17d:[36] 168.7, 161.8, 161.4 (J = 245.0 Hz), 136.2, 134.9, 134.3, 130.1, 129.7 (J = 8.4 Hz), 129.6, 127.7, 127.1, 115.2 (J = 22.0 Hz), 33.8, 29.0, 26.5. **17e:**[36] 168.6, 162.7, (J = 245.0 Hz), 161.7, 143.0 (J = 7.5 Hz), 134.9, 134.2, 130.0, 129.7 (J = 8.6 Hz), 129.5, 127.6, 127.1, 124.0 (J = 2.4 Hz), 115.2 (J = 20.7 Hz), 113.0 (J = 20.7 Hz), 34.2 (J = 2.5 Hz), 28.9, 25.9. **24a:** 168.9, 161.9, 141.7, 135.0, 134.3, 130.2, 129.7, 128.4, 128.3, 127.8, 127.3, 125.9, 35.4, 30.6, 29.8, 24.4. **24b:** 168.8, 161.7, 138.4, 135.2, 134.9, 134.1, 130.1, 129.6, 128.9, 128.1, 127.7, 127.1, 34.7, 30.5, 29.8, 24.3, 20.8. **24c:** 168.8, 161.7, 157.6, 134.8, 134.1, 133.7, 130.0, 129.5, 129.1, 127.6, 127.1, 113.6, 55.1, 34.3, 30.7, 29.7, 24.2. **24d:**[36] 169.0, 161.9, 161.1 (J = 247.0 Hz), 137.2 (J = 2.4 Hz), 135.1, 134.4, 130.3, 129.5 (J = 7.5 Hz), 129.3, 127.7, 127.1, 115.8 (J = 22.0 Hz), 34.4, 30.4, 29.8, 24.2. **31a:** 168.3, 166.0, 139.2, 128.6, 128.2, 126.6, 31.5, 30.5, 16.4. **31f:** 168.2, 166.1, 137.7, 132.5, 129.6, 128.7, 31.4, 29.9, 16.5. **32a:** 168.8, 166.0, 140.5, 128.3, 128.3, 126.0, 34.7, 28.9, 26.2, 16.3. **32b:** 168.9, 166.0, 137.5, 135.6, 129.9, 128.3, 34.2, 29.1, 28.4, 20.9, 16.4. **32d:**[36] 168.8, 166.0, 161.3 (J = 242.8 Hz), 136.2, 129.8 (J = 7.4 Hz), 115.1 (J = 21.7 Hz), 33.7, 28.9, 26.4, 16.4. **32e:**[36] 168.6, 165.9, 162.7 (J = 237.3 Hz), 143.1 (J = 7.3 Hz) 129.7 (J = 7.4 Hz), 124.0 (J = 2.5 Hz), 115.1 (J = 20.8 Hz), 112.8 (J = 20.7 Hz), 34.1, 28.8, 25.9, 16.2. **33a:** 169.0, 165.9, 141.5, 128.1, 128.1, 125.7, 35.1, 30.4, 29.6, 24.2, 16.4. **33b:** 168.9, 166.0, 138.5, 135.1, 128.9, 128.0, 34.7, 30.5, 29.7, 24.2, 20.8, 16.4. **33d:**[36] 168.9, 166.1, 164.6 (J = 245.0 Hz), 137.2, 129.7 (J = 7.4 Hz), 114.9 (J = 20.8 Hz), 34.4, 30.5, 29.7, 24.2, 16.5.

General Procedure for [13]C **CIDNP Studies.** Neat cyclohexanone or hexachloroacetone (~1.0 mL) in an NMR tube was preheated to ~100 °C inside the probe of a Varian FT-80 NMR spectrometer. A concentrated solution (or a slurry) of ~250 mg of the peroxide in the same solvent was added all at once into the NMR tube. The lock was held externally and each FID was time averaged for 20 (90° flip angle) consecutive pulses with 0.8 s of acquisition time per pulse. Ten consecutive FID's were stored in a Sykes Flexidisk Accessory. The FID's were Fourier transformed at the end of the reaction and plotted. Each experiment was approximately 5 min in length. However, polarized signals were observed only for about 1–2 min. The identity of the signals were established by comparison with the spectra of authentic samples[10] or with literature data.[11]

Solid-State Chemistry, Kinetics, and Electron Spin Resonance Spectroscopy of 2-Biphenylmethylene

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The chemistry and kinetics of 2-biphenylmethylene have been examined in low-temperature glasses and polycrystals. Photolysis of 2-biphenyldiazomethane at 77 K produces a single set of triplet carbene resonance peaks. They have been assigned to the unresolved superposition of syn and anti rotamers of the carbene. The carbene kinetics are fastest in diethyl ether glass. The decay rates of **4T** in diethyl-d_{10} ether and in a perfluorinated alkane polycrystal are comparable. This indicated that the main carbene reaction in diethyl ether is hydrogen atom abstraction. The reaction of **4T** in diethyl-d_{10} ether is a mixture of reaction with solvent and cyclization to fluorene. These interpretations are consistent with the observed product distributions. Matrix effects on the observed chemistry are discussed.

Electron spin resonance spectroscopy has been used successfully to characterize carbenes which are ground-state triplets.[2] Through the analysis of the zero-field parameters and hyperfine splitting parameters of diphenylcarbene, fluorenylidene, and methylene it was determined that carbenes are substantially bent.[3] This value is in good agreement with more recently determined results

(1) Fellow of the Alfred P. Sloan Foundation.
(2) Trozzolo, A. M.; Wasserman, E. "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1975.

(3) (a) Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* 1969, *51*, 3327. (b) Wasserman, E.; Trozzolo, A. M.; Yager, W. A.; Murray, R. W. *Ibid.* 1964, *40*, 2408. (c) Brandon, R. W.; Closs, G. L.; Davoust, C. E.; Hutchison, C. A., Jr.; Kohler, B. E.; Silbey, R. *Ibid.* 1965, *43*, 2006. (d) Hutchison, C. A., Jr., Parson, G. A. *Ibid.* 1965, *43*, 2545; 1967, *47*, 520. (e) Wasserman, E.; Yager, W. A.; Kuck, V. J. *Chem. Phys. Lett.* 1970 *7*, 409. (f) Wasserman, E.; Kuck, V. J.; Hutton, R. S.; Anderson, E. D.; Yager, W. A. *J. Chem. Phys.* 1971, *54*, 4120.

with other techniques.[4] A consequence of the bent carbene geometry is the possibility of inequivalent rotomeric forms in methylene derivatives. This was discovered in 1965 by Trozzolo and Wasserman in a study of 1- and 2-naphthylmethylene.[5] In each case two well-resolved triplet spectra were observed due to the syn and anti ro-

tomers. Only a single triplet ESR spectrum was observed for 9-anthrylmethylene (1) as expected, for equivalent rotomers. In subsequent work two rotomeric spectra were observed for vinylmethylene 2,[6] carbomethoxymethylene
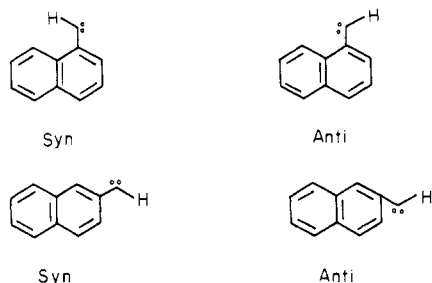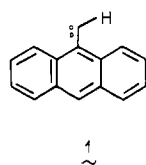
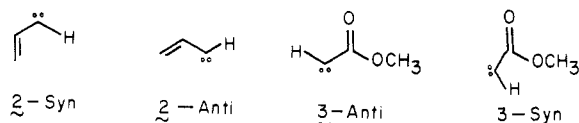(3),[7] and the isomeric 2-, 3-, 4-, and 8-quinolylmethylenes.[8] Schaefer has calculated a barrier of 4.93 kcal/mol to rotation in the carboxylic acid derivative of 3.[9] Senthilnathan and Platz have established that reactions of 1- and 2-naphthyl carbene with host matrices (2-propanol or toluene) are much more rapid than syn–anti interconversion at 77 K.[10] The mechanism of carbene reaction with the matrix was attributed to hydrogen atom abstraction via quantum mechanical tunneling. The lower limit of the barrier to syn–anti interconversion was found to be 4.5 kcal/mol for triplet 1- and 2-naphthylmethylene triplets. This work prompted a study of 2-biphenylmethylene (4). In principle, carbene 4 should also display
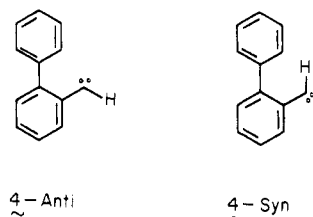
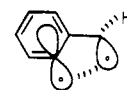two rotomeric spectra, as well as conformationally dependent chemistry. Klemchuk has generated carbene 4

in solution, at room temperature, photolytically.[11] Fluorene was the only volatile product formed (69% material balance). The closely related species 2-biphenylnitrene was studied by Swenton.[12] Direct photolysis of 2-azidobiphenyl gave carbazole as the predominant product in solution.

It is now well-known that the solution chemistry of carbenes is very different than that obtained in low-temperature solids.[13] We felt that this might be particularly true with 2-biphenylmethylene upon freezing out the different rotomeric forms.

ESR Spectroscopy

Photolysis of 2-biphenyldiazomethane 5 at 77 K in glassy diethyl ether (ether) produced a single set of triplet carbene resonance absorptions at 2151.3, 4876.9, and 5737.5 G: $|D/hc| = 0.510$ cm^{-1}, $|E/hc| = 0.020$ cm^{-1}. Extensive photolysis at 77 or even 4 K did not produce a second set of rotomeric spectra. Several other matrices were studied (ethanol, benzene, cyclohexane, hexafluorobenzene). In no case did we observe a second set of triplet spectra. Ether gave the most intense spectra for a given period of irradiation. Logically, the observed triplet spectrum may be due to a single rotomer or the unresolved superposition of both conformational isomers. The latter belief is plausible based on the following PMO argument.

The magnitude of ΔD (the difference in zero-field parameter D between the two conformational isomers) can be predicted by molecular orbital theory.[5,8] The zero-field parameter D can be simply thought of as proportional to $1/r^3$, where r is the spatial separation of the two unpaired electrons. In an aromatic carbene, one can picture the spin distribution in the following manner: one electron is essentially localized in the pseudo sp^2 σ orbital on the carbene center. The other unpaired electron is delocalized throughout the π system which should resemble that of benzyl radical. In benzyl radical itself, the spin density is concentrated on the benzylic carbon, but there is substantial spin density at the ortho and para positions. The main contribution to the zero-field parameter in phenylmethylene will be the interaction between the unpaired electron in the σ orbital and the unpaired electron in the π orbital on the carbene center. To a lesser extent, there will be a contribution to the D value from the interaction of the unpaired electron in the σ orbital on the carbene center and the π electron at the ortho carbon. The in-

teraction between the unpaired electrons in the σ orbital and in the other ortho position and that in the para position will be negligible.

In the case of 2-biphenylmethylene, the dominant contribution to the D value will also arise from the interaction of the unpaired electron in the σ orbital on the carbene

(4) Engelking, P. C.; Corderman, R. R.; Wendoloski, J. J.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C. *J. Chem. Phys.* **1981**, *74*, 5460.

(5) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129.

(6) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wasserman, E. *J. Am. Chem. Soc.* **1974**, *96*, 4680.

(7) Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 4324.

(8) Hutton, R. S.; Roth, H. D.; Schilling, M. L. M.; Suggs, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 5147.

(9) K. S.; Kim, Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 5389.

(10) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5503.

(11) Denney, D. B.; Klemchuk, P. P. *J. Am. Chem. Soc.* **1958**, *80*, 3289.

(12) Swenton, J. S.; Ikeler, T. J.; Williams, B. H. *J. Am. Chem. Soc.* **1970**, *92*, 3103.

(13) (a) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475–4480. (b) Moss, R. A.; Huselton, J. K. *Ibid.* **1978**, *100*, 1314–1315. (c) Moss, R. A.; Joyce, M. A. *Ibid.* **1977**, *99*, 1262–1264. (d) Moss, R. A.; Dolling, U. H. *Ibid.* **1971**, *93*, 954–960. (e) Tomioka, H.; Inagaki, T.; Nakamura, S.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 130–134. (f) Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128–6129. (g) Omioka, H. *Ibid* **1979** *101*, 256–257. (h) Tomioka, H.; Inagaki, T.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 1023–1024. (i) Tomioka, H.; Ueda, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7817. (j) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *Ibid.* **1979** *101*, 6009. (k) Tomioka, H.; Suzuki, H.; Izawa, Y. *Chem. Lett.* **1980**, 293.

center with the other unpaired electron in the π orbital on the carbene center. The interactions of the unpaired electron of the σ orbital on the carbene center with other centers of π electron density in 2-biphenylmethylene are not equivalent in the two conformers. In principle this will lead to distinct ESR spectra with measurably different D values. The spin density in 2-phenylbenzyl radical is readily calculated from perturbational molecular orbital (PMO) theory and is shown below.[14] The two interactions

Anti   Syn

denoted by A in the syn and anti conformers are exactly the same by PMO theory and cannot contribute to ΔD. The only difference between the conformational isomers is interaction B. It is solely this effect which will give rise to any difference in ESR spectra between these two carbenes. As shown by PMO theory, there is very little spin density at the 2'-position in planar 2-phenylbenzyl

$$a = \frac{1}{\sqrt{31}}$$

radical, hence even in the optimal planar geometry ΔD should be small. It is undoubtedly true that this carbene is not planar, further reducing the spin density at the 2'-position and hence further reducing the size of ΔD. PMO theory predicts that ΔD will be vanishingly small for 2-biphenylmethylene.

ESR Kinetics

The time dependence of the ESR spectrum of 2-biphenylmethylene was studied following a specified period of irradiation of the diazo compound in diethyl ether. As expected for a reaction in a glassy solid the kinetics did not follow a simple first-order rate law. It was empirically determined that a plot of ln I (where I is the signal intensity of the carbene) vs $t^{1/2}$ gave excellent straight-line plots. This analysis gives "rate constants" in units of $s^{1/2}$, which cannot be related to a true rate constant for an elementary reaction. It is, however, the most accurate and precise means of reporting the data and provides a qualitative basis for discussing carbene reactivity under various sets of experimental conditions. The $t^{1/2}$ rate law is well-known for free radical,[15] carbene,[16] and excited-state processes[17] in viscous glasses. It has been theoretically justified by Förster.[18] The nonexponential decay of radicals in solids has usually been ascribed to a multiple site problem. A matrix contains different reaction sites. The reactivity of the nascent carbene will depend on its fixed orientation relative to the host. Some matrix sites will have

Table I. Dependence of the Matrix Rate Constants of 4T in Diethyl Ether upon Photolysis Time at 77 K

photolysis time, min	k, $s^{-1/2}$
3	0.025 ± 0.001
5	0.023 ± 0.003
15	0.015 ± 0.001

a superior orientation for reaction relative to others. Molecular nitrogen is a byproduct of the carbene forming photochemical reaction and may sterically block carbene reactions in different matrix sites to a variable extent. In the early stages of the reaction the reactive carbene sites are quickly depleted and are not regenerated. The remaining carbenes exist in less reactive sites. Consequently, the apparent reaction rate decreases during the course of the reaction, and the apparent pseudo-first-order rate constant (defined by tangents to the ln I vs. time plots) decreases. The effect of the history of the glass on the matrix rate constants is clearly evident in Table I. A 1 M solution of 5 in ether was photolyzed at 77 K for 3, 5, or 15 min to build up the carbene ESR signal for kinetic analysis. The longer the sample is irradiated, the larger the initial carbene concentration and the slower the matrix rate constant. At short irradiation times, a given distribution of matrix sites are created photochemically. At long irradiation times the same distribution is created, but the fast-reacting sites are largely depleted during the course of irradiation. This leaves the ensemble enriched in slower reacting sites which ultimately determine the observed rate constants. The chemistry observed in polycrystalline solids and glasses must also represent a summation of the different environments experienced by the ensemble of carbenes. The chemistry of different sites within the same matrix may vary considerably. It is important to bear in mind that the conclusions drawn from the ESR kinetics are valid only for those sites containing triplet 2-biphenylmethylene which can be time resolved by CW ESR. It is conceivable that there are sites in the matrix in which the carbenes react too fast to measure by CW ESR. Those carbene sites which are detected by ESR represent a subset of unknown proportion of the total component of triplet carbene reaction. The total triplet component of the reaction does not represent all carbenic reaction in the solid state, of course, as nascent singlet 2-biphenylmethylene can react rapidly prior to intersystem crossing to the triplet.
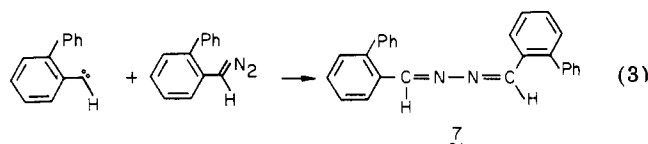
The decay of the triplet carbene at low temperature may originate in several ways. The carbene may react intramolecularly to give fluorene (eq 1), dimerize to alkene 6
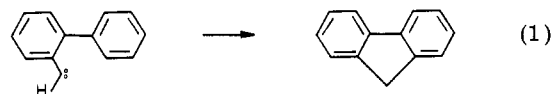
(eq 2), or react with diazo precursor to form azine 7 (eq
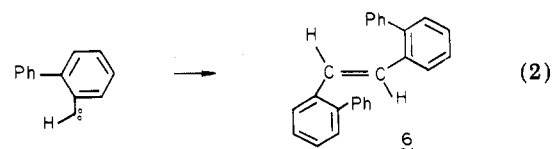
3). Alternatively, 2-biphenylmethylene may react with

(14) Dewar, M. J. S.; Dougherty, R. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975.

(15) (a) Sprague, E. D. *J. Phys. Chem.* **1973**, *77*, 2066–2070. (b) Neiss, M. A.; Willard, J. E. *Ibid.* **1975**, *79*, 783–791. (c) Neiss, M. A.; Sprague, E. D.; Willard, J. E. *Ibid.* **1972**, *76*, 546–1121. (d) French, W. A.; Willard, J. E. *Ibid.* **1968**, *72*, 4604–4608. (e) Hudson, R. L.; Shiotan, M.; Williams, F. *Chem. Phys. Lett.* **1977**, *48*, 193–195. (f) Bol'Shakov, Z. V.; Tolkatchen, V. A. *Ibid.* **1976**, *40*, 468–470. (g) Bol'Shakov, Z. V.; Fuks, M. P.; Tolkatchev, V. A.; Burstein, A. I. *Radiol. Chem. 4th*, **1976**, *4*, 723–725.

(16) (a) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7637. (b) Line, C. T.; Gaspar, P. P. *Tetrahedron Lett* **1980**, *21*, 3553.

(17) Yardley, J. T. "Introduction to Molecular Energy Transfer"; Academic Press: New York, 1980; pp 239–241.
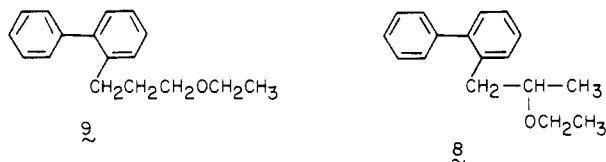
(18) Förster T. *Z. Naturforsch.* **1949**, *49*, 3217.

Table II. Pseudo-First-Order Matrix Rate Constants of
Carbene 4T in Low-Temperature Glasses[a]

matrix	temp, K	k, s$^{-1/2}$
diethyl ether	97	0.030 ± 0.003
	93	0.022 ± 0.001
	89	0.020 ± 0.001
	77	0.014 ± 0.002
diethyl-d_{10} ether	97	0.022 ± 0.002
	92	0.016 ± 0.002
	89	0.010 ± 0.002
	77	0.007 ± 0.001

[a] Fifteen minutes of irradiation of precursor.

the matrix to give matrix-incorporated compounds **8** and **9** or with trace amounts of water or oxygen to give **10** and


11 (eq 4), respectively.
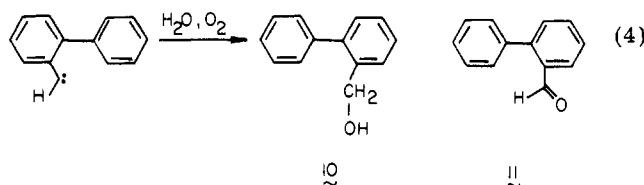


Chemical analysis of the reaction mixture formed in the glass reveals the formation of only fluorene and matrix-incorporated adducts **8** and **9**. This supports reactions 1 and 5 as possible decay mechanisms of the ESR active triplet. Further evidence in support of the reaction giving **8** and **9** is provided by the observation of kinetic isotope effects in diethyl-d_{10} ether (ether-d_{10}). The decay of the triplet signal is definitely slower in the deuterated matrix (Table II). The magnitude of the isotope effect (averaged over the ensemble of sites in the matrix) does not allow one to quantify what percentage of the ESR signal decays by the reaction giving **8** and **9** relative to the ring closure reaction (eq 1).

Further information on the solid-state chemistry of 2-biphenylmethylene is obtained by kinetic studies in perfluorinated alkane (PFA) matrices. In this matrix addition and abstraction reactions involving the carbene and the solvent are unlikely or impossible. These conditions would afford the best opportunity for monitoring the kinetics of ring closure of the carbene. Accordingly, the ESR signal decay of 2-biphenylmethylene is slower in PFA (24% signal decay in 30 min at 77 K) than in ether (53% signal decay in 30 min), but comparable to the stability found in ether-d_{10} (25% signal decay in 30 min). Evidence that the decay reaction of 2-biphenyl methylene in PFA is indeed ring closure, is provided by a similar kinetic study of 4-biphenylmethylene.[2] The isomeric carbene **12** cannot
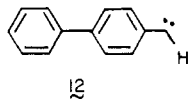
undergo intramolecular reaction comparable to that of 2-biphenylmethylene and has a much longer lifetime in PFA under identical experimental conditions (15% signal decay after 180 min at 77 K). On this basis the signal decay of 2-biphenylmethylene **4T** in PFA is assigned to ring closure. It is not clear from the limited kinetic data whether the mechanism involves triplet addition to the
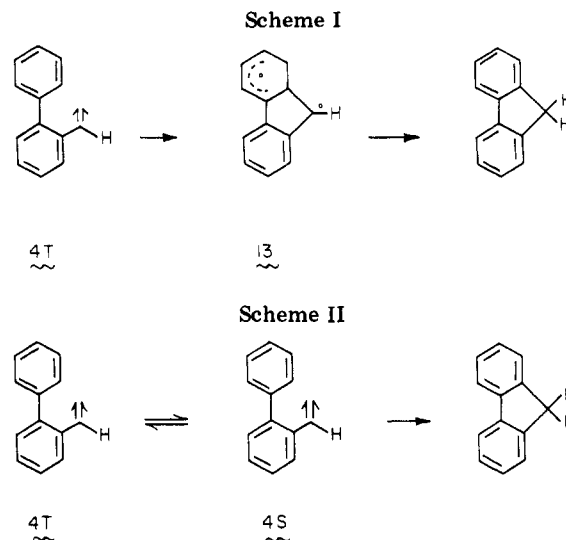
Scheme I

Scheme II

ortho phenyl ring (Scheme I) or whether the reaction proceeds through the small equilibrium population of singlet carbene present at 77 K (Scheme II). Triplet biradical **13** was not detected. This is not surprising as it is likely to have a singlet ground state by analogy to other o-xylylenes.[19] The slow decay of 4-biphenylmethylene may be due to reactions 2–4 or due to reaction of the carbene with nitrogen to regenerate the diazo precursor. A very similar pattern of kinetic results with 2- and 4-biphenylmethylene was obtained in hexafluorobenzene.

The $|D/hc|$ value of 2-biphenylmethylene is 0.510 cm^{-1}. This is virtually the same as phenylmethylene itself (0.5098 cm^{-1}) and substantially larger than that for 4-biphenylmethylene (0.4788 cm^{-1}).[5] $|D/hc|$ decreases with increased delocalization, and separation, of the two unpaired electrons. The zero-field parameters therefore indicate that in the para compound there is considerable interaction between the phenyl and methylene substituents and essentially no extra π interaction in 2-biphenylmethylene, relative to phenylmethylene. The two phenyl rings in **4** may be close to orthogonal. In this context it is not surprising that syn-**4** and anti-**4** could not be resolved in glasses and polycrystalline solids.

At the outset of this work it was anticipated that site problems would be less severe in intra- rather than intermolecular reactions in disordered solids. This did not prove to be the case. The decay kinetics of 2-diphenylmethylene in PFA or hexafluorobenzene did not follow any simple rate law and could not be analyzed. If, as is likely, the two phenyl rings of 2-biphenylmethylene are not coplanar, then cyclization of the carbene will require considerable molecular motion in the solid. This motion can be blocked to a variable extent by solvent molecules and molecular nitrogen. The rate of cyclization of 2-biphenylmethylene in different sites in the matrix must be quite variable and gives rise to complex overall kinetics.

The kinetic studies definitely indicate both intramolecular and intermolecular decay routes for triplet 2-biphenylmethylene. However, it is not possible to quantitatively dissect the kinetic data into its various components. This is a consequence of both the complex kinetics and the different "hardness" of glassy ether and PFA. These two matrices may not be equally permissive of carbenic motion. Therefore, the rate of cyclization of anti **4T** may differ in glassy ether and PFA. The kinetic data

(19) (a) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436. (b) Flynn, C. R.; Michl, J. *Ibid.* **1974**, *96*, 3280.

support the ESR spectral assignment as an unresolved superposition of the syn and anti conformers. Anti triplet carbene 4 must be present to account for the intramolecular decay component, as the syn form cannot cyclize directly, and our work with naphthyl methylenes at 77 K
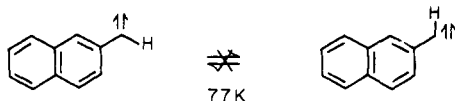
demonstrated that they do not undergo syn–anti isomerization at an appreciable rate, at low temperature. Extension of these results makes it unlikely that triplet 2-biphenylmethylene will isomerize at a useful rate in the matrix.
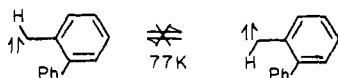
Analysis of the steric preferences of 2-biphenyldiazomethane indicates that the pro-syn conformer should be



Pro — Anti   Pro — Syn

more prevalent than the pro-anti form. It is usually assumed that the relative yields of syn and anti carbene reflect the relative proportions of their respective precursors.[5] The kinetic data strongly suggest the presence of *anti*-4; the preceeding argument suggests that *syn*-4 is present in the matrix as well.

Product Studies

Photolysis of 2-biphenyldiazomethane in ether at 25 °C produces flourene as the major volatile product (70%). Small amounts of 2-methylbiphenyl (0.1%) and the branched (8, 3%) and straight-chain (9, 2%) solvent-insertion adducts are observed. The low material balance may be due to our inability to remove all traces of solvent from the viscous oil 2-biphenyldiazomethane (see Experimental Section).

The identities of 8 and 9 were established by their isolation by preparative gas chromatography and their subsequent spectral characterization. The structures were confirmed by independent syntheses (eq 5 and 6).

$$(5)$$

$$(6)$$
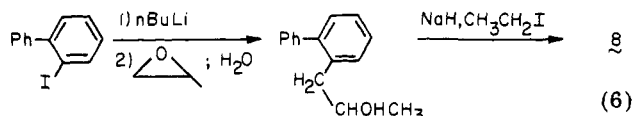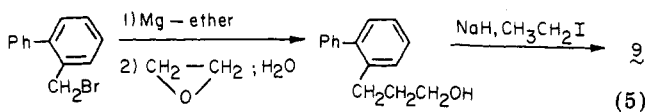
Sensitized photolysis of (2-biphenyl)diazomethane in ether was complicated by reactions of triplet benzophenone with the solvent. Control experiments demonstrated that flourene was the only carbenic product formed. There was no evidence of 2-methylbiphenyl, 8, or 9 formed in the sensitized photolysis. Photolysis of (2-biphenyl)diazomethane and benzophenone at 298 K gives flourene as the only detectable product.

Photolysis of (2-biphenyl)diazomethane in ether at 77 K gives rise to a very different product distribution than that observed in solution. The combined yields of solvent insertion compounds 8 and 9 are more than 4 times that of fluorene, in the glassy matrix (Table III). There is a

Table III. Relative Product Yields Obtained from Photolysis of 2-Biphenyldiazomethane in Diethyl Ether and Diethyl-d_{10} Ether at 77 K[a]

matrix	product	yield, %
diethyl ether	2-methylbiphenyl	1
	8	44
	9	38
	fluorene	17
diethyl-d_{10} ether	2-methylbiphenyl	1
	8	30
	9	22
	fluorene	47

[a] The material balance was ~70% based upon diazo compound.

Scheme III
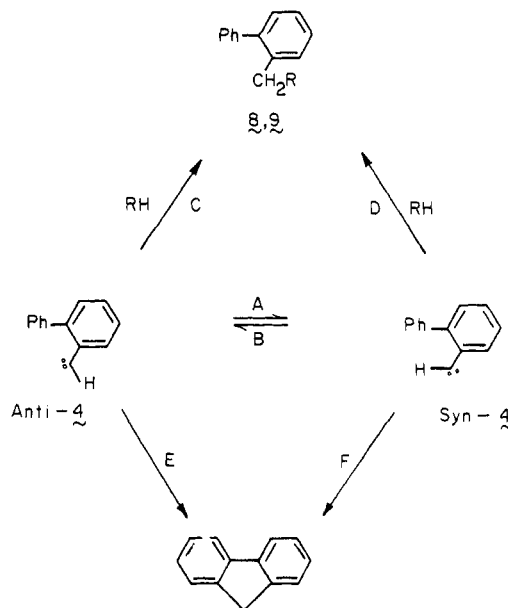
considerable matrix isotope effect on the product composition. In ether-d_{10} the combined yields of 8 and 9 are about the same as that of fluorene.

Discussion

The ether and ether-d_{10} product studies are consistent with the ESR kinetics. The kinetic studies revealed that the triplet decay in ether was faster than in inert matrices. Therefore, abstraction–recombination is predicted to be the major decay route of the triplet carbene in ether glass. A substantial kinetic isotope effect was observed in ether-d_{10}, making the triplet lifetime comparable to that found in perfluorinated matrices. It is not surprising then that the yields of inter- and intramolecular products are more evenly balanced in ether-d_{10}. This may be fortuitous as we have no knowledge as to how much of the chemistry of 4 is triplet derived.

A simplified mechanistic picture of the matrix chemistry is shown in Scheme III which momentarily neglects the multiplicity of the carbene rotomers. Processes A and B are considered to be unimportant in the triplet state on the basis of analogy with the naphthyl carbene work. There is no corresponding data for singlet syn-anti isomerization. However, we feel justified in neglecting processes A and B for 4S, on the basis of the rapidity of singlet processes and the fact that ab initio calculations of singlet methylene find barriers to geometric distortion.[20] We feel it is also valid to neglect process F for both 4S and 4T.

The observation of a matrix isotope effect on the product distribution means that process C must be significant.[20]

If all of the anti rotomer (both **4S** and **4T**) gave only fluorene and all of the syn form reacts with the matrix, then the rate of *syn*-4-reaction with the ethereal matrix would be retarded upon isotopic substitution of the solvent. However, the ultimate yield of **8** and **9** would not be effected by isotopic substitution, and there would be no change in product distribution. Our data does not indicate whether process C is important in only **4S** or **4T** or in both spin states. In solution the chemistry of 2-biphenylmethylene is almost purely intramolecular. In the matrix there are many sites in which the nonplanar carbene is prevented from cyclizing due to the local environment. It is conceivable that all of the ESR-active triplet carbene detected corresponds to only those sites in which the conformation and environment about the carbene retards the unimolecular process. Those matrix sites which are more permissive of the motions needed in ring closure would have been depleted by the rapid reaction of either **4S** or **4T**. If this view obtains, then the slow rate of cyclization of **4T** observed by CW ESR in inert matrices in unsurprising.

Experimental Section

The ESR system used for spectroscopic and kinetic studies has been described elsewhere.[10] Product analyses were measured by using a Hewlett-Packard 5830A gas–liquid chromatograph on a 6-ft 10% FFAP column. Peak identities were established by GC/MS and coinjection with authentic samples. Response factors were determined from authentic samples relative to naphthalene as standard. Material balances were typically 70% based upon the isolated weight of diazo compound. Preparative GLC was performed with a Varian Aerograph. Photolyses for both ESR kinetics and product analyses utilized a 1000-W Hg–Xe arc lamp. The light output was collimated and passed through a copper sulfate filter to reduce sample heating. Samples were kept at 77 K for 24 h following photolysis to ensure complete thermal reaction of the carbenes prior to thawing the matrix. At this point the tubes were opened, and excess diazo compound was consumed by the addition of acrylonitrile. Control experiments indicated that all of the photolysis products were stable to extended photolysis.

2-Biphenylcarboxaldehyde. A stirred suspension of wet manganese dioxide (14.07 g, 162 mmol) in 100 mL of toluene was azeotropically distilled with a Dean–Stark trap to remove water. After the mixture was cooled to room temperature, a 50 mL solution of 2-biphenylmethanol (2.49 g, 13.5 mmol) in toluene was added dropwise over a period of 15 min. The reaction was brought to reflux and allowed to stir overnight. The mixture was cooled to room temperature and suction filtered to remove MnO_2. The filtrate was treated with decolorizing carbon, filtered through Celite, and treated with anhydrous $MgSO_4$. Toluene solvent was removed in vacuo, rendering a yellow oil. Vacuum distillation of this oil (100–110 °C, 0.10 mm) gave 1.53 g (62%) of a colorless liquid: IR (neat) 2760 (aldehyde CH), 1690 cm^{-1} (C=O); NMR (CDCl$_3$) δ 10.00 (s, 1 H), 7.35 (m, 9 H); mass spectrum, *m/e* (relative intensity) 182 (94), 181 (100), 166 (3), 155 (22), 154 (32), 153 (38), 100 (75), 99 (54), 77 (21); calcd for C$_{13}$H$_{10}$O *m/e* 182.0732, found *m/e* 182.0736.

2-Biphenylcarboxaldehyde *p*-Toluenesulfonylhydrazone. 2-Biphenylcarboxaldehyde (2.26 g, 12.4 mmol) was dissolved in 100 mL of ethanol at room temperature, and *p*-toluenesulfonhydrazide (97%, 2.31 g, 12.4 mmol) was added to this solution. The solution was concentrated with heating to 25 mL, cooled to room temperature, and placed in the freezer compartment of a refrigerator overnight. The precipitated crystals were filtered off and recrystallized from ethanol to give 2.92 g (67%) of white prisms: mp 178–181 °C, with decomposition to an orange liquid; IR (KBr) 3210 (NH), 1345 (SO$_2$NH), 1165 (SO$_2$NH), 830 cm^{-1} (para disubstituted); NMR (acetone-d_6) δ 7.10–7.90 (m, 14 H), 2.73 (br s, 1 H, exchangeable), 2.36 (s, 3 H); mass spectrum, *m/e*

(relative intensity) 350 (12), 349 (8), 195 (15), 194 (10), 167 (23), 166 (94), 165 (100), 156 (9), 139 (10), 92 (13), 91 (26); calcd for C$_{20}$H$_{18}$O$_2$N$_2$S *m/e* 350.1089, found *m/e* 350.1081. Anal. Calcd for C$_{20}$H$_{18}$O$_2$N$_2$S: C, 68.55; H, 5.18; N, 7.99; S, 9.15. Found: C, 68.52; H, 5.25; N, 8.02; S, 9.24.

(2-Biphenyl)diazomethane (5). Method A. To a stirred solution of 2-biphenylcarboxaldehyde *p*-toluenesulfonylhydrazone (0.16 g, 0.457 mmol) in 35 mL of THF at room temperature was quickly added an unknown excess of solid sodium hydride (scoopula tip full). The mixture was gently heated until the incipient orange-red color no longer darkened, usually 20 min. The reaction mixture was cooled to 0 °C, and water was slowly added dropwise with a pipet to consume unreacted NaH. The mixture was suction filtered, and the filtrate was treated with anhydrous sodium sulfate followed by anhydrous sodium carbonate. The THF solvent was evaporated, and the remaining dark red oil was placed under high vacuum at 0 °C for 30 min. The crude yield was 72 mg (81%). The light, heat, and acid sensitivity of **5** precluded additional purification. For minimization of premature decomposition, **5** and solutions of **5** were handled expeditiously, below 25 °C, and in the dark, i.e., no fluorescent light exposure.

Method B. A solution of 2-biphenylcarboxaldehyde *p*-toluenesulfonylhydrazone (0.23 g, 0.656 mmol) in 10 mL of 1,1,3,3-tetramethylguanidine (TMG; 9.16 g, 79.5 mmol) was heated on a steam bath until the incipient orange-red color no longer darkened, usually 5 min. The red solution was poured onto 100 mL of an ice–water slush. This entire mixture was transferred to a separatory funnel. Ether extraction (2 × 250 mL) removed all of the pink coloration from the aqueous phase into the organic phase. The organic phase was washed with 5% aqueous sodium carbonate solution (3 × 100 mL) to remove untreated TMG and poured through fluted filter paper containing anhydrous MgSO$_4$. Ether solvent was removed in vacuo, and the remaining oil, contaminated with residual water, was taken up in hexane. The red hexane phase was separated from the colorless aqueous phase. Hexane solvent was removed in vacuo, affording 70 mg (55%) of crude **5** as a deep red oil. At this point, **5** was ready for immediate use in photolysis experiments: IR (neat) 2060 cm^{-1} (C=N=N); NMR (CDCl$_3$) δ 7.20 (m), 4.87 (s).

4-Biphenylcarboxaldehyde *p*-Toluenesulfonylhydrazone. 4-Biphenylcarboxaldehyde (1.34 g, 7.35 mmol) was dissolved in 100 mL of ethanol at room temperature, and *p*-toluenesulfonohydrazide (1.38 g, 7.41 mmol) was added to this solution. Upon heating of the solution to the boiling point of ethanol, off-white crystals precipitated. The mixture was cooled to room temperature. The crystalline product was filtered off and recrystallized from ethanol to give 1.99 g (77%) of white needles: mp 182–185 °C, with decomposition to an orange liquid; IR (KBr) 3190 (N—H), 1330 (SO$_2$NH), 1170 (SO$_2$NH), 825 cm^{-1} (para disubstituted).

(4-Biphenyl)diazomethane (12). To a stirred solution of 4-biphenylcarboxaldehyde *p*-toluenesulfonylhydrazone (0.16 g, 0.457 mmol) in 35 mL of THF at room temperature was quickly added solid sodium hydride (70 mg, 2.92 mmol). The mixture was gently heated until the incipient orange-red color no longer darkened, about 20 min. The reaction was cooled to 0 °C, and water was slowly added dropwise to consume excess NaH. The mixture was suction filtered, and the filtrate was treated with anhydrous sodium sulfate followed by anhydrous sodium carbonate. The THF solvent was removed in vacuo, and the remaining rich red crystals were treated with high vacuum at 0 °C for 15 min. The crude yield was not determined. The aforementioned diazo handling precautions also applied to this compound as well. IR (neat) 2065 cm^{-1} (C=N=N).

1-Methyl-2-(1,1′-biphen-2-yl)ethanol. To a −78 °C stirred solution of 2-iodobiphenyl (Pfaltz and Bauer; 1.13 g, 4.03 mmol) in 25 mL of THF was slowly added over a period of 5 min a solution of *sec*-butyllithium in cyclohexane (6 mL, 1.25 M, 7.50 mmol). The mixture turned cloudy yellow before complete addition of the *sec*-butyllithium. After the mixture was stirred for an additional 5 min at −78 °C, propylene oxide (4 mL, 59.2 mmol) was syringed into the reaction mixture as rapidly as possible. The mixture was allowed to warm to room temperature. After 10 min of stirring at room temperature, water (4 mL, 222 mmol) was added whereupon the solution turned from cloudy yellow to clear

(20) (a) Shih, S. K.; Poyerimhoff, S. D.; Buenker, R. J.; Peric, M. *Chem. Phys. Lett.* **1978**, *55*, 206 and references therein.

light yellow in appearance. The solution was transferred to a separatory funnel, taken up in several volumes of ether, and washed with a 10% aqueous NaHCO$_3$ solution. The organic phase was dried by filtration through anhydrous MgSO$_4$ and evaporated down in vacuo to give 0.55 g of a yellow oil, the TLC (20% ethyl acetate in hexane) of which revealed several components. Column chromatography (20% ethyl acetate in hexane) on silica gel gave 0.46 g (54%) of the title compound as a light yellow oil. Additionally, the lead TLC spot was identified as biphenyl on the basis of its melting point (71 °C) and mass spectrum (base and parent at m/e 154). For the secondary alcohol: IR (neat) 3350 (OH), 1070 cm^{-1} (C–O); NMR (CDCl$_3$) δ 7.25 (m, 9 H), 3.77 (m, 1 H, J = 6 Hz), 2.73 (d, 2 H, J = 6 Hz), 2.20 (br s, 1 H, exchangeable), 1.00 (d, 3 H, J = 6 Hz); mass spectrum, m/e (relative intensity) 212 (13), 194 (3), 179 (7), 178 (4), 169 (16), 168 (100), 167 (47), 166 (10), 165 (23), 154 (10), 153 (12), 152 (13), 115 (3), 83 (3), 81 (5), 44 (13), 42 (12), 40 (6), 38 (6); calcd for C$_{15}$H$_{16}$O m/e 212.1201, found 212.1207.

2-(2-Ethoxypropyl)-1,1'-biphenyl (8). To a stirred suspension of sodium hydride (0.26 g, 10.8 mmol) in 2 mL of THF at room temperature was added a solution of 1-methyl-2-(1,1'-biphen-2-yl)ethanol (46 mg, 0.217 mmol) in 2 mL of THF. The mixture was heated to a gentle reflux and allowed to stir for 10 min to promote alkoxide formation. After the mixture cooled to near room temperature, neat ethyl iodide (1.11 g, 7.12 mmol) was added. The reaction was returned to reflux and allowed to stir overnight. After cooling to room temperature, the mixture was suction filtered, and the insoluble white salts were copiously washed with ether. The clear filtrate was washed with a 10% aqueous sodium bicarbonate solution and dried over anhydrous MgSO$_4$. The solvents were removed in vacuo, leaving 30 mg of a colorless oil, the TLC (5% ethyl acetate in hexane) of which revealed one major component and several minor components. Preparative layer chromatography (5% ethyl acetate in hexane) on silica gel gave 16 mg (31%) of the title compound as a colorless oil which was one spot by analytical TLC (5% ethyl acetate in hexane, R$_f$ = 0.5): IR (neat) 1095 cm^{-1} (C=O); NMR (300 MHz, CDCl$_3$) δ 7.28 (m, 9 H), 3.34 (m, 1 H), 3.19 (m, 2 H), 3.04 (dd, 1 H), 2.58 (dd, 1 H), 1.03 (t, 3 H), 0.97 (d, 3 H); mass spectrum, m/e (relative intensity) 240 (10), 210 (0.4), 195 (2), 194 (2), 179 (5), 178 (3), 168 (5), 167 (6), 166 (4), 165 (10), 152 (4), 115 (1), 91 (2), 89 (1), 74 (4), 73 (100), 46 (1), 45 (56); calcd for C$_{17}$H$_{20}$O m/e 240.1514, found m/e 240.1521.

o-Phenylbenzyl Bromide. To a stirred 0 °C solution of 2-biphenylmethanol (21.41 g, 116 mmol) and pyridine (9.21 g, 116 mmol) in 150 mL of ether was slowly added dropwise over a period of 20 min neat phosphorus tribromide (11 mL, 116 mmol). A white precipitate formed immediately. The reaction was brought to reflux and allowed to stir overnight. The mixture was cooled to room temperature and poured onto 250 mL of ice. The entire ether–ice mixture was transferred to a separatory funnel, and ether and water were added to achieve a phase separation. The phases were separated, and the ether layer was washed with water followed by a 10% aqueous sodium bicarbonate solution. After the mixture was dried over anhydrous MgSO$_4$, the ether solvent was evaporated in vacuo, leaving a yellow, lachrymose oil. Vacuum distillation of this oil (82 °C at 0.15 mm) gave 19.40 g (68%) of o-phenylbenzyl bromide as a colorless liquid: IR (neat) 1600 cm^{-1} (C=C); NMR (CDCl$_3$) δ 7.30 (m, 9 H), 4.35 (s, 2 H); mass spectrum, m/e (relative intensity) 248 (9), 246 (10), 168 (16), 167 (100), 166 (23), 165 (40), 163 (4), 152 (12), 83 (12), 82 (8); calcd for C$_{13}$H$_{11}$ ^{79}Br m/e 246.0045, found m/e 246.0052.

3-(1,1'-Biphen-2-yl)-1-propanol. To a vigorously stirred suspension of freshly ground magnesium (0.36 g, 14.8 mmol) in 30 mL of ether at room temperature was slowly added dropwise over a period of 30 min a solution of o-phenylbenzyl bromide (3.01 g, 12.2 mmol) in 20 mL of ether. The dark green solution was

maintained at reflux for 10 min with a heating mantle. After the mixture was cooled to 0 °C, the Grignard reagent was quenched by a 20-min dropwise addition of an unknown excess of ethylene oxide, condensed into the reaction flask from a gas cylinder fitted with a needle valve attached to a –78 °C Dewar condenser. The solution turned clear light green and was returned to reflux for 45 min, whereupon water was quickly added. A white emulsion appeared. The entire reaction mixture was transferred to a separatory funnel, and a 1% aqueous sulfuric acid solution was added. The separated organic layer was dried over anhydrous MgSO$_4$, and ether solvent was removed in vacuo, leaving a colorless oil, the TLC (10% ether acetate in hexane) of which showed no starting material bromide. All of the oil was vacuum distilled to give two fractions. A considerable amount of brown residue would not distill. The first fraction (62 °C at 0.20 mm, identified by NMR) contained 2-methylbiphenyl, and the second fraction (124–128 °C at 0.20 mm) contained 2-methylbiphenyl, the title compound, and 2-biphenylmethanol. Because the two alcohols could not be separated by TLC, the previously described manganese dioxide oxidation procedure was employed to selectively oxidize 2-biphenylmethanol to 2-biphenylcarboxaldehyde, leaving the title compound untouched. For the reaction, 0.78 g of the vacuum distillate and 4.01 g of wet MnO$_2$ were used. After the workup, a yellow oil (IR 1690 cm^{-1}) was isolated, and TLC (30% ethyl acetate in hexane) on silica gel gave 0.16 g of 3-(1,1'-biphen-2-yl)-1-propanol as a light yellow oil: IR (neat) 3340 (OH), 1060 cm^{-1} (C–O); NMR (CDCl$_3$) δ 7.19 (m, 9 H), 3.39 (t, 2 H, J = 6 Hz), 2.62 (t, 2 H, J = 8.4 Hz), 1.66 (m, 2H), 1.44 (br, 2, 1 H, exchangeable); NMR decoupling experiments (CDCl$_3$) irradiated δ 1.66, obsd δ 3.39 (s), 2.62 (s); irradiated δ 3.39, obsd δ 2.62 (t), 1.66 (t); mass spectrum, m/e (relative intensity) 212 (91), 194 (28), 180 (20), 179 (100), 178 (25), 168 (36), 167 (75), 166 (38), 165 (80), 152 (28); calcd for C$_{15}$H$_{16}$O m/e 212.1201, found 212.1197.

2-(3-Ethoxypropyl)-1,1'-biphenyl (9). To a stirred suspension of sodium hydride (0.14 g, 5.83 mmol) in 2 mL of THF at room temperature was added a solution of 3-(1,1'-biphen-2-yl)-1-propanol (22 mg, 0.104 mmol) in 2 mL of THF. The mixture was heated to a gentle reflux whereupon it turned yellow. Reflux was maintained for 10 min and after cooling to near temperature, neat ethyl iodide (0.48 g, 3.08 mmol) was added. The reaction was returned to reflux and allowed to stir for 3 h. After cooling to room temperature, the mixture was suction filtered and the insoluble white salts were washed with ether. The filtrate was washed with a 10% aqueous sodium bicarbonate solution and dried over anhydrous MgSO$_4$. The solvents were evaporated leaving 17 mg (68%) of a light yellow oil. IR (neat) 1070 cm^{-1} (C–O); NMR (300 MHz, CDCl$_3$) δ 7.30 (m, 9 H), 3.34 (q, 2 H, J = 7.2 Hz), 3.27 (t, 2 H, J = 7.5 Hz), 2.65 (t, 2 H, J = 7.5 Hz), 1.72 (quintet, 2 H, J = 7.5 Hz), 1.15 (t, 3 H, J = 7.2 Hz); mass spectrum, m/e (relative intensity) 240 (36), 220 (6), 205 (17), 195 (14), 194 (78), 193 (15), 180 (17), 179 (100), 178 (15), 168 (17), 167 (31), 166 (28), 165 (60), 153 (6), 152 (13), 115 (6), 91 (6), 77 (5), 71 (14), 59 (8), 57 (6), 55 (5), 43 (5), 41 (8), 40 (6), 39 (6); calcd for C$_{17}$H$_{20}$O m/e 240.1514, found m/e 240.1521.