of EtOAc, and washed with 3 × 10 mL of 10% HCl and 10 mL each of saturated $NaHCO_3$ and brine. The organic layer was dried, concentrated, and purified on a 20 × 20 cm 250 μm silica gel prep-TLC plate eluted with 50% EtOAc/CH_2Cl_2 which afforded 30 mg (94%) of psiAβ 2 as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.48 (1 H, ddt, J = 0.5, 11.0, 7.5 Hz, 10-H), 5.35 (1 H, ddt, J = 10.8, 8.8, 1.5 Hz, 9-H), 4.44 (1 H, ddd, J = ~8.0, 6.0, 6.0 Hz, 8-H), 4.30 (1 H, m, 5-H), 2.57 (1 H, m, 2-H), 2.44 (1 H, m, 2-H′), 2.06 (2 H, m, 11-H, H′), 1.95–1.45 (8 H, m), 1.40–1.20 (12 H, m), 0.86 (3 H, t, J = 6.9 Hz, 18-CH_3); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 171.8, 132.9, 131.9, 80.3, 67.2, 32.6, 31.8, 31.5, 29.7, 29.4, 29.3, 29.2, 27.8, 27.7, 22.6, 18.5, 14.1; IR (film) 3430 (br), 2924, 2854, 1732, 1463, 1378, 1246, 1181, 1047, 932, 724 cm^{-1}; HRMS (EI) m/e 296.2357 (M^+; $C_{18}H_{32}O_3$, calcd 296.2351); $[\alpha]^{29}_D$ = +59.3 (c = 0.0076 g mL^{-1}, CH_3CN).

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Supplementary Material Available: ^{1}H NMR spectra of **4a,b**, **5**, **7a,b**, **8a,b**, **10**, **11**, **12**, and **2** (11 pages). Ordering information is given on any current masthead page.

Carboxylation of Carbenes in Low-Temperature Matrices

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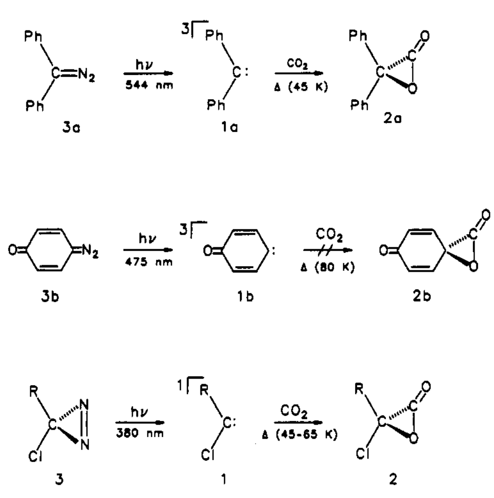
Oxiranones (α-lactones) are low-temperature species that can be generated by photodecarboxylation of malonyl peroxides[1,2] or by epoxidation of ketenes.[3,4] Two derivatives have been reported to be stable at ambient temperature (one of them in solution, only).[4,5] A matrix isolation study of the reaction of methylene with carbon dioxide has been described by Milligan and Jacox.[6]

Recently we reported on the carboxylation of diphenylcarbene **1a** in carbon dioxide doped argon and xenon matrices (0–10% CO_2).[7] The thermal reaction at low temperature (25–70 K) as well as the photochemical reaction at 10 K lead to diphenyloxiranone **2a**, which was characterized spectroscopically and through its subsequent photochemistry. The reaction between a triplet carbene and CO_2 is remarkable because it can be classified as formally "spin-forbidden". Thus, intersystem crossing (ISC) must occur on one of three possible pathways: (i) on the reactant side, which means thermal population of excited singlet diphenylmethylene (S-**1a**), (ii) on the product side, which means formation of triplet **2a**, or (iii) somewhere along the reaction coordinate (nonequilibrium surface crossing[8,9] or formation of a short-lived intermediate, e.g., a diradical with rapid spin equilibration). To study the influence of the spin state of carbenes on their reactivity, we have now investigated the kinetics of carboxylation of two triplet carbenes and two singlet carbenes in solid carbon dioxide: diphenylcarbene (**1a**), 4-oxo-2,5-cyclohexadienylidene (**1b**), phenylchlorocarbene (**1c**), and (*p*-nitrophenyl)chlorocarbene (**1d**). The formally "spin-allowed" reactions of the singlet carbenes **1c** and **1d** are expected to be fast compared to the carboxylation of triplet carbenes **1a** and **1b**.

Scheme I



c: R = Ph
d: R = (p-NO_2)-Ph

Triplet Carbenes 1a and 1b. Matrix isolation of **1a** in CO_2-doped argon matrices has already been described.[7] The IR spectra in solid CO_2 are similar to those in argon, the major difference being line broadening and small shifts of several absorptions. The thermal reaction of **1a** in solid CO_2 is described below. Irradiation (λ = 543 nm) of quinone diazide **3b**, matrix-isolated in CO_2 at 10 K, produced carbene **1b** which has been identified by comparison of its IR spectra with the argon spectra.[10-12] The C=O str vibration shows large line broadening, indicating a strong interaction of the C=O bond and CO_2 molecules in the matrix cage. Other bands are much less perturbed and were used to monitor the carbene concentration. In the temperature range between 45 and 80 K, **1b** is, unlike **1a**, unreactive toward CO_2.

Singlet Carbenes 1c and 1d. On irradiation (λ = 380 nm) of chlorophenyldiazirine (**3c**) in CO_2 (or CO_2-doped Ar matrices) at 10 K, carbene **1c** was formed as the major product.[13-17] A minor product with a predominant IR

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(12) **1b**: IR (CO_2, 10 K) 1503.7 (41.4), 1497.4 (100), 1491.1 (96.5), 1384.1 (42.7), 1371.6 (26.8), 1257.8 (62.3), 1081.3 (14.1), 939.6 (16.7), 828.2 (93.4) cm^{-1} (rel intensity).

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absorption at 1920.2 cm^{-1} was identified as chlorophenyloxiranone **2c**.[1,2,4,5] Isotopic labeling using $^{13}CO_2$ and $C^{18}O_2$ caused a shift of the absorption at 1920.2 cm^{-1} of −56.4 and −27.9 cm^{-1}, respectively, and confirmed the assignment of this high frequency band to the C=O stretching mode of the α-lactone moiety, in accordance with established precedent.[7,18]

No thermal reaction of **1c** and CO_2 was observed at matrix temperatures below 30 K. This clearly indicates a thermal barrier for the reaction of carbene **1c** and CO_2. The small amount of **2c** observed after irradiation of **3c** is produced by the reaction of electronically or vibrationally excited carbene **1c**. Warming above 40 K caused a decrease of the carbene IR bands and the concomitant growth of absorptions assigned to **2c**.

Irradiation of chloro(*p*-nitrophenyl)diazirine (**3d**) (λ = 380 nm), matrix isolated in Ar at 10 K, cleanly gave carbene **1d**.[19-21] **1d** was identified by the characteristic thermal reaction with O_2[22] to give *p*-nitrobenzoyl chloride *O*-oxide.[23] Carbene **1d** is remarkably unreactive in solid CO_2; at 50 K, conditions under which **1a** and **1c** are readily carboxylated, no reaction was observed. Upon warming the CO_2 matrix above 60 K, however, a new product with an intense IR absorption at 1927.5 cm^{-1} is formed.[24] By comparison with the spectra of **2a** and **2c**, the thermal product was identified as chloro(*p*-nitrophenyl)oxiranone **2d**.

Kinetic Studies. To gain insight into the consequences of the carbene spin state on the carboxylation reaction, kinetic studies at several temperatures (45, 55, 65, and 80 K) in solid CO_2 were carried out (Figure 1). The data were evaluated assuming pseudo-first-order kinetics by using the empirical eq 1 described by Siebrand and Wildman.[25]

$$[A]_t = [A]_0 \exp[-(k_1 t)^{\beta}] \qquad (1)$$

The "stretched exponent" β is a measure for the distribution of matrix sites exhibiting different rate constants k_1. For an exponential process in solution β is 1, while in matrices having multiple matrix sites, typical values are close to 0.5.[25] In our experiments β varied between 0.3 and 0.95, an indication of the nonuniform distribution of reactive sites. Due to the approximate nature of this approach, k_1 from different carbenes at various temperatures are only compared qualitatively.

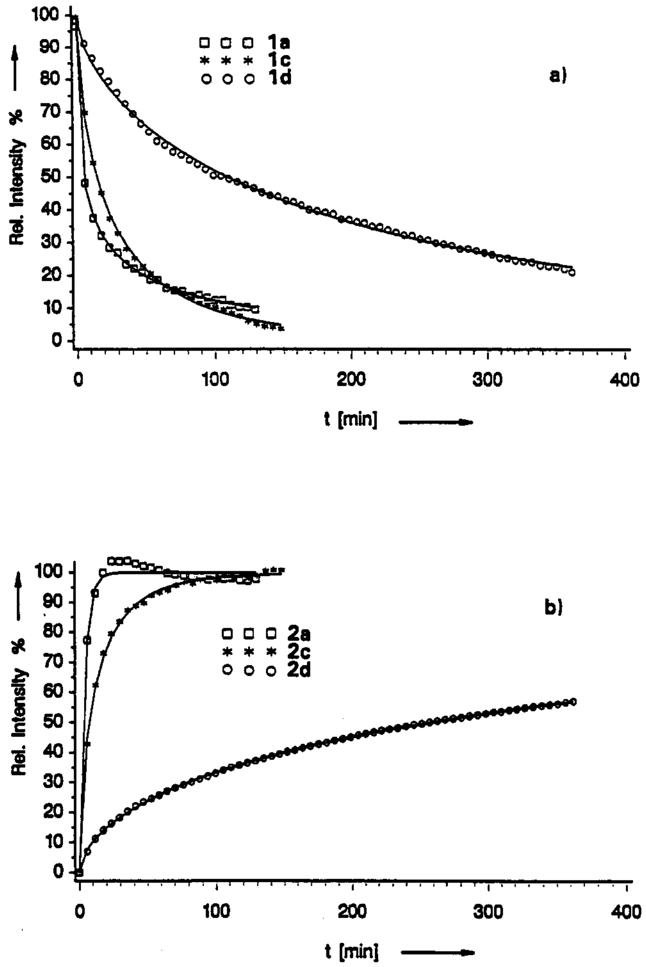

Figure 1. IR peak integral of carbenes **1** (a) and oxiranones **2** (b) vs time at 80 K in solid CO_2. Solid lines are calculated on assuming nonexponential kinetics (see eq 1). The graph reflects decay and growth of the following peaks (cm^{-1}): 1466 (**1a**), 1230 (**1c**), 1212 (**1d**), 1888 (**2a**), 1920 (**2c**), 1927 (**2d**). The decay of **2a** from >100% to <95% is due to CO_2-matrix degradation during annealing.

The difference in reactivity of carbenes **1** toward CO_2 is striking.[26] In solid CO_2 at 80 K, triplet carbene **1a** and singlet carbene **1c** exhibit approximately the same reactivity, while **1d** reacts slower by 2 orders of magnitude (rate constants for **1a** and **c** approximately 10^{-3} s^{-1} compared to 10^{-5} s^{-1} for **1d**)[26] and **1b** is completely unreactive. Thus, there is no indication that the reactivity is influenced by the spin state of carbene **1**. Rather, the data suggest that the carboxylation is dominated by the philicity of the carbene. The electron-withdrawing nitro group causes **1d** to be less nucleophilic than **1c**, and **1b** is less nucleophilic than **1a**. The relative reactivity order **1b** < **1d** < **1c** ≈ **1a** indicates that the nucleophilic attack on the CO_2 carbon atom is rate determining.

For the electrophilic attack of **1c** and **1d** on molecular oxygen, just the opposite order of reactivity is observed: in Ar matrices doped with 1% O_2 the half-life at 35–40 K for **1d** is in the order of minutes, while for **1c** in the order of hours.[14,16] Time-resolved laser flash spectroscopy in O_2-containing solvents at 25 °C gave a rate constant of 2.24

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(17) **1c**: IR (CO_2, 10 K) 1586.1 (70.8), 1451.1 (60.3), 1324.3 (22.0), 1307.0 (25.5), 1230.8 (100), 1172.0 (54.5), 998.4 (11.6), 848.5 (56.9), 569.3 (53.4) cm^{-1} (rel intensity).

(18) **2c**: IR (CO_2, 10 K) 1920.2 (100), 1495.0 (19.8), 1450.6 (36.9), 1256.8 (22.1), 1136.3 (14.3), 1066.9 (16.2), 1030.7 (11.3), 1001.8 (10.9), 916.5 (20.6), 869.7 (12.0), 862.9 (13.9), 602.1 (16.4), 574.2 (12.4) cm^{-1} (rel intensity).

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(21) **1d**: IR (Ar, 10 K) 1601.5 (8.2), 1588.0 (9.9), 1540.3 (27.1), 1354.7 (16.3), 1342.2 (14.2), 1322.9 (9.6), 1206.7 (100), 1168.1 (12.1), 831.1 (35.9), 828.7 (34.5) cm^{-1} (rel intensity); IR (CO_2, 10 K) 1603.0 (15.9), 1587.6 (26.8), 1540.8 (100), 1363.9 (22.2), 1349.4 (58.0), 1324.8 (22.2), 1212.0 (74.0), 1167.2 (11.5), 832.6 (71.2) cm^{-1} (rel intensity). **3d**: IR (Ar, 10 K) 1613.1 (7.2), 1605.9 (6.5), 1584.2 (22.5), 1538.9 (53.4), 1365.3 (9.5), 1347.5 (100), 1321.4 (7.3), 1024.0 (33.8), 1008.1 (12.1), 851.9 (37.8), 849.9 (26.5), 844.1 (9.2) cm^{-1} (rel intensity); IR (CO_2, 10 K) 1613.6 (7.7), 1607.8 (5.5), 1586.6 (22.1), 1539.3 (100), 1366.8 (9.3), 1350.4 (50.1), 1323.4 (8.5), 1024.9 (22.2), 1009.0 (4.1), 852.8 (34.8), 845.1 (13.3) cm^{-1} (rel intensity).

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(23) *p*-Nitrobenzoyl chloride *O*-oxide: IR (Ar, 1% O_2, 10 K) 1421.2 (10.0), 1328.2 (100), 1300.7 (33.8), 1257.3 (81.9), 1002.3 (50.3), 992.6 (15.7), 918.9 (87.2), 909.7 (81.9), 680.2 (13.5) cm^{-1} (rel intensity).

(24) **2d**: IR (CO_2, 10 K) 1942.9 (37.6), 1927.5 (64.0), 1544.3 (100), 1355.2 (100), 1256.8 (11.2), 1072.7 (7.3), 860.0 (19.9), 851.9 (49.3) cm^{-1} (rel intensity).

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(26) Rate constants k_1 (s^{-1}) for the carboxylation reaction of carbenes **1** in CO_2 at 80 K have been calculated (i) from the decay of several IR bands of **1** and (ii) from the formation of IR bands assigned to **2** (standard deviation in brackets). The data have been evaluated according to eq 1: **a**, 1.28 (0.10) × 10^{-3} (i) and 4.19 (0.55) × 10^{-3} (ii); **c**, 0.64 (0.02) × 10^{-3} (i) and 1.31 (0.03) × 10^{-3} (ii); **d**, 8.57 (0.80) × 10^{-5} (i) and 3.43 (0.21) × 10^{-5} (ii).

$\times 10^7\ M^{-1}\ s^{-1}$ for **1d**[27] but no measurable reaction (rate constant $<10^4\ M^{-1}\ s^{-1}$) for **1c**.[28] A similar dependency of the reactivity of singlet aryl carbenes on para substituents has been described by Moss et al.[29]

It can be asked whether the carboxylation of carbenes **1** is a concerted reaction or not. For triplet carbenes **1a** and **1b**, there is no experimental evidence for the formation of an intermediate or carbene complex even if the carbene is isolated in pure CO_2. The small frequency shifts and line broadening of IR bands in CO_2 relative to Ar—which have been observed as well for singlet carbenes **1c** and **1d**—are attributed to unspecific matrix effects rather than to the formation of defined molecular complexes. On the other hand, we cannot exclude intermediates in the carboxylation of **1a** which are short-lived under the conditions of matrix isolation and rapidly rearrange to **2a**. The singlet–triplet gap ΔH_{ST} of **1a** in an unpolar solvent (isooctane) is 4.0 ± 0.3 kcal/mol[30] and therefore the thermal population of the excited singlet state is too small to account for the observed reactivity toward CO_2 at temperatures below 50 K. It is therefore reasonable to assume that the carboxylation of **1a** does not procede via thermally populated singlet **1a**. Crossover to the singlet manifold occurs at an unspecified stage along the reaction coordinate, and short-lived triplet diradicals having high ISC rates are possible intermediates.

The only hint for the formation of an ylide-type intermediate in the reaction of singlet carbenes **1c** and **1d** comes from the observation of a pale blue-green color when the carbenes are produced in the presence of CO_2. From our experiments there is no indication whether the colored compound is an intermediate on the path to oxiranones **2c** and **2d** or rather a side product. No colored product is observed during the carboxylation of **1a**.

In summary, this study suggests that the reactivity of carbenes **1** toward CO_2 is determined by their philicity rather than by their spin state. The reactivity is decreased by electron-withdrawing substituents, and the only products identified are oxiranones **2**. Short-lived triplet diradicals might be involved in the ISC, although there is no experimental evidence for the formation of these species.

Experimental Section

Diazo compounds **3a**[31] and **3b**[32] and diazirines **3c** and **3d**[33] have been synthesized according to literature procedures. The setup for matrix experiments has been described elsewhere.[16,34] Carbon dioxide (Messer Griesheim, 99.995%) was deposited at 80 K, yielding sufficiently transparent matrices and still matrix-isolated samples (the degree of matrix isolation was monitored by observing the line width of IR bands as function of the temperature of matrix deposition). The line width of IR bands increased during irradiation or annealing of the CO_2 matrices.

Other gases used were argon (Messer Griesheim, 99.9999%), oxygen (Messer Griesheim, 99.998%), $C^{18}O_2$, and $^{13}CO_2$ (MSD Isotopes 99.75% and 99.3% isotopic purity, respectively). Infrared spectra were recorded on a Bruker IFS 66 FT-IR spectrometer in the range 4000–450 cm^{-1}; the standard resolution was set to 1 cm^{-1}. Irradiation was performed by using a 500-W high-pressure mercury arc lamp, dichroic mirrors to preselect the range of irradiation, and appropriate cut-off filters.

Acknowledgment. Financial support was given by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. **1a**, 3129-17-7; **1b**, 3225-37-4; **1c**, 19807-41-1; **1d**, 102146-13-4; **2a**, 30436-19-2; **2c**, 138061-24-2; **2d**, 138061-25-3; **3a**, 883-40-9; **3b**, 932-97-8; **3c**, 4460-46-2; **3d**, 39184-67-3.

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Regioselective α-Methoxycarbonylsulfenylation of Ketones and Aldehydes: A Versatile Method for Preparation of Thiazolones, Thiadiazinones, and 3-Indolethiols[1]

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The characteristic properties of α-sulfenylcarbonyl compounds have led to the development of a number of useful transformations in organic synthesis.[3] In the area of heterocyclic chemistry, it is well documented that α-(acylthio)- and α-(cyanatothio)carbonyl compounds can serve as the precursor of 2-substituted thiazole derivatives (i.e., Hantzsch synthesis).[4] In addition, α-sulfenylcarbonyl compounds play also an important role in the synthesis of indole derivatives.[5]

In general, the most common method for the synthesis of α-sulfenylcarbonyl compounds involves the reaction of lithium enolates or trimethylsilyl enol ethers and organic disulfides,[5a–d] sulfenyl chlorides,[5a,e] or *S*-phenylthiosulfonates.[5b] Other methods for the synthesis of α-sulfenylcarbonyl compounds involve the reaction of α-halo ketones with thiolate anions or sulfenyl chlorides in the presence of zinc.[7] Methods for the synthesis of α-sulfenylated ketones include the reaction of 1,3,2-dioxophospholes[8] or α-diazoketones[9] with sulfenyl chlorides.

In this paper, we report a novel and regioselective α-methoxycarbonylsulfenylation of a variety of ketones and aldehydes employing (methoxycarbonyl)sulfenyl chloride **1**[10] as an electrophilic sulfenylating agent. Furthermore, the cyclization reactions of the resultant α-methoxycarbonylsulfenylated carbonyl compounds **2** with amines

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