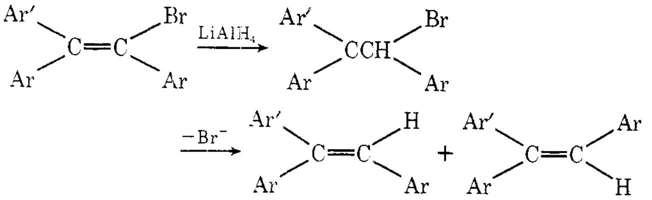
and these results are in agreement with expectations from the reported conversion of β-bromostyrene to styrene.[5] A similar treatment with *cis*-**4** or *cis*-**5** gave an essentially 1:1 mixture of the cis and trans olefins, *cis*- and *trans*-1-phenyl-1,2-di-*p*-tolylethylene (*cis*- and *trans*-**9**) from *cis*-**4** and *cis*- and *trans*-1,2-di-*p*-anisyl-1-phenylethylene (*cis*- and *trans*-**10**) from *cis*-**5**. Identification of the olefinic products in all of these reactions was made by comparison of their ^{1}H NMR spectra with known spectral data or with those of authentic samples prepared from dehydration of the corresponding 1,1,2-triarylethanols[6] by treatment with H_3PO_4.[7]

The formation of a mixture of *cis*- and *trans*-**9** from *cis*-**4** and *cis*- and *trans*-**10** from *cis*-**5** definitely eliminated a direct backside displacement as the mechanism for the $LiAlH_4$ reduction of triarylvinyl bromides, thus giving further confirmation to earlier conclusions that the S_N2 reaction at vinylic carbon is energetically unfavorable. The observed results, however, may be reasonably explained by an addition–elimination route[8] as shown below.



Experimental Section

Reaction of Triarylvinyl Bromide with $LiAlH_4$. A solution of 200 mg of triarylvinyl bromide **1**, **2**, **3**, *cis*-**4**, or *cis*-**5** in 25 mL of anhydrous ether was placed in a round-bottom flask fitted with a reflux condenser. $LiAlH_4$ (1.0 g) was added in small portions over a period of about 10 min. The mixture was then refluxed for 12 h and cooled in an ice bath and the excess $LiAlH_4$ was destroyed by the slow addition of 50 mL of H_2O. The ether layer was separated and the aqueous layer was extracted with ether (3 × 50 mL). The combined ether solution was dried over $MgSO_4$ and the ether was removed, giving a residual triarylethylene in yields ranging from 50–65%. The mass spectrum of each product showed the expected molecular ion for the triarylethylene and the absence of any unreacted triarylvinyl bromide.

From bromides **1**, **2**, and **3**, the products triphenylethylene (**6**), tri-*p*-tolylethylene (**7**), and tri-*p*-anisylethylene (**8**), respectively, were crystallized from CH_3OH. Olefin **6** melted at 67–68 °C (lit.[9] mp 67–68 °C) and showed an ^{1}H NMR spectrum identical with that reported previously for an authentic sample of **6**.[9] Olefin **7** melted at 113–114 °C (lit.[10] mp 114 °C): ^{1}H NMR ($CDCl_3$) δ 2.25, 2.34, 2.37 (CH_3, 3 s), 6.8–7.2 (aromatic + C=CH, m). This spectrum was the same as that of an authentic sample of **7** prepared from the H_3PO_4 dehydration[7] of 1,1,2-tri-*p*-tolylethanol.[6e] Olefin **8** melted at 100–101 °C (lit.[7] mp 100–101 °C): ^{1}H NMR ($CDCl_3$) δ 3.74, 3.80, 3.83 (CH_3O, 3 s), 6.6–7.3 (aromatic + C=CH, m). These spectral absorptions were essentially the same as those reported for **8** by Rappoport et al.[11] and were identical with the spectrum of **8** prepared from dehydration[7] of 1,1,2-tri-*p*-anisylethanol.[6c]

The product from *cis*-**5** was an oil. It was identified as a mixture of *cis*- and *trans*-1,2-di-*p*-anisyl-1-phenylethylene (*cis*- and *trans*-**10**) since its ^{1}H NMR spectrum showed four CH_3O singlets at ($CDCl_3$) δ 3.69, 3.77 (for *trans*-**10**), and 3.71 and 3.80 (for *cis*-**10**), with the aromatic and vinyl protons at δ 6.5–7.3. The four CH_3O absorptions observed were essentially the same as those for *cis*-**10** and *trans*-**10** reported by Rappoport and Apeloig.[12] 1-Phenyl-1,2-di-*p*-tolylethylene (**9**) (stereochemistry not specified) has been prepared as an oil, bp 182–183 °C (0.01 Torr).[13] In the present work, the product from *cis*-**4** was also an oil. Its ^{1}H NMR spectrum showed three singlets in the CH_3 region at ($CDCl_3$) δ 2.22 (6 H), 2.30 (3 H), and 2.34 (3 H) while the aromatic and vinyl protons absorbed at δ 6.8–7.3. These data indicated that the olefinic product from *cis*-**4** was a mixture of *cis*- and *trans*-**9**, with the CH_3 absorptions at δ 2.22 and 2.30 for *trans*-**9** and at δ 2.22 and 2.34 for *cis*-**9**.

Registry No.—**1**, 1607-57-4; **2**, 66184-02-9; **3**, 25354-46-5; *cis*-**4**, 64833-13-2; *cis*-**5**, 26326-64-7; **6**, 58-72-0; **7**, 6629-83-0; **8**, 7109-27-5; *cis*-**9**, 66184-01-8; *trans*-**9**, 66184-00-7; *cis*-**10**, 26326-61-4; *trans*-**10**, 15789-91-0.

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The Triphenylmethyl Radical: Equilibrium Measurements and the Reaction with Thiophenol[1]

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Received March 13, 1978

Rate constants for hydrogen atom transfer reactions to organic free radicals are usually determined only by rather complex methods with considerable uncertainties. However, an incidental observation during a study of the isotope effect for the reaction of thiophenol with the triphenylmethyl radical (the trityl radical) led to an order of magnitude estimation of the rate constant. That is, the color of the radical was not instantaneously discharged upon mixing the reagents at 0 °C.[4] It was clear that a careful measurement could yield a more precise value.

At the same time, it was clear that the determination of the rate constant required values for the equilibrium constant. In order to use the earlier isotope effect work, it was necessary to use toluene as the solvent. Previous determinations had been made in benzene and other solvents, but not toluene.[5] Depending upon the method of measurement, there was also an uncertainty of a factor of 2.[5] The availability of an apparatus that would allow us to handle and accurately dispense volumes of air and moisture-sensitive solutions prompted us to remeasure the dissociation constant in toluene by spectrophotometric methods, as originally done by Ziegler.[5] The discrepancy between spectrophotometric and magnetic measurements has now been resolved.[1] It arose primarily from the diamagnetic susceptibility of the dimer. Subsequently, the same apparatus was used to measure the rate of reaction of the trityl radical with thiophenol.

Dissociation of 1-Diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene. The measurements were made at the 516-nm maximum absorbance of the trityl radical. At this wavelength the dimer does not significantly absorb, so the absorbance in the 1-cm cell used is

$$A = \epsilon(\mathrm{R}\cdot) \qquad (1)$$

0022-3263/78/1943-2722$01.00/0

Table I. Equilibrium Constants for the Dissociation of the Trityl Dimer in Toluene

T, °C	$K \times 10^4$,[a] M	ϵ[a]
−5	0.516	635
0	0.808	651
10	1.49	652
20	3.09	661
30	5.86	656

[a] These values differ slightly from those in ref 1 because of the application of a correction for thermal expansion or contraction of the solvent.

where (R·) is the radical concentration. This can be related to the dimer concentration (D) and the total stoichiometric dimer concentration (D_0) as shown:

$$(D) = (D_0) - (R\cdot)/2 \tag{2}$$

The desired equilibrium constant is given by the expression

$$K = (R\cdot)^2[(D_0) - (R\cdot)/2] \tag{3}$$

Rearranging this expression and substituting for (R·) gives

$$(D_0)/A = (A/K\epsilon^2) + (1/2\epsilon) \tag{4}$$

Thus, a plot of $(D_0)/A$ vs. A should be linear with a slope of $1/K\epsilon^2$ and an intercept of $1/2\epsilon$. A plot of this sort is shown in Figure 1, corresponding to measurements made in toluene solution at 20 °C. A least-squares fit to the straight line yields $K = 3.08 \times 10^{-4}$ mol/L and $\epsilon = 661$. Determinations made at −5, 0, 10, and 30 °C were likewise satisfactorily linear. In order to extract equilibrium and extinction coefficient data, it is necessary to allow for thermal expansion or contraction of the toluene[7] since the solutions were made at room temperature and then brought to the measurement temperature. The results are presented in Table I; the extinction coefficient is 655 ± 4 L/mol cm^{-1}, and the equilibrium constants are reasonably well fitted by the equation $K = (5.56 \pm 2.66) \times 10^4 \exp[(-11\,075 \pm 130\ \text{cal/mol})/RT]$. The results differ slightly from the preliminary report[1a] because of the thermal expansion correction. From magnetic susceptibility measurements[8] there is an indication that the equilibrium constant in toluene solution should be approximately 73% as large as the equilibrium constant in benzene.[8] Applying this correction to the results of Ziegler and Ewald in benzene[5] leads to an expected value of 3×10^{-4} mol/L at 20 °C in toluene, in good agreement with the value obtained in the present work. The value of ΔH in benzene from Ziegler, 11.5 kcal/mol, is likewise in reasonable agreement considering the solvent change and the combined experimental errors.

Reaction of the Trityl Radical with Thiophenol. The reaction of the triphenylmethyl radical with thiophenol is as follows:

$$\begin{aligned} D &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2R\cdot \\ R\cdot + PhSH &\overset{k_2}{\rightleftharpoons} RH + PhS\cdot \\ PhS\cdot + R\cdot &\overset{k_3}{\rightleftharpoons} PhSR \end{aligned} \tag{5}$$

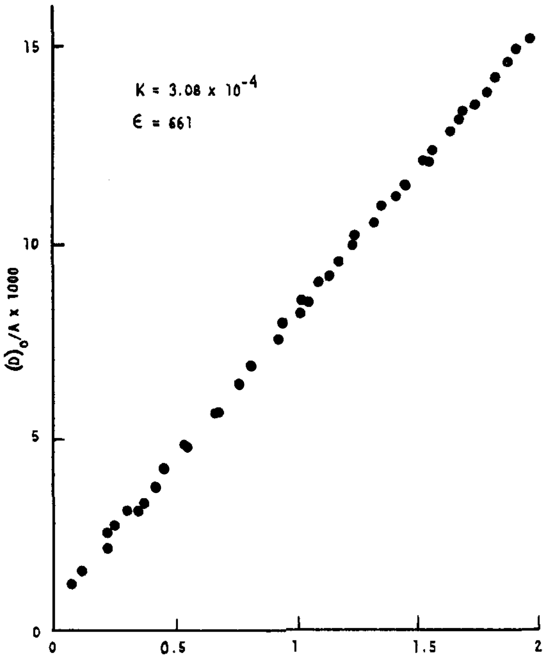

Figure 1. (D_0)/A vs. A plot of dimer at 20 °C in toluene.

The reaction of the phenylthiyl radical with undissociated dimer is possible,[4] but with an insufficient amount of thiol this side reaction and the reversal of the hydrogen transfer are unimportant under the conditions employed. Assuming that a steady state in phenylthiyl radicals is achieved, the following may be derived:

$$-d(R\cdot)/dt = 2k_{-1}(R\cdot)^2 - 2k_1(D) + 2k_2(R\cdot)(PhSH) \tag{6}$$

If the initial equilibrium is fast compared to the reaction of the radical with thiophenol, the first two terms cancel, leaving a second-order expression:

$$-d(R\cdot)/dt = 2k_2(R\cdot)(PhSH) \tag{7}$$

which because of the prior equilibrium cannot be integrated in the usual way. However, it was found upon mixing solutions of the triphenylmethyl radical and thiophenol in toluene that the reaction did not proceed according to this expression. Thus, the complete eq 6 must be used. A computer was used to integrate this equation numerically by the Runge–Kutta method[9] given values for k_1, k_1, k_2, (D_0), and (S_0). From the literature values for k_1[10] and the equilibrium constants measured in this work, values for k_{-1} could be calculated. The experimental and calculated curves of the radical absorbance vs. time were compared for various values of k_2. The results presented in Table II correspond to the values of k_2 which best fit the observed curves. An example of such a determination is shown in Figure 2. The rate constants are adequately fitted by eq 8.

$$k_2 = (2.65 \pm 1.76) \times 10^7 \exp[(-9060 \pm 178\ \text{cal/mol})/RT] \tag{8}$$

Table II. Rate Constants and Isotope Effects for the Reaction of the Trityl Radical with Thiophenol

T, °C	k^{H}_{obsd}[a]	k^{H}_{calcd}[b]	k^{D}_{obsd}[a]	k^{D}_{calcd}[c]	k^H/k^D	k^H/k^D[d]
0	1.63	1.48	0.245	0.227	4.54	5.60
10	2.36	2.67	0.407	0.452	5.38	6.82
20	4.58	4.63	0.861	0.860	5.91	7.61
40	13.5	12.5	2.87	2.75	6.52	8.56

[a] In M^{-1} s^{-1}; the average of about 10 independent measurements. [b] Calculated from eq 8. [c] Calculated from eq 9. [d] Calculated using the Swain–Schaad equation from the tritium isotope effects of ref 4.

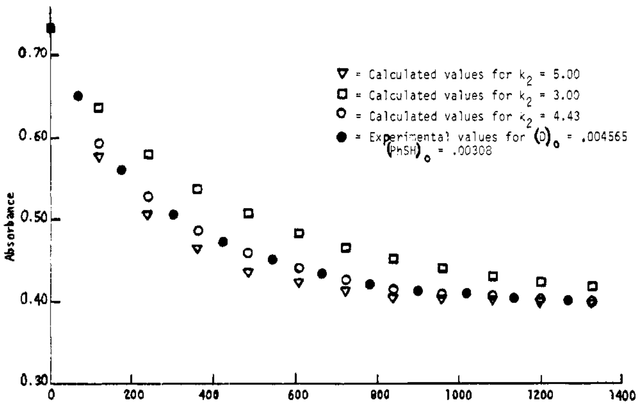

Figure 2. Typical plot of absorbance vs. time for observed and calculated values of triphenylmethyl concentration in its reaction with thiophenol in toluene.

Table II also shows results with deuterated thiophenol and the isotope effects. Since there was only 92% deuteration, the results do not have great quantitative significance; lower values than are predicted from the application of the Swain–Schaad[11] equation to the tritium isotope effects[4] are thus to be expected. The data are reasonably fit by the equations

$$k_2{}^{\mathrm{D}} = (6.8 \pm 3.8) \times 10^7 \exp[(-10\,600 \pm 151 \text{ cal/mol})/RT] \quad (9)$$

$$k^{\mathrm{H}}/k^{\mathrm{D}} = 0.4 \exp(1540/RT) \quad (10)$$

The temperature dependence of the isotope effect could confirm the suggestion of tunneling[12] made from the tritium data[4] and strengthened by the more extreme result with mesityl mercaptan.[13] The incomplete deuteration makes such arguments far from compelling, but the conclusion that the reaction being followed is indeed the hydrogen atom transfer is incontrovertible.

The precision of the rate constants measured here appears to be good, perhaps within ±10%. The temperature was controlled to within ±0.1 °C except at 0 °C, where the control was ±0.2 °C. Individual runs were fit by the computer program to better than 10%, but the overall range of rate constants is sensitive to the accuracy of the earlier rate constants as well as the equilibrium constant. In work to be published in a related system, we avoid this problem.

Conclusion

The equilibrium constant for the dimerization of the triphenylmethyl radical has been measured over the temperature range of −5 to 30 °C. The values agree well with those measured in a different solvent in the same way by Ziegler but are not in agreement with the magnetic measurements in which the wrong dimer structure was used. The rate constant for the reaction of the trityl radical with thiophenol has been measured. The measurements on incompletely deuterated thiophenol confirm that the rate constants measured are indeed for the hydrogen atom transfer and are in imperfect but adequate agreement with the earlier tritium isotope effect measurements.

Experimental Section

Kinetic Measurements. The solutions for kinetic measurements were prepared using an automatic sampling system constructed by P. S. Glaspie. (The details of this apparatus are presented in ref 1b.) The device consists of two specially constructed syringes driven by reversible motors acting on precision screws. A disc with a number of evenly spaced holes is attached to the back of each screw. This chops the beam of light between a light-emitting diode and a phototransistor. The pulses are counted using transistor–transistor logic circuits. The amount of fluid to be delivered from each syringe is independently preset. The device causes the delivery of a predetermined amount from each syringe and automatically refills the syringes from a reservoir. Each syringe delivers its fluid through a glass capillary tip into a thermostatted cell in a Cary 14 spectrophotometer. The temperature was measured using a Wheatstone bridge and a calibrated thermistor which extended into the solution in the cell. Argon gas was used continually to sweep the cell compartment.

Materials. Commercial triphenylmethyl chloride (Aldrich) was recrystallized from acetyl chloride, mp 113–114 °C (uncor) (lit.[15] mp 112.5–113 °C). Toluene was dried over Linde 4A molecular sieves and bulb-to-bulb distilled immediately before use. Acetone was refluxed with potassium permanganate until the purple color persisted for hours. It was then distilled under nitrogen onto 4A molecular sieves and bulb-to-bulb distilled.

1-Diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene. Under a vigorous nitrogen flow, mercury (46 g, 0.228 mol) was added to a solution of 15.9 g (0.057 mol) of triphenylmethyl chloride in 150 mL of purified acetone in a 250-mL flask equipped with a vacuum stopcock. The flask was pumped on for several minutes and the stopcock closed. It was stirred magnetically overnight in the dark. The flask was then placed in a glovebag which was purged with argon at least six times. The flask was opened, and the mixture was filtered to remove excess mercury and mercurous chloride and concentrated to 40 mL. The resulting solid was collected on a sintered glass filter. After recrystallizing in a similar manner five times from purified acetone, the white solid, mp 152–153 °C (uncorr) (lit.[16] mp 150–152 °C), was then placed in an ampule fitted with a vacuum stopcock. The ampule was evacuated, removed from the glovebag, and sealed. Due to the light sensitivity of the triphenylmethyl radical in solution, the above procedure was performed in a darkened room. This procedure is an adaptation of that used by Leftin and Lichtin.[15]

An alternative procedure is the use of an apparatus similar to that of Dorfman.[17] Essentially, it is a large scale Schlenk tube. The apparatus consisted of two 500-mL round-bottom flasks whose necks had been extended. The necks were joined by a short length of 25-mm tubing containing a sintered glass disc. One of the flasks was fitted with a 24/40 male joint so it could be removed. Rather than opening the flask containing the radical solution in a glovebag, it was opened by pressurizing it with argon and filtered directly into the recrystallizer. One neck was stoppered, the other was fitted with a vacuum stopcock, and the system was evacuated and closed off. By tilting the apparatus, the radical solution was filtered through the glass disk into the other flask. The acetone was then bulb-to-bulb distilled back into the other flask until the dimer precipitated out. The slurry was then filtered through the disk. Fresh acetone was distilled back onto the solid, and the procedure was repeated several times. After the dimer was sufficiently pure, it was rinsed off of the disk with fresh acetone. At this point, all of the acetone was distilled into the other flask. The apparatus was placed in a glovebag. It was opened under argon, the flask containing the purified solid was removed, and the dimer was loaded into ampules as before.

Thiophenol. Reagent grade thiophenol was dried over Linde 4A molecular sieves for 10 days. The thiophenol was then decanted into a round-bottom flask and distilled under a nitrogen atmosphere taking only a small middle fraction. This procedure was repeated twice, each time taking only the middle fraction. Final distillation gives material of bp 168.5–169 °C (uncor).

Deuterium-Labeled Thiophenol. Thiophenol was refluxed with 99% D_2O for 3 h, the water was distilled out, and the procedure was repeated three times with fresh 99% D_2O. The thiophenol was then dried over magnesium sulfate for 24 h and distilled as described previously for thiophenol. Comparison of the S–H signal with the C_6H_5 signals using proton NMR spectroscopy was used to assay the protium and hence the deuterium content. The thiophenol contained 8% H on S. The step in which deuterium is lost is believed to be on drying over magnesium sulfate, and the procedure is therefore not recommended. We have since obtained thiophenol-*d* with less than 1% protium content by various distillation procedures.

Acknowledgment. Support of this work by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

Registry No.—1-Diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene, 18909-18-7; triphenylmethyl chloride, 76-83-5; triphenylmethyl, 2216-49-1; thiophenol, 108-98-5; trityl dimer, 31713-29-8.

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Singlet Ethoxycarbonylnitrene Stabilization by Dichloromethane. Thermolysis of Ethyl Azidoformate in Adamantane and Ethylbenzene

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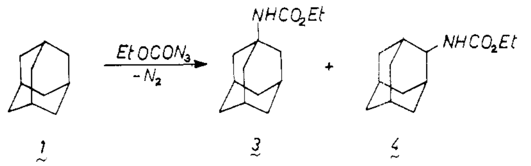
Received August 9, 1977

Some evidence was gained in favor of the formation of a solvent–singlet ethoxycarbonylnitrene complex. It has been reported that dichloromethane,[1,2] hexafluorobenzene,[3,4] and 1,4-dioxan[5] stabilize the singlet state of EtOCON, generated by ethyl azidoformate, during the C–H insertion reaction. Quite recently Takeuchi et al.[6] discussed the situation for EtOCON generated in the THF–CH_2Cl_2–cyclohexane system and their conclusions were against a stabilizing effect during thermolysis.

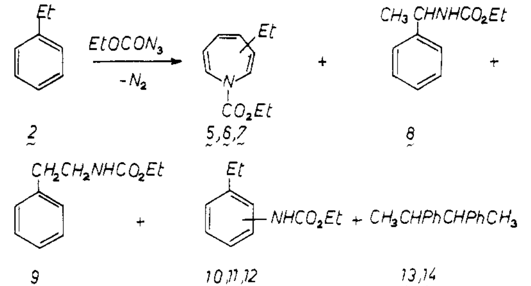
We now report on some more data supporting our opinion on this matter for the thermal decomposition of $EtOCON_3$ in adamantane (**1**) and in ethylbenzene (**2**). This choice was suggested for the former hydrocarbon by the low steric hindrance for the bridgehead C–H bonds compared to that of the CH_2 groups and for the latter one by the high stability of the radical $Ph\dot{C}HCH_3$, in connection with the possibility of the triplet EtOCON participation in the C–H insertion reaction.[7] The reaction between adamantane and $EtOCON_3$ in CH_2Cl_2 has been reported and a 6.0 tertiary/secondary reactivity ratio was found.[8]

We confirmed this figure and found a 23% yield (based on ethyl azidoformate) of 1-adamantylurethan (**3**) and 2-adamantylurethan (**4**). The reactivity ratio for the thermolysis of $EtOCON_3$ in a cyclohexane solution[9] of adamantane was 4.0. In this case the absolute yield of **3** and **4** was 7% while a 11% yield of cyclohexylurethan was found. The decrease in the reactivity ratio and in the yield is in agreement with the formation of a dichloromethane–singlet nitrene complex with a steric demand larger than that of a free nitrene, and it is consistent with our first results on decalins[1] as well as with Belloli's finding on *trans*-1,2-dimethylcyclohexane.[2] In fact in the case of *cis*- and *trans*-decalin, where the tertiary C–H bonds are the most crowded ones, we observed an increased tertiary/secondary reactivity ratio when the thermolysis was run in the absence of CH_2Cl_2. The above interpretation is corroborated by the results we obtained in the photolysis of $EtOCON_3$ in a cyclohexane solution of adamantane. Under these conditions the value of reactivity ratio was 4.1 which was quite close to that (4.0) of the thermolysis in cyclohexane. Since it is known that about 30% of the photolytically generated EtOCON is formed in the triplet state, this should not be involved in the insertion reaction giving the 1- or 2-adamantylurethan.

Scheme I



Scheme II



The thermolysis of $EtOCON_3$ in ethylbenzene has been previously described by Photis[10] and azepines **5–7** were recognized as the main products. We reinvestigated the above thermolysis and compared the results with those of the thermolysis carried out in the presence of CH_2Cl_2. From careful GC analysis, GC–MS study, and comparison with authentic samples we are able to give a more complete picture of the actual situation. Observed products **5–14** are indicated in Scheme II and their relative amounts and absolute yields are shown in Table I.

N-Ethylphenylurethans **10–12** are the isomerization[11] products of azepines **5–7** in the reaction with CH_2Cl_2, as confirmed by heating the products of the thermolysis of $EtOCON_3$ in ethylbenzene after addition of CH_2Cl_2. Urethan **8** arising from EtOCON insertion into benzylic CH_2 is formed in low yield (5%) in thermolysis with CH_2Cl_2, i.e., under the stabilization conditions of the singlet ethoxycarbonylnitrene. The amount of this urethan rises to 16% in the thermolysis without solvent. It is noteworthy that the parallel increase from 6 to 23% of hydrocarbons **13** and **14** comes from the coupling of $Ph\dot{C}HCH_3$ in the absence of dichloromethane. In our opinion this trend is confirmed by the consideration that the ratio of insertion product **8** to the sum of **5, 6, 7, 10, 11,** and **12** products, derived from the singlet EtOCON addition to the benzene ring,[12] goes from 0.056 to 0.26 and seems to indicate

Table I. Thermolysis of $EtOCON_3$ in Ethylbenzene

	Products, %[a]				Ratio
Reaction conditions	5 + 6 + 7	8	10 + 11 + 12	13 + 14	8/(5 + 6 + 7 + 10 + 11 + 12)
90 °C, 15 h, CH_2Cl_2	9 (4.5)	5 (2.5)	80 (41)	6 (3)	0.056
90 °C, 15 h, neat	61 (21.5)	16 (5.5)		23 (8)	0.26

[a] Relative yields; absolute yields are given in parentheses (see Experimental Section).

0022-3263/78/1943-2725$01.00/0