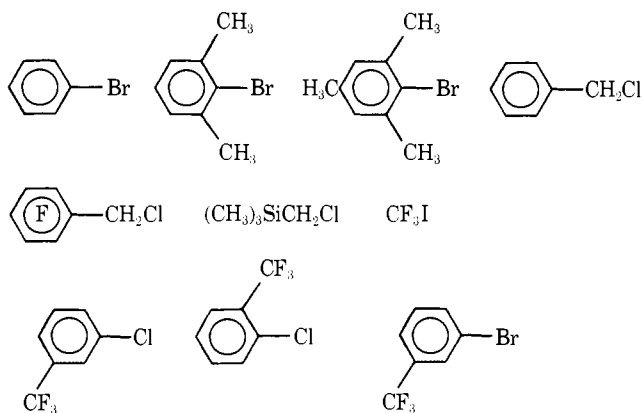


Chart I



tions.⁷ At this time, in view of the electronegativity of C_6F_5 and the higher stabilities of the complexes when more electron-rich π -arenes are employed, the stabilization of the complex is a delicate balance of "push-pull" electronic configuration. This delicate stabilizing "balancing act" is needed in spite of the fact that **1** is a closed shell diamagnetic 18-electron configuration. Thus, strongly electronegative σ -bonded ligands with supposedly strong π -acceptor characteristics are required, and another good candidate is the pentachlorophenyl group, in light of the recent work of Wada and coworkers.⁸

The preparative details for synthesizing **1** are very similar to those previously described for the analogous Co complex.¹ Vaporizing 1.5 g of Ni and depositing with 50 mL of C_6F_5Br and 15 mL of dry toluene yields ~3.5 g of product crystallized from toluene: mp 137–140 °C (darkens at 125 °C); IR (KBr pellet, cm^{-1}) 3120 (w), 2940 (w), 1640 (w), 1615 (w), 1535 (m, sh), 1505 (vs), 1470 (vs), 1440 (vs, sh), 1390 (m), 1360 (m), 1280 (w, sh), 1260 (w), 1215 (w), 1180 (w), 1120 (w), 1060 (s), 1040 (m, sh), 1005 (w), 985 (w), 960 (vs), 875 (w), 800 (s), 790 (s), 730 (w). Anal. Calcd for $\eta^6-C_6H_5CH_3(C_6F_5)_2Ni$: C, 47.06; H, 1.66; F, 39.17. Found: C, 47.10; H, 1.70; F, 39.20.

Additional chemistry, x-ray structures, and syntheses of other metal(II)-arene complexes (both by metal vapor means and conventional means) will be reported soon.

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References and Notes

- B. B. Anderson, C. Behrens, L. J. Radonovich, and K. J. Klabunde, *J. Am. Chem. Soc.*, **98**, 5390 (1976).
- K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975); also P. S. Skell, *ibid.*, **14**, 195 (1975); P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965); P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972); K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975); M. Moskovits and G. Ozin, Ed., "Cryochemistry", Wiley-Interscience, New York, N.Y., 1976.
- Cf. F. J. Hirsekorn, M. C. Rakowski, and E. L. Muettterties, *J. Am. Chem. Soc.*, **97**, 237 (1975); E. L. Muettterties and F. J. Hirsekorn, *ibid.*, **96**, 4063 (1974), and references therein.
- K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, **98**, 1021 (1976).
- K. J. Klabunde, S. C. Davis, H. Hattori, and Y. Tanaka, *J. Catal.*, submitted for publication.
- Cf. M. L. Churchill and M. V. Veidis, *Chem. Commun.*, 1099 (1970).
- L. J. Radonovich, F. Koch, M. Bader, B. B. Anderson, and K. J. Klabunde, unpublished work.
- M. Wada and K. Oguro, *Inorg. Chem.*, **15**, 2346 (1976); M. Wada, Kusabe, and K. Oguro, *ibid.*, **16**, 446 (1977).

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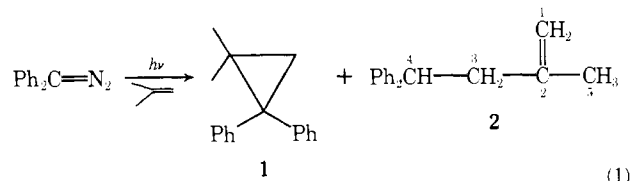
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Reactions of Carbenes at Low Temperatures. Diphenylcarbene and Isobutene

Sir:

Reactions of triplet diphenylcarbene, Ph_2C , with olefins are readily observable at ambient temperature,^{1,2} whereas the analogous chemistry of phenylcarbene and phenylmethylcarbene becomes dominant only at very low temperatures.^{3,4} Notwithstanding the report that Ph_2C reacts with isobutene only by addition at 25 °C,^{1d} we find that both addition and "insertion" reactions compete effectively at 0 °C, albeit the former is dominant; cf. eq 1. We now report that (a) reaction



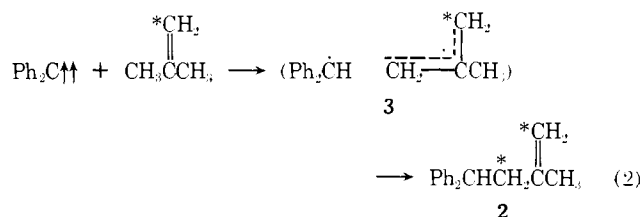
1 is dramatically temperature dependent, with **2** becoming the near-exclusive product at -196 °C; (b) alkene **2** is a true abstraction-recombination (a-r) product at -77 °C and probably also at -196 °C, although there the matrix imposes a "memory" effect on radical-pair recombination; and (c) the observed relation between $\ln(2/1)$ and T^{-1} implies that there is no enhancement of olefin formation³ when Ph_2C and isobutene react in the solid phase.

Photolysis at 0 °C of 0.116 M solutions of diphenyldiazomethane⁵ in isobutene gave 1,1-dimethyl-2,2-diphenylcyclopropane (**1**) and 2-methyl-4,4-diphenyl-1-butene (**2**) in a ratio of 3.2:1, eq 1.⁶ Also formed were benzophenone, benzophenone ketazine, and (<1%) diphenylmethane. Cyclopropane **1** was identified by NMR,^{1d} whereas authentic **2** was prepared by Yates' method,⁷ and was identical (GC, NMR,⁷ IR) with **2**⁸ isolated from reaction 1.

The temperature dependence of reaction 1 is illustrated by Table I; at -196 °C, olefin **2** was almost the sole $C_{17}H_{18}$ product detectable.⁹

To investigate the origin of **2**, diphenyldiazomethane was photolyzed in $^{13}CH_2=C(CH_3)_2$.¹⁰ In the ^{13}C NMR spectrum of **2**, C_1 and C_3 appear at δ_C^{TMS} 112.62 and 43.96, respectively. Intensity analyses of these signals, in standard and reaction product samples of **2**, afforded $^{13}C_3:^{13}C_1$ label distributions of 50:50 and 28:72, respectively, in **2** from -77 °C (solution) and -196 °C (matrix) photolyses.¹¹

The equidistribution of ^{13}C between C_1 and C_3 , observed in product **2** formed at -77 °C, establishes an a-r mechanism operating with complete equilibration of radical pair **3**; cf. eq 2. Label equilibration is significantly incomplete in the -196



°C matrix photolysis, with the direction of inequality suggesting a partial inhibition, by the matrix, of the relative motions needed within **3** to geometrically equilibrate C_3 and C_1 , relative to $Ph_2C\dot{H}$. There is no evidence for triplet Ph_2C addition, followed by H migration, as an important origin of **2**.^{4,12} Such a mechanism would require an excess of ^{13}C at C_3 .

Figure 1 presents $\ln(2/1)$ as a function of T^{-1} . A least-squares correlation based on all five points ($r = 0.988$, significant at the 99% confidence level) yields $\Delta E_{app}^{a(arent)} = 1.1$

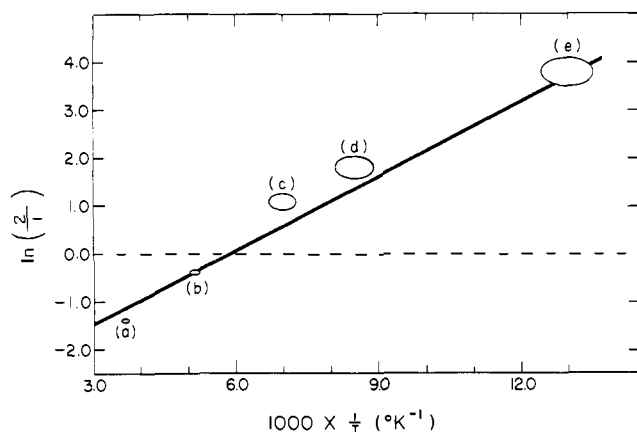


Figure 1. $\ln(2/1)$ vs. T^{-1} (K^{-1}) for reaction 1; cf. Table I. Points a-c represent solution experiments; points d and e refer to matrix photolyses.

Table I. Product Ratios from Ph_2C and Isobutene as a Function of Temperature^a

Temp, °C	2/1	Av dev _n ^b
0	0.243	0.008 ₄
-77	0.682	0.007 ₂
-130	3.07	0.04 ₃
-155 ^c	6.25	0.14 ₃
-196 ^c	44.6	7.57 ₆

^a Values were determined by GC⁶ and are corrected for relative detector response. ^b Average deviation of n experiments. ^c Solid isobutene matrices were formed.

kcal/mol. However, $\Delta E_{\text{app}}^{\text{a}}$ contains contributions from at least four sources: activation energies for singlet addition ($E_{\text{ad}}^{\text{a,S}}$), triplet abstraction ($E_{\text{abst}}^{\text{a,T}}$), and triplet addition ($E_{\text{ad}}^{\text{a,T}}$), as well as the differential singlet-triplet energy ($\Delta E_{\text{S-T}}$). If $E_{\text{ad}}^{\text{a,T}}$ is the largest of the activation energies,¹³ and triplet addition is neglected, then $\Delta E_{\text{app}}^{\text{a}} \sim (E_{\text{ad}}^{\text{a,S}} - E_{\text{abst}}^{\text{a,T}}) + \Delta E_{\text{S-T}}$. Taking an upper limit of 3 kcal/mol for $\Delta E_{\text{S-T}}$,^{1a,2c} and recalling that $\Delta E_{\text{app}}^{\text{a}} = 1.1$ kcal/mol, we estimate that $(E_{\text{abst}}^{\text{a,T}} - E_{\text{ad}}^{\text{a,S}}) \leq 1.9$ kcal/mol.¹⁴ That is, the activation energy for triplet abstraction¹⁵ is greater than that for singlet addition, but the difference is *smaller* than $\Delta E_{\text{S-T}}$.¹⁶ Thus, as temperature decreases for reaction 1, triplet abstraction gains relative to singlet addition, because the increase in triplet population more than offsets the higher activation energy needed for abstraction.

Analogous behavior may well be common for other arylcarbenes, viz., phenylcarbene,³ phenylmethylcarbene,⁴ and fluorenylidene.¹⁷ More generally, we should expect similar temperature dependent phenomena with other carbenes and for other types of competitive singlet and triplet reactions.^{18,19}

Finally, it will be noted from Figure 1, that *less* olefin is formed in the -196 °C matrix experiment (point e) than is predicted by simple extrapolation of the solution points: 2/1 predicted by extrapolation of points a-c is ~290 at -196 °C, whereas the observed value is 44.6. With Ph_2C and isobutene, it is clear that temperature effects (i.e., differential energy factors) are largely, if not exclusively, responsible for the ultimate dominance of the triplet abstraction reaction in both very cold solutions and frozen matrices. The suspicion is strong that temperature effects must also be major influences in the previously observed, analogous reactions of phenylcarbene³ and phenylmethylcarbene.⁴

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References and Notes

- (1) (a) G. L. Closs and B. E. Rabinow, *J. Am. Chem. Soc.*, **98**, 8190 (1976). (b) G. L. Closs, L. E. Closs, and B. E. Rabinow, unpublished results; we thank Professor Closs for a summary of this work. (c) D. Bethell, M. R. Brinkman, J. Hayes, and K. McDonald, *J. Chem. Soc., Perkin Trans. 2*, 966 (1976). (d) W. J. Baron, M. E. Hendrick, and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 6286 (1973). (e) G. L. Closs and L. E. Closs, *ibid.*, **91**, 4549 (1969).
- (2) (a) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. I, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973, pp 73-79; (b) G. L. Closs, *Top. Stereochem.*, **3**, 224f (1968); (c) G. L. Closs in "Carbenes", Vol. II, R. A. Moss and M. Jones, Jr., Ed., Wiley, New York, N.Y., 1975, pp 174-183.
- (3) R. A. Moss and U-H. Dolling, *J. Am. Chem. Soc.*, **93**, 954 (1971).
- (4) R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, **99**, 1262 (1977).
- (5) L. I. Smith and K. L. Howard, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 351.
- (6) Photolyses were run on degassed samples, sealed into Pyrex tubes, using a Rayonet reactor fitted with 3000-Å lamps. Excess diazo compound was destroyed with maleic anhydride (neither 2 nor 1 was formed during this process), and products were analyzed by GC on a 12 ft X 0.25 in., 5% Carbowax 20M column at 200 °C.
- (7) P. Yates, G. D. Abrams, M. J. Betts, and S. Goldstein, *Can. J. Chem.*, **49**, 2850 (1971).
- (8) Exact mass: calcd for $\text{C}_{17}\text{H}_{18}$, m/e 222.1408; found, 222.1410.
- (9) Control experiments established that 2 was a primary product. Photolysis of diphenyldiazomethane and 1 in 1-octene, at either 0 or -196 °C, gave no 2. Inclusion of excess benzophenone in 0 and -155 °C photolytic runs gave ratios of 2/1 of 0.268 and 6.60, respectively, not markedly different from the "normal" values; cf. Table I.
- (10) NMR analyses showed 11.1-11.2 at. % ¹³C at C₁; isobutene recovered after several photolyses showed 11.2-11.8 at. % ¹³C at this position. For preparative details, see ref 4, note 9.
- (11) Duplicate runs, at each temperature, agreed to within ±1%. NMR analyses were relative to C₆ at $\delta_{\text{C}}^{\text{TMS}}$ 22.58; analyses based on C₄ ($\delta_{\text{C}}^{\text{TMS}}$ 49.40) gave comparable results.
- (12) Reinvestigation of $\text{PhCCH}_3 + {}^{13}\text{CH}_2=\text{C}(\text{CH}_3)_2$ matrix reactions has shown the label distribution reported in ref 4 to be in serious error and the suggested addition-H migration mechanism has been withdrawn: R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, **99**, 7399 (1977) (correction).
- (13) In reactions of diphenylcarbene and *cis*-butene, $(E_{\text{ad}}^{\text{a,T}} - E_{\text{ad}}^{\text{a,S}}) \sim 3.6$ kcal/mol and $(E_{\text{ad}}^{\text{a,T}} - E_{\text{abst}}^{\text{a,T}}) \sim 0.9$ kcal/mol.^{1b} We assume, with Closs,^{2b} that equilibration of singlet and triplet Ph_2C is the fastest process in the system.
- (14) With Ph_2C and *cis*-butene, this value is estimated to be ≤ 2.8 kcal/mol.^{1b}
- (15) We assume that all radical pairs 3 recombine to give 2; note that little Ph_2CH_2 , which would represent escaped $\text{Ph}_2\text{CH}^\cdot$, is formed.
- (16) A similar conclusion follows if only solution data, points a-c, Figure 1, are used to determine $\Delta E_{\text{app}}^{\text{a}}$. In this case, $\Delta E_{\text{app}}^{\text{a}} = 1.5$ kcal/mol and $(E_{\text{abst}}^{\text{a,T}} - E_{\text{ad}}^{\text{a,S}}) \leq 1.5$ kcal/mol.
- (17) R. A. Moss and M. A. Joyce, unpublished work.
- (18) For examples, see H. Tomioka, T. Inagaki, and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, 1023 (1976); and H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99**, 6128 (1977). The latter work, published after completion of the experiments reported herein, employs similar interpretations applied to the reactions of arylcarbenes with alcohols.
- (19) Similar conclusions follow from the work of Closs et al.^{1b}

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Selective Olefin Dimerization via Tantalocyclopentane Complexes

Sir:

We have shown recently that a neopentylidene complex, $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$, reacts with ethylene to give 4,4-dimethyl-1-pentene,¹ probably by transfer of a β -hydrogen atom selectively to the substituted α -carbon atom in an intermediate tantalocyclobutane complex.² If the organometallic product of the initial reaction, $\text{CpCl}_2\text{TaCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ (1), were to decompose similarly,³ it would be a catalyst for dimerizing ethylene selectively to 1-butene, an almost unknown result for metal hydride based homogeneous catalysts.⁴ We present re-