCl_3$ or $C_6D_6$ as solvents, we feel confident that these effects are real and that our assignment is reliable.




(1)

**C. Trimer 7.** Perhaps the most exciting discovery in this project is trimer **7** (21% yield), which has not been observed in any of the other bi(benzocyclobutenylidene) preparations. Indeed, even previous attempts to add cyclobutylidene carbene to bicyclobutylidene have reportedly failed.[7] While the reaction of **6a-*E*** with benzocyclobutenylidene carbene **5a** can only yield trimer **7** in an *anti* (cis–trans) configuration, **6a-*Z*** could theoretically generate either the sterically congested *syn* (cis–cis) isomer or it's thermodynamically more stable *anti* analog; only the latter is observed, however. Thus, the $^1H$ NMR spectral data for the six methylene protons of the trimer show the 4 hydrogens of the cis methylenes as an AB

(5) (a) Similarly, in the case of ethylidenebenzocyclobutene,[5b] the *E*-isomer in which the exocyclic methyl group points toward the cyclobutyl ring appears upfield (at 1.76 ppm) as compared to *Z*-isomer in which this methyl group faces the aromatic ring (1.94 ppm). (b) Newsoroff, G. P.; Sternhell, S. *Aust. J. Chem.* **1972**, *25*, 1669–1693, Table 1 (p 1672), entries 15 and 16.

(6) Sanders, J. K.; Mersh, J. P. *Prog. NMR Spectrosc.* **1982**, *15*, 353–400.

(7) (a) Bee, L. K.; Everett, J. W.; Garratt, P. J. *Tetrahedron* **1977**, *33*, 2143–2150. (b) See also Brinker, U. H.; Boxberger, M. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 974–975, footnote 3.

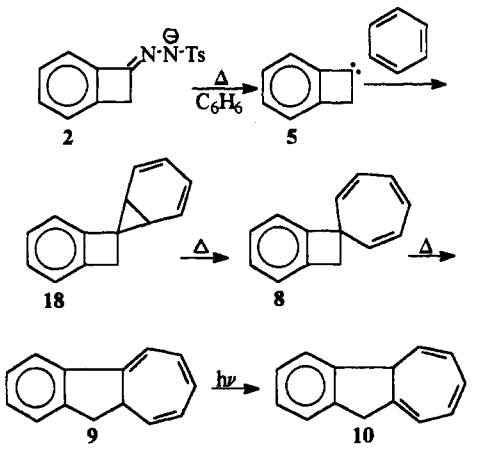



**Figure 3.** O'Leary's scheme for product formation in the thermolysis of **2**.

quartet at 3.48 and 3.41 ppm ($J$ = 13.5 Hz) with a 2H singlet for the trans methylene falling at 3.45 ppm. Similarly the $^{13}C$ NMR reveals two separate sets of benzocyclobutenyl carbons.

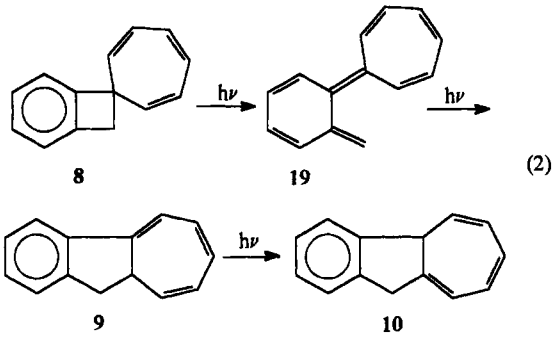
This *anti* stereospecificity is a bit surprising. Previous investigations on the addition of arylcarbenes to alkenes revealed preferential formation of the more-hindered products![8] Closs and Moss[8b,8d,9] have suggested that this phenomenon results from a transition state in which the polarizable aryl electrons interact via van der Waals and London forces with the cis olefinic alkyl substituents. Nevertheless, the secondary interactions involved in the addition of arylcarbenes to arylolefins may be quite different. Indeed, Durr[2d,10] reports that carbene **5b** reacts with styrene yielding the *anti* and *syn* products in a 4:1 ratio. With such a large *anti* preference, it is not surprising that in our case, where two phenyl groups are present in the starting olefin, the addition is essentially stereospecific.

**D. Cycloheptatrienes 8–10.** We turn now to the formation of cycloheptatrienes **8–10**. O'Leary et al.[2b,4] obtained green 9,10-dihydrobenzazulene (**9**) (51% yield) as the sole isolable product from the thermal decomposition of hydrazone **2a** in benzene (see Figure 3). They postulate the intermediacy of spironorcaradiene **18** and spiroheptatriene **8**; the latter, upon independent synthesis, does indeed thermally rearrange to **9** exclusively. In addition, the Australian group reports that **9**, though thermally stable, undergoes facile photochemical rearrangement (even under laboratory light) to the photochemically stable **10**.

As can be seen from Figure 2, the photolysis of **2a** in benzene yields **8**, **9**, and **10** in a 7:1:3 ratio. Upon standing in an NMR tube at room temperature in laboratory light, this ratio becomes 1:1:1 after 30 days and 1:4:4 after 2 months. On the basis of O'Leary's results above, **8** is generating **9** thermally, while **9** produces **10** photochemically, at about the same rate.

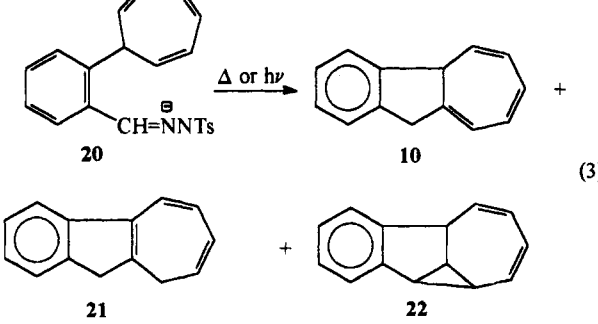
Unlike O'Leary, we are able to isolate **8** in our photochemical system, apparently because of the reduced reaction temperature (ca. 10 °C).[11] Furthermore, the small amount of **9** obtained in the initial reaction mixture is presumably formed thermally during the workup and is not a primary reaction product. Indeed, if care is taken to keep the product mixture below 25 °C during solvent removal, no **9** is observed at all.

In light of the observations described in the previous paragraph, it is unlikely under our reaction conditions (10 °C for 2 h) that **9** is formed thermally in sufficient quantities to be the precursor of **10**. It is probable, then, that **8** is photochemically converted to its *o*-quinodimethane form **19** (eq 2),[12] which cyclizes in turn to **9**. The latter is immediately transformed photochemically into **10**. Consistent with this suggestion, we have found that the product ratio at longer radiation times favors increased formation of **10** at the expense of 8.




(2)

Further, though circumstantial, evidence for this mechanism comes again from the laboratory of O'Leary,[4] who studied the thermolysis and photolysis of the sodium salt of tosylhydrazone **20** in which **10**, **21**, and **22** were formed (eq 3). The product ratio (**10**:**21**:**22**) from the *thermolysis*




(3)

under a variety of conditions is on the average 1:2:5. Were a carbene formed, it would be expected to insert into the benzylic C–H bond generating **8**, which should thermally rearrange in turn to **9**. However, since no **9** is observed, the results were explained by the Australian group by invoking the intermediacy of a pyrazoline. By contrast, when **20** is *photolyzed*, the product ratio is 5:2:6. The dramatic rise in the yield of **10** suggests to us that at least a partial change of mechanism is occurring to generate

(8) (a) Wentrup, C. In *Methoden der Organischen Chemie (Houben-Weyl) – Carbene (Carbenoide)*; Regits, M., Ed.; Georg Thieme: Stuttgart, 1989; Vol. E19b1, pp 824–1021. (b) Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, p 153; see especially pp 187–191. (c) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; p 288. (d) Moss, R. A. *Chem. Eng. News* **1969**, *47* (June 16), pp 60–68; (June 30), pp 50–58.

(9) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042–4053.

(10) (a) Much to our surprise, there do not seem to be any other examples in the literature of the addition of monoarylcarbenes to arylolefins. Prof. Robert Moss (Rutgers) has brought to our attention the work of Doyle et al.[10b] who report that the addition of phenyl chloro carbene (PhCCl) to styrene yields the corresponding diphenylcyclopropane in a *trans*/*cis* ratio of 1.6. However, this carbene always gives *trans* in preference to *cis* and may well involve intermediate ylide formation. (b) Doyle, M. P.; Terpstra, J. W.; Winter, C. H. *Tetrahedron Lett.* **1984**, *25*, 901–904.

(11) Surprisingly, O'Leary and Wege[2b] report that the photochemical decomposition of methylated **2c** in benzene at 10 °C yields only **6c**.

(12) Cf. McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270–276.

carbene. The latter initially forms **8** which is photolyzed, as suggested above, ultimately yielding **10**.

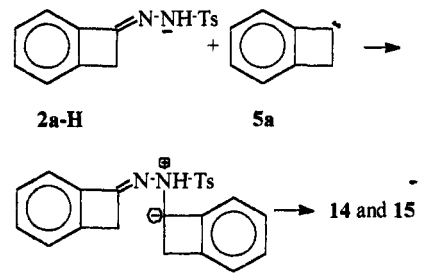
**E. Ketazines 11-13.** Ketazines **11-13** have been suggested,[2d] though never before isolated, as intermediates in the decomposition of **2a**, and are presumably formed via the reaction of carbene **5a** with diazobenzocyclobutene (**3a**).[13] As might be expected this coupling could yield products with either a *syn* or *anti* conformation around the carbon–nitrogen double bond. As seen from Figure 2, all three possible products, **11** (*anti–anti* conformation),[14] **12** (*anti–syn* or *syn–anti*), and **13** (*syn–syn*), are formed. The $^1$H NMR spectrum of the isomeric mixture revealed four methylene singlets at 3.985, 4.005, 4.045, and 4.060 ppm. Four methylene absorptions are also observed in the $^{13}$C NMR spectrum at 41.18, 41.35, 41.58, and 41.64 ppm. Symmetrical isomers **11** and **13** are expected to show only one absorption each for their benzocyclobutenylidene methylenes, while the asymmetrical **12** should have two different methylene resonances. Since the observed peaks are of almost equal size, **11**, **12**, and **13** are presumably formed in a 1:2:1 ratio. The same ratio is obtained when these ketazines are synthesized from benzocyclobutenone and hydrazine.[2d]

This ratio is somewhat surprising, for although this is what would be predicted statistically, it is rarely observed for steric reasons.[15] Thus, in the analogous case of the azines of benzaldehyde, acetophenone, or propiophenone, the only isomer observed has an *anti–anti* arrangement,[15] in which the smaller substituent (H, $CH_3$, or $C_2H_5$) is *syn* to the $\beta$-nitrogen.[14] The controlling factor in the special case of ketazines **11-13** seems to be the 90° angle of the cyclobutyl ring, which pulls the phenyl ring back and thus minimizes its steric contribution.

**F. Tosylhydrazones 14 and 15.** The literature is replete with examples of the electrophilic attack of a carbene on the lone pair of nitrogen in a variety of compounds including amines (eq 4), azo and diazo compounds, and nitriles.[16] Work carried out on the thermal or photochemical decomposition of sulfonylhydrazones sodium salts indicates that a similar alkylation occurs at the singly bonded nitrogen when free hydrazone is present, i.e., when conversion to the salt has been incomplete.[17] A similar sequence involving tosylhydrazone **2a-H** and carbene **5a** could readily explain the formation of isomeric hydrazones **14** and **15** (eq 5).

The two isomers were characterized by their spectral data. The $^1$H and $^{13}$C NMR both reveal the presence of two different cyclobutyl methylene groups in the molecule. Thus, the protons on the methylene to the carbon–nitrogen double bond appear downfield, ca. 3.8 ppm, which is approximately where the methylene protons of hydrazone

$$R_2HN: + R_2C: \rightarrow R_2HN\text{-}\overset{+}{C}R_2\text{-}\overset{-}{:} \rightarrow R_2N\text{-}CHR_2 \quad (4)$$




(5)

**2a** absorb. The protons on the methylene to the carbon–nitrogen single bond absorb more upfield at ca. 3.2 ppm and are coupled to the cyclobutyl methyne hydrogen to nitrogen which is located at ca. 5.4 ppm (approximately where the methyne of benzocyclobutenylhydrazine (**16**) is found; *vide infra*).

We have tentatively assigned **15** the more-congested *syn* conformation based on chemical and spectral considerations. Regarding the former, we have found that **15** slowly isomerizes in chloroform solution at room temperature to **14**, suggesting that the former is in the less thermodynamically stable *syn* conformation. In addition, in the *anti* conformation, the cyclobutyl methylene to the carbon–nitrogen double bond is turned toward the locus of steric congestion; the resulting $\gamma$-effect would be expected to shift the $^{13}$C NMR absorption of this methylene upfield as compared to the *syn* analog. Indeed, this methylene appears at 41.88 ppm in **14** as compared to 43.22 ppm in **15**. While this effect may seem small, we note that all the other corresponding cyclobutyl ring carbons of the two isomers have *identical* absorptions (±0.05 ppm).

**G. Benzocyclobutenone 1, Hydrazine 16, and *p*-Tolyl Sulfone 17.** Benzocyclobutenylhydrazine (**16**) was identified based on its spectral data which is comparable to that observed for the corresponding amine.[18] The formation of hydrazines in the decomposition of tosylhydrazones is unprecedented, nor can we suggest a straightforward mechanism for the surprising formation of this product.

Regarding the generation of benzocyclobutenone **1**, Durr,[2d] Nozaki,[17c] and Wilt[17f] have also observed the formation of ketone in the decomposition of their respective tosylhydrazones. They attribute this to an electophilic attack of the carbene on an oxygen of the tosyl group of the starting material[2d] or the sulfinate ion (**4**),[17c,17f] formed during carbene generation, followed by disproportionation. In support of the latter suggestion, Nozaki and Wilt have isolated *p*-tolyl *p*-toluenethiosulfonate (*p*-Tol-SO-S-*p*-Tol) and/or *p*-tolyl disulfide (*p*-Tol-SS-*p*-Tol), presumably the products of an oxidation–reduction process, from their reaction mixtures (eqs 6 and 7).[17c,17f]

$$RCH: + {}^-O\text{-}SO\text{-}p\text{-}Tol \rightarrow RCH\text{-}O\text{-}SO\text{-}p\text{-}Tol \rightarrow \quad (6)$$

$$RCH{=}O + [{}^-O\text{-}S\text{-}p\text{-}Tol] \rightarrow p\text{-}Tol\text{-}SO\text{-}S\text{-}p\text{-}Tol + p\text{-}Tol\text{-}SS\text{-}p\text{-}Tol \quad (7)$$

*p*-Tolyl sulfone formation in the course of the photochemical or thermal decomposition of tosylhydrazone salts

(13) See ref 2d and ref 8c, pp 415–417.

(14) Unfortunately, there is little uniformity in the literature regarding the assignment of *syn* and *anti*. In this paper, we have utilized the Cahn–Ingold–Prelog rules. Thus, based on an analogy to the azine of acetophenone, the aromatic ring of the benzocyclobutenylidene moiety has been given priority over the cyclobutyl methylene.

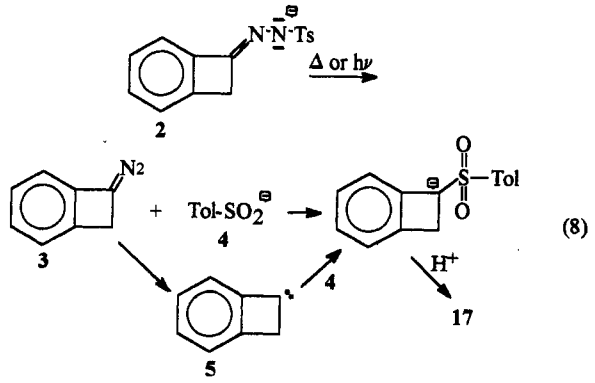
(15) (a) Fleming, I.; Harley-Mason, J. *J. Chem. Soc* **1961**, 5560–5561. (b) Elguero, J.; Jacquier, R.; Marzin, C. *Bull. Soc. Chim. Fr.* **1968**, 713–732; **1969**, 1375–1378. (c) Kolbah, B.; Koruncev, D. In *Methoden der Organischen Chemie (Houben-Weyl) – Stickstoff Verbindungen I*; Stroh, R., Ed.; Georg Thieme: Stuttgart, 1967; Vol. 10, part 2, pp 89–120.

(16) See ref 8c, pp 409–420.

(17) (a) Dornow, A.; Bartsch, W. *Justus Leibigs Ann. Chem.* **1957**, *602*, 23–36. (b) Lemal, D. M.; Fry, A. J. *J. Org. Chem.* **1964**, *29*, 1673–1676. (c) Nozaki, H.; Noyori, R.; Sisido, K. *Tetrahedron* **1964**, *20*, 1125–1132. (d) Wilt, J. W.; Schneider, J. A.; Dabek, H. F., Jr.; Kraemer, J. F.; Wagner, W. A. *J. Org. Chem.* **1966**, *31*, 1543–1551. (e) Leznoff, C. C. *Can. J. Chem.* **1968**, *46*, 1152–1153. (f) Reference 17d, footnote 14.

(18) Bubb, W. A.; Sternhell, S. *Aust. J. Chem.* **1976**, *29*, 1685–1697.

is also well documented.[2a,17b,19] It presumably involves the reaction of the carbene **5a** (or alternatively, diazobenzocyclobutene (**3a**)) with the sulfur[17f] of the sulfinate ion (**4**) (see eq 8).[17b] The identification of **17** was based initially




(8)

based on its spectral data[20] which revealed a triplet at 4.91 ppm in the $^1$H NMR spectrum assigned to the cyclobutyl methyne proton to the sulfone moiety. As expected,[21] this absorption is slightly downfield of the related alcohol (5.19 ppm);[18] were **17** a sulfinate ester, this methyne should appear upfield of the alcohol.[22] The corresponding $C_1$ carbon absorbs in the $^{13}$C NMR spectrum at 63.88 ppm; considering that sulfones are only shifted ~5 ppm downfield from the related sulfoxides,[23] this value compares favorably to 60.1 ppm reported for benzyl methyl sulfoxide.[23] Sulfone **17** was also independently synthesized from benzocyclobutenyl bromide[3,18] (**23**) and sodium *p*-toluenesulfonate in DMF.[24] Interestingly, the nucleophilic substitution was substantially more sluggish than expected. As a result, a 10-fold excess (rather than the usual[24] equimolar amount) of sodium *p*-toluenesulfonate was used and the reaction mixture was stirred for 1 week (rather than 24 h) at room temperature.

## Conclusion

The above results indicate that benzocyclobutene dimers **6a-*E*** and **-*Z*** are indeed the major products from the photochemical decomposition of hydrazone salt **2a**. Nevertheless, a variety of carbene coupling (**7**), carbene addition (**1**, **11-17**), and solvent addition (**8–10**) products are formed as well. Many of these types of products have been previously observed in various other carbene-generating reactions, but this system is unique in having all these varied reaction pathways occurring simultaneously.

The various products formed shed new light on the secondary interactions in arylcarbene additions, as well as insight into the surprisingly small steric size of the benzocyclobutenyl moiety. Regarding the former, we have seen that while the addition of arylcarbenes to alkenes results in the preferential formation of the more-hindered *syn* products,[8,9] arylcarbene **5** adds to aryl olefins (styrenes[2d] and dimer **6**) in a stereospecific *anti* orientation to give the less-hindered product. Thus, the secondary interactions involved in the addition of arylcarbenes to arylolefins would appear to be quite different from the van der Waals and London forces[8,9] presumed to be involved in the addition to alkylolefins. Much to our surprise, there do not seem to be any further examples in the literature of the addition of monoarylcarbenes to arylolefins and this observation deserves further investigation before a true generalization is justified.

Regarding the relatively small steric size of the unsubstituted benzocyclobutenyl moiety, this finds expression in the addition of carbene **5a** to dimers **6a** yielding trimer **7**. This fascinating compound is unreported among the reaction products of the methylated analogs **5b** and **5c**. Similarly, we have noted that the coupling of carbene **5a** with diazobenzocyclobutene (**3a**) gives all three possible ketazine conformations (**11–13**) in a statistical distribution, while generally only the most-stable conformation is observed for steric consideration. As noted above, the controlling factor in these cases seems to be the 90° angle of the cyclobutyl ring, which pulls the phenyl ring back and thus minimizes its steric contribution.

## Experimental Section

$^1$H and $^{13}$C NMR spectra were obtained on a Bruker AM 300 Fourier transform spectrometer. Assignments were facilitated by correlating proton and carbon chemical shifts through analysis of residual couplings in off-resonance decoupled spectra. In all cases, TMS served as the internal standard. In the case of known compounds, the previously published NMR spectral data were often obtained on a 60-MHz instrument and/or lacking the corresponding $^{13}$C data and are, therefore, recorded below. Mass spectra were run on a Finnigan-4000 GC/MS machine. High resolution mass spectra (HRMS) for the determination of exact masses were performed at the Mass Spectroscopy Center at the Technion, Haifa. UV-visible spectra were taken with a Varian DMS-100 spectrometer. Preparative thin-layer chromatography (TLC) was carried out on Merck silica gel $F_{254}$ precoated plates, and the products were extracted from the silica by stirring overnight in a solution of 10% $CH_3OH$ in $CHCl_3$. Analytical runs were performed using Riedel-De Haen micro cards and the retention times given are for the latter. For column chromatography separations, Fluka neutral alumina (type 507C) was used.

**Photolysis of the Sodium Salt of Benzocyclobutenone Tosylhydrazone (2).** Benzocyclobutenone (**1a**), its hydrazone (**2a-H**), and the corresponding hydrazone sodium salt (**2a**) were prepared according to Durr and co-workers.[2d] A 500-mL Pyrex immersion well photolysis apparatus, fitted with a 450-W Hanovia lamp and a magnetic stirrer, was charged with dry and finely ground hydrazone salt **2a** (7.5 g, 0.0243 mol) and 400 mL of dried (sodium wire) benzene. In order to maintain the reaction temperature below 10 °C, both the reaction vessel and the recirculated cooling water were chilled in an ice-bath. The reaction mixture was bubbled with oxygen-free nitrogen for 20 min and then irradiated under a nitrogen atmosphere for approximately 2 h. The yellowish product mixture was filtered from the white inorganic salts, and the filtrate yielded 2.8–3.0 g of yellow solid upon rotary evaporation. TLC (5% acetone in hexane) revealed the absence of starting material and the presence of approximately seven spots (although in several cases, a single spot corresponded to several products). The product mixtures from several such reactions were combined and the products separated as described below. Once the various products were identified, the product distribution and yields could be determined from the $^1$H NMR of the crude product mixture, based on the number of cyclobutylidene units incorporated in the product. From the above data we could also verify that nearly

(19) Bramford, W. R.; Stevens, T. S. *J. Chem. Soc.* **1952**, 4735–4740.
(20) The spectral data of the ring-dimethylated analog of **17**, obtained from the decomposition of **6b**, has been reported by Blomquist and Heins.[2a] Although the spectral pattern is comparable, their 60-MHz spectral data seems to be erroniously shifted upfield by ~0.3 ppm.
(21) Oae, S.; Uchida, Y. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C., Eds.; Wiley: New York, 1988; p 583; see especially p 593.
(22) Bassindale, A. R.; Iley, J. N. In *The Chemistry of Sulphinic Acids, Esters and their Derivatives*; Patai, S., Ed.; Wiley: New York, 1990; pp 130–184; see especially Table 3, p 133.
(23) Kalinowski, H. O.; Berger, S.; Braun, S. *$^{13}$C-NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1984; Table 3.35, pp 166–168.
(24) Meek, J. S.; Fowler, J. S. *J. Org. Chem.* **1968**, *33*, 3422–3424.

all the cyclobutylidene units in the starting material could be accounted for in the isolated products and, hence, that the overall product yield was almost quantitative.[25]

***E*- and *Z*-1,1'-Bi(benzocyclobutenylidene) [6a-*E* and -*Z*].** The aforementioned yellow product mixture from the photolysis of tosylhydrazone salt **2** was dissolved in a minimum of $CHCl_3$, and acetone was added dropwise until crystallization of cream-colored platelets commenced. The crystals were vacuum filtered, washed with a small amount of cold $CCl_4$, and identified by its $^1H$ NMR spectral data[2d,3] as **6a-*E***. Concentration of the mother liquor yielded more crystals of **6a-*E***, contaminated with 30% of the *Z*-isomer. Dropwise washing of this fraction with cold $CCl_4$ substantially increased the purity of the sample. The mother liquor and $CCl_4$ washings were loaded on an alumina column (200:1 alumina to sample ratio) and eluted with a 5% ether in hexane solvent mixture. The first set of fractions proved to be **6a-*Z***. Extensive NMR double resonance analysis of **6a-*E*** in $CDCl_3$ and $C_6D_6$ allowed us to assign the various aromatic hydrogens and splitting constants. The subsequent NOE analysis of this isomer confirmed its absolute assignment (see Results and Discussion). The physical properties and spectral data (numbering as shown above in Figure 2) of the two isomers are essentially those reported previously.[2d,3]

**6a-*E*:** $R_f$ (5% ether in hexane) 0.743; $^1H$ NMR ($C_6D_6$) 7.10 (tdt; $J_{4,5}$ and $J_{3,4}$ = 7.0, $J_{4,6}$ = 2.1 and $J_{4,CH_2}$ = 0.8 Hz; 2H; $H_4$ and $H_{4'}$), 7.05 (td, $J_{5,6}$ and $J_{4,5}$ = 7.0 and $J_{3,5}$ = 1.4 Hz, 2H, $H_5$ and $H_{5'}$), 7.02 (dddt, $J_{5,6}$ = 7.0, $J_{4,6}$ = 2.1, $J_{3,6}$ = 1.0 and $J_{6,CH_2}$ = 0.6 Hz, 2H, $H_6$ and $H_{6'}$), 6.98 (dddt; $J_{3,4}$ = 7.0, $J_{3,5}$ = 1.4, $J_{3,6}$ = 1.0 and $J_{3,CH_2}$ = 0.3 Hz; 2H; $H_3$ and $H_{3'}$), 3.64 (bs, 4H, methylenes); the coupling constants given are only approximate, since the spectrum shows extensive distortion due to second-order effects; $^1H$ NMR ($CDCl_3$) 7.25 ($H_4$ and $H_{4'}$), 7.23 ($H_6$ and $H_{6'}$), 7.19 ($H_5$ and $H_{5'}$), 7.13 ($H_3$ and $H_{3'}$), 3.81 (methylenes); HRMS *m/z* ($M^+$) calcd for $C_{16}H_{12}$ 204.0939, obsd 204.0979.

**6a-*Z*:** $R_f$ (5% ether in hexane) 0.743; $^1H$ NMR ($CDCl_3$) 7.35–7.27 (m, 2H), 7.27–7.18 (m, 2H), 3.71 (s, 2H).

**Trispiro[cyclopropene-1,1':2,1'':3,1'''-trisbenzocyclobutene] (7), Spiro[benzocyclobutene-1,7'-cyclohepta-1',3',5'-triene] (8), 9a,10-Dihydrobenz[*a*]azulene (9), and 4a,10-Dihydrobenz[*a*]azulene (10).** The above chromatography column was further eluted with 5% ether in hexane to give a second group of bluish fractions, which upon TLC analysis showed two spots with $R_f$ values of 0.722 and 0.635. Preparative TLC (silica; eluting again with 5% ether in hexane) enabled the separation of these two components. The major component corresponded to the faster running band ($R_f$ 0.722) which proved to be a mixture of compounds. These were readily identified as cycloheptatrienes **8**, **9**, and **10** in a 7:1:3 ratio by comparing their spectral data with previously published values.[2b,4]

The third set of fractions from the above column was further purified via preparative TLC (as above) and the major component ($R_f$ 0.635) was a yellow solid but gave a greenish $CHCl_3$ solution. This fraction was identified as trimer **7**, based on the spectral data (numbering of carbons as shown above in Figure 2).

**7:** $^1H$ NMR ($CDCl_3$) 7.24–7.04 (m, 11H), 6.92 (dt, $J_{6',m}$ = 7 Hz, $J_{6',CH_2}$ = 1.5 Hz, 1H, $H_{6'}$ [*ortho* to methylene on trans-oriented benzocyclobutenylidene]), 3.48 and 3.41 (AB q split into t, $J_{gem}$ = 13.5 Hz, $J_{3,CH_2}$ = 1.5 Hz, 4H, cis $CH_2$), 3.45 (bs overlapping AB q, 2H, trans $CH_2$); $^{13}C$ NMR ($CDCl_3$) 148.1 ($2C_2$), 147.9 ($C_{2'}$), 143.8 ($C_{7'}$), 143.6 ($2C_7$), 127.2 ($2C_4$ and $C_{4'}$), 126.7 ($C_{5'}$), 126.6 ($2C_5$), 122.4 ($2C_6$ and $C_{6'}$), 119.8 ($2C_3$), 119.1 ($C_{3'}$), 44.5 ($2C_1$), 44.3 ($C_{1'}$), 35.7 ($2C_8$), 34.8 ($C_{8'}$); MS (CI, isobutane, 70 ev), *m/z* 363 (M + $C_4H_9^+$, 2.501%), 307 ($MH^+$, 100%), 229 ($M^+ - C_6H_5$, 15.70%), 215 ($M^+$ – tropylium, 12.45%), 205 (**6a** + $H^+$, 12.40%), 103 ($C_6H_4CH_2CH^+$, 10.74%), 91 (tropylium, 97.52%); MS (EI, 70 ev) *m/z* 306 ($M^+$, 16.02%), 305 (M – 1, 12.04%), 291 (M – $CH_2$ – H, 5.7%), 215 (M – tropylium, 4.43%), 204 (**6a**, 93.17%), 203 (**6a**-H, 100%), 202 (64.55%); HRMS *m/z* ($M^+$) calcd for $C_{24}H_{18}$ 306.1409, obsd 306.1386.

**Benzocyclobutenone (1) and *anti-anti*-, *anti-syn*-, and *syn-syn*-Benzocyclobutenone Azines (11–13).** The above column was eluted further with 30% ether in hexane yielding the next set of product-containing fractions, which was deep yellow in color. The $^1H$ NMR spectrum revealed the presence of cyclobutenone **1**[2d,26] as well as the known[2d] isomeric azines **11**, **12**, and **13** in a 1:2:1 ratio (see Results and Discussion). The same ratio is obtained when these ketazines are synthesized from benzocyclobutanone and hydrazine.[2d] In the NMR data below, the numbering of carbons is as shown above in Figure 2.

**1:** $^{13}C$ NMR ($CDCl_3$) 188.58 ($C_1$), 151.29 ($C_7$), 147.87 ($C_2$), 135.12 ($C_5$), 128.64 ($C_4$), 123.65 ($C_6$), 120.47 ($C_3$), 52.32 ($C_8$).

**11, 12, and 13** (1:2:1): $^1H$ NMR ($CDCl_3$) 7.58 (dt, $J$ = 7.0 and 0.75 Hz, 1H), 7.53–7.44 (m, 3H), 7.44–7.28 (m, 12H), 4.060, 4.045, 4.005 and 3.985 (each s, each 2H, methylenes); $^{13}C$ NMR ($CDCl_3$) 163.53, 162.53, 161.11 and 159.72 ($C_1$), 146.83, 146.76, 146.76 and 146.65 ($C_7$), 143.14, 143.02, 141.59 and 141.59 ($2C_2$), 132.18, 132.18, 132.03 and 132.03 ($C_5$), 128.26, 128.26, 128.13 and 128.05 ($C_4$), 123.27, 123.27, 122.94 and 122.94 ($C_6$), 123.73, 123.50, 120.35 and 120.19 ($C_3$), 41.64, 41.58, 41.35 and 41.18 ($C_8$); MS (CI, 70 ev), *m/z* 233 ($MH^+$, 68.2%); MS (EI, 70 ev), *m/z* 233 ($MH^+$, 63.58%), 116 (M/2, 100%), 103 ($C_6H_4CH_2CH^+$, 19.7%), 91 (tropylium, 35.91%).

***anti*- and *syn*-Benzocyclobutenone *N*-Tosyl-*N*-benzocyclobutenylhydrazone (14 and 15) and 1-Benzocyclobutenyl *p*-Tolyl Sulfone (17).** Eluting the above column with 25% ethyl acetate in hexane yielded a further set of yellow fractions. Upon concentration of the solvent, a small amount *p*-toluenesulfonic acid precipitated out. $^1H$ NMR of the filtrate revealed the presence of three components. This product mixture was then loaded onto an alumina column and eluted with hexane. This resulted in fractions that were enriched in the various components, identified as *anti*- and *syn*-tosylhydrazones **14** and **15**, as well as sulfone **17**. NMR samples in $CDCl_3$ were allowed to stand at room temperature for several days and then reexamined, revealing that **15** gradually isomerizes to **14**.

For the purpose of identification, an authentic sample of sulfone **17** was prepared from the known benzocyclobutenyl bromide (**23**)[3,18] and sodium *p*-toluenesulfonate in DMF at room temperature.[24] Because the bromide reacts only sluggishly, Meek and Fowler's procedure[24] was modified as follows: a 10-fold excess (rather than an equimolar amount) of sodium *p*-toluenesulfonate was used and the reaction mixture was stirred for 1 week (rather than 24 h). The crude product was separated by preparative TLC eluting with 10% acetone in hexane. In the NMR data below, the numbering of carbons is as shown above in Figure 2.

**14:** $^1H$ NMR ($CDCl_3$) 7.89 and 7.39 (AA'XX', $J$ = 9 Hz, 4H, tosyl), 7.74 (d, $J$ = 8 Hz, 1H), 7.45 (m, 1H), 7.31 (d, $J$ = 8 Hz, 1H), 7.0–6.9 (m, 4H), 6.40 (d, $J$ = 7 Hz, 1H), 5.43 (dd, $J_{vic}$ = 5 and 3 Hz, 1H, CH-N), 3.90 and 3.82 (AB q, $J_{gem}$ = 16 Hz, 2H, $CH_2C{=}N$), 3.19 (dd, $J_{gem}$ = 14 Hz, $J_{vic}$ = 5 Hz, 1H of $CH_2CHN$), 3.08 (dd, $J_{gem}$ = 14 Hz, $J_{vic}$ = 3 Hz, 1H of $CH_2CHN$), 2.47 (bs, 3H, tosyl $CH_3$); $^{13}C$ NMR ($CDCl_3$) 147.22 (C=N), 144.31, 144.31, 143.75, 143.73, 142.45 and 141.36 (aromatic quaternary), 136.66, 129.68, 129.68, 129.05, 129.05, 128.94, 128.52, 127.08, 124.25, 123.11, 123.06 and 122.64 (aromatic CH), 60.01 (CHN), 41.88 ($CH_2C{=}N$), 35.38 ($CH_2CHN$), 21.67 (tosyl $CH_3$); MS (CI, $CH_4$, 70 ev), *m/z* 417 ($MC_2H_5^+$, 2.3%), 389 ($MH^+$, 100%), 272 ($MH^+ - C_6H_4CH_2CH{=}N$, 1.17%), 233 ($MH^+$ – TosH, 46.10%); HRMS *m/z* ($M^+$ not observed) calcd for $C_{16}H_{13}N_2$ ($M^+ - PhSO_2$) 233.1080, obsd 233.1084.

**15:** $^1H$ NMR ($CDCl_3$) 7.85 (d, $J$ = 9 Hz, 2H), 7.60–6.9 (m, 9H), 6.72 (d, $J$ = 7 Hz, 1H), 5.25 (t, $J_{vic}$ = 3.75 Hz, 1H, CHN), 4.08 (s, 2H, $CH_2C{=}N$), 3.20 (d, $J_{vic}$ = 3.75 Hz, 2H, $CH_2CHN$), 2.50 (s, 3H, tosyl $CH_3$); $^{13}C$ NMR ($CDCl_3$) 147.17 (C=N), 144.31, 144.31, 143.74, 143.74, 142.65 and 141.47 (aromatic quaternary), 133.50, 132.37, 130.02, 130.02, 129.12, 128.25, 128.25, 127.13, 123.46, 123.03, 122.73 and 121.06 (aromatic CH), 60.05 (CHN), 43.22 ($CH_2C{=}N$), 35.38 ($CH_2CHN$), 21.70 (tosyl $CH_3$). Samples of compound **15** contain small amounts of **14** as a result of thermal rearrangement.

**17:** $R_f$ (10% acetone in hexane) 0.56; $^1H$ NMR ($CDCl_3$) 7.75 and 7.32 (AA'XX', $J$ = 8 Hz, 4H, tosyl), 7.3–7.2 (m, 2H, $H_4$ and $H_5$), 7.06 and 6.99 (each bd, $J$ = 7 Hz, 2H, $H_3$ and $H_6$), 4.91 (t, $J_{vic}$ = 3.75 Hz, 1H to Tos), 3.50 (d, $J_{vic}$ = 3.75 Hz, 2H), 2.44 (s, Tos $CH_3$); $^{13}C$ NMR ($CDCl_3$) 144.82 and 143.84 ($C_2$ and $C_{12}$),

(25) We note in passing that GC-MS analysis of the crude product mixture revealed the presence of several additional unidentified minor products, altogether representing <1%.

(26) Lau, K. S. Y. *Chemistry, Characterization and Processing of IMC Curing Polymers*; Air Force Wright Aeronautical Laboratories Technical Report, AFWAL-TR-83-4063, July 1983, pp 117–118.

138.29 ($C_9$), 134.63 ($C_7$), 129.87 and 127.96 ($C_4$ and $C_5$), 129.71 ($C_{11}$), 128.91 ($C_{10}$), 123.19 and 123.05 ($C_3$ and $C_6$), 63.88 ($C_1$), 33.29 ($C_8$), 21.66 ($C_{13}$); MS (CI, 70 ev), *m/z* 259 ($MH^+$, 100%), 227 ($M - SO$, 8.32%), 139 ($CH_3C_6H_4SO$, 35.43%), 119 ($M - CH_3C_6H_4SO$, 10.88%), 103 ($C_6H_4CH_2CH^+$, 22.31%), 91 (tropylium, 6.98%); MS (EI, 70 ev), 258 ($M^+$, 36.34%), 179 ($M - CH_3 - SO_2$, 18.96%), 178 ($M - CH_3 - HSO_2$, 37.51%), 103 ($C_6H_4CH_2CH^+$, 100%), 102 ($C_6H_4CHCH^+$, 100%), 92 ($C_7H_8$, 10.28%); HRMS calcd ($C_{15}H_{14}O_2S$, $M^+$) 258.0715, obsd 258.0741.

**23:** $^1H$ NMR ($CDCl_3$) 7.29 (m, 2H), 7.14–7.04 (m, 1H), 7.04–6.96 (m, 1H), 5.35 (dd, $J_{1,8} = 5$ Hz, $J_{1,8'} = 2$ Hz, 1H, $H_8$), 3.80 (dd, $J_{gem} = 15$ Hz, $J_{1,8} = 5$ Hz, 1H, $H_8$), 3.40 (dd, $J_{gem} = 15$ Hz, $J_{1,8'} = 2$ Hz, 1H, $H_{8'}$); $^{13}C$ NMR ($CDCl_3$) 145.97 ($C_2$), 141.90 ($C_7$), 130.05, 128.14, 123.23, 122.49 (aryl), 43.87 ($C_8$), 41.84 ($C_1$).

**Benzocyclobutenylhydrazine (16).** Eluting the above column with 35% ethyl acetate in hexane yielded a greenish set of fractions, which upon spectral analysis was identified as hydrazine **16**. Assignments were aided by comparison of these data with those of the related amine.[18] Attempts to prepare an authentic sample by reacting benzocyclobutenyl bromide[3] with hydrazine gave a mixture of products, whose spectral data (MS and NMR) suggested that it was composed primarily of *N,N*-bis(benzocyclobutenyl)hydrazine accompanied by ca. 10% of **16**.

**16:** $^1H$ NMR ($CDCl_3$) 7.4–6.8 (m, 4H, aromatic), 5.28 (dd, $J_{vic} = 4.0$ and 1.75 Hz, 1H, $H_1$ to NH), 3.62 (dd, $J_{gem} = 14$ Hz, $J_{vic} = 4$ Hz, 1H, $H_8$ trans to hydrazine), 3.04 (dd, $J_{gem} = 14$ Hz, $J_{vic} = 1.75$ Hz, 1H, $H_8$ cis to hydrazine), 2.48–2.22 (m, 3H, $NHNH_2$); $^{13}C$ NMR ($CDCl_3$) 142.30 ($C_2$), 135.10 ($C_7$), 129.66, 129.49, 127.21, 123.59 (aryl), 76.9 ($C_1$), 42.5 ($C_8$); MS (CI, 70 ev), *m/z* 135 ($MH^+$, 100%), 119 ($MH^+ - NH_2$, 21.63%), 103 ($M - NHNH_2$, 32.03%); MS (EI, 70 ev), *m/z* 134 ($MH^+$, 10.44%), 118 ($M - NH_2$, 86%), 103 ($M - NHNH_2$, 33.12%), 91 (tropylium, 100%), 77 ($C_6H_5^+$, 53.39%); HRMS calcd ($C_8H_{10}N_2$, $M^+$) 134.0844, obsd 134.0840.

**Supplementary Material Available:** 300-MHz $^1H$ NMR spectra of **7**, a mixture of **14**, **15**, and **17**, and **16** as well as a $^{13}C$ NMR spectrum of **17** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the misrofilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.