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Stereoselectivity of Carbene Intermediates. I. *p*-Tolylcarbene

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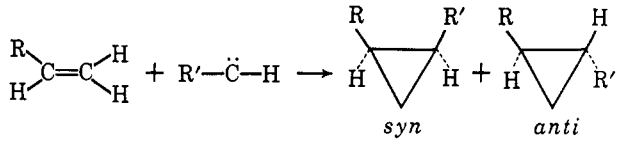
p-Tolyl carbenoid has been generated from various precursors and added to propene, butene-1, *i*-propylethylene, and *t*-butylethylene. The stereochemistry and rates (relative to *trans*-butene) of these additions are discussed in terms of steric hindrance to carbenoid addition.

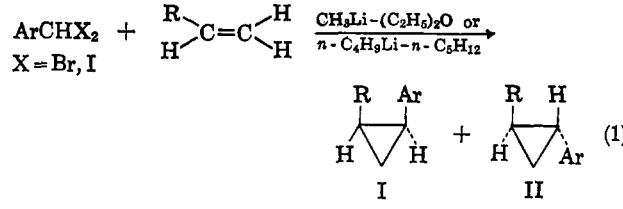
The addition of unsymmetrically substituted carbenes and carbenoids to olefins which have neither a center of symmetry, nor a twofold rotational axis defined by the carbon–carbon double bond, affords isomeric cyclopropane products. For monosubstituted carbenes, the *stereoselectivity* of addition can be described as net *syn* if, in the product mixture, that cyclopropane predominates, in which the carbene substituent is *cis* to the largest number of olefinic substituent groups. Predominance of that cyclopropane in which the carbene substituent is *trans* to the largest number of olefin substituents represents net *anti* addition.[1]



Monosubstituted arylcarbenes and carbenoids[2–4] and alkylcarbenes and carbenoids[5–7] generally exhibit *syn* stereoselectivity. To learn something of the limits of *syn* stereoselectivity in aryl carbenoid addition, we have added *p*-tolyl carbenoid to a series of increasingly hindered alkylethylenes, determining, in each case, resultant *syn*/*anti* ratio, as well as over-all rate of addition relative to a *trans*-butene standard. Both kinds of data were studied as a function of solvent and carbenoid leaving group.

Results

Synthesis of 1-Alkyl-2-*p*-Tolylcyclopropanes.—The reaction studied is described in eq. 1.[2] The *p*-methylbenzal iodide employed in eq. 1 was obtained *via* the action of iodine on *p*-methylphenyldiazomethane. For synthetic purposes, the cyclopropanes were best prepared by action of methyllithium in ether on requisite olefinic solutions of *p*-methylbenzal bromide.[2] In this case, yields of isomer pairs a, c, and d were 37, 48, and 28%, respectively (determined on distilled product, purity greater than 90% by v.p.c.). Preparation of Ib–IIb has been described.[2]



a, R = CH_3
b, R = C_2H_5
c, R = *i*-C_3H_7
d, R = *t*-C_4H_9

(Ar = *p*-$CH_3C_6H_4$)

Use of butyllithium in pentane as generative base in eq. 1 led to by-products which codistilled with desired cyclopropanes.[8] Though these products were cleanly separated *via* the gas chromatograph, they made butyllithium unattractive for synthetic purposes. Final purification of all cyclopropanes was effected by preparative v.p.c.

Stereochemistry.—The stereochemistry of each cyclopropane was assigned most readily *via* n.m.r. It has been established that, in arylalkylcyclopropanes, alkyl groups *cis* to aryl substituents experience net shielding due to aryl ring currents, while alkyl groups *trans* to aryl substituents experience a (smaller) net

(1) Only carbene additions which are highly stereospecific will be discussed in this paper. The term carbenoid is used in the sense defined in ref. 2.

(2) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(3) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962).

(4) A reported example of *anti*-arylcarbene addition [J. E. Hodgkins, J. D. Woodyard, and D. L. Stephenson, *ibid.*, **86**, 4080 (1964)] has recently been questioned: G. L. Closs, Carbene Symposium at Lewis College, Lockport, Ill., April 3, 1965.

(5) H. M. Frey, *J. Chem. Soc.*, 2293 (1962).

(6) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 4876 (1964).

(7) See below for further discussion of alkyl carbenoid stereoselectivity.

(8) Though these by-products have not been fully characterized, their n.m.r. spectra, v.p.c. retention times, and absence when methyllithium is used suggest that they arise by combination of *n*-butyl- and *p*-methylbenzal moieties.

Table I

N.m.r. Data for Newly Prepared Isomeric 1-Alkyl-2-*p*-tolylcyclopropanes[a]

Compd.	Config.	Signals, (integrals), assignments[b]
Ia	*syn*	419 s, (4.0), aryl; 137 s and 137–107 m, (4.2), *p*-methyl and benzylic; 66–21 m and 48 s, (6.1), cyclopropyl and methyl
IIa	*anti*	425–400 m, (4.0), aryl; 133 s, (3.0), *p*-methyl; 102–78 m and 69 s (broad) and 69–30 m, (6.6), benzylic, methyl, and cyclopropyl
Ic	*syn*	418 s, (4.0), aryl; 137 s and 137–115 m, (3.9), *p*-methyl and benzylic; 68–30 m, (9.8), cyclopropyl and alkyl[c]
IIc	*anti*	411 s, (4.0), aryl; 135 s and 101–83 m, (4.0), *p*-methyl and benzylic; 61 s and 61–31 m, (10.7), isopropyl and cyclopropyl
Id	*syn*	435–407 m, (4.0), aryl; 137 s and 137–102 m, (3.9), *p*-methyl and benzylic; 60–42 m and 42 s, (11.9), cyclopropyl and *t*-butyl
IId	*anti*	412 s, (4.0), aryl; 135 s and 113–90 m, (4.0), *p*-methyl and benzylic; 55 s and 62–36 m, (12.2), *t*-butyl and cyclopropyl

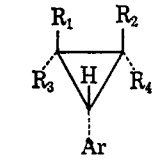
[a] Varian A-60 spectrometer was used. [b] Spectra determined in CCl_4 and reported in c.p.s. downfield from internal TMS; m = multiplet, s = singlet. [c] In this case, the poorly resolved signal of the isopropyl methyls occurs at the highfield end of the multiplet, *ca.* 42 c.p.s.

deshielding.[9] The stereochemistry indicated in Table I follows from the observed alkyl group resonance positions.

An independent check on these assignments is possible from the data. In all compounds to which *anti* stereochemistry has been assigned by the above method, it is found that the multiplet due to the benzylic proton appears at higher field than in the corresponding *syn* isomer. Examination of models of Ia and IIa indicates that the effect of ring-carbon–alkyl-carbon bond anisotropy on the benzylic proton should be shielding when this proton is *cis* and deshielding when it is *trans* to the alkyl substituent (*i.e.*, when the cyclopropane is of the *anti* and *syn* series, respectively).[10] There are further effects from the α-methyl groups in the c and d isomer pairs. These added anisotropies, together with the general problem that the preferred aryl conformation (with respect to the cyclopropane ring, and, hence, with respect to the benzylic proton) is probably not the same in *syn* and *anti* isomers,[2] make difficult calculations of expected chemical shift differences for the benzylic protons. Nonetheless, the observed differences are fully consistent with stereochemistry assigned on the basis of alkyl resonance positions.

Two peculiarities of the n.m.r. data required special note. In IIc, no splitting is observed for the methyl protons of the isopropyl group. This situation is not unprecedented[11] and could be the case if the chemical shifts of the carbinyl proton and *gem*-methyl protons have become equal. A combination of conformational and shielding effects might lead to such equivalence.

Of further interest are the observed aryl proton multiplicities. Previous data for compounds of structure III[2] indicate a singlet aryl resonance where $R_3 = R_4 = CH_3$ (or $R_3 = C_2H_5$, $R_4 = H$) and $R_1 = R_2 = H$, but a multiplet where $R_3 = R_4 = H$. (In the latter case, $R_1 = R_2 = CH_3$ or $R_1 = C_2H_5$, $R_2 = H$.) Present data reveal that, while Ia and IIa follow the previous pattern, compounds Ic and IIc both exhibit aryl singlets, while in Id and IId the expected pattern is reversed. Though a full discussion of the origin of these effects is here deferred, it is clear that aryl multiplicities in III should not be employed as sole evidence for stereochemistry.



III, Ar = C_6H_5 or *p*-$CH_3C_6H_4$

Independent checks on n.m.r. stereochemical assignments were carried out for the c and d isomer pairs. (Stereochemistry of IIb had been previously established by alternate synthesis.[2]) Thus, in both cases, it was possible to isomerize *syn* to *anti* adduct by treatment with 2 *N* potassium *t*-butoxide in dimethyl sulfoxide at 100°.

***syn/anti* Ratios and Relative Addition Rates.**—*syn/anti* ratios and rates of addition to the various 1-alkylethylenes (relative to *trans*-butene) were determined at −10° in the usual manner.[2] Control experiments established product stability to reaction and chromatographic conditions. Competition experiments were carried out for three methods of carbenoid generation: *p*-methylbenzal bromide with methyllithium in ether, with butyllithium in pentane, and *p*-methylbenzal iodide with butyllithium in pentane. Final competition values were obtained on crude reaction products by v.p.c. with flame ionization detector calibrated by standard adduct mixtures. All values, unless noted, are averages of at least two experiments; reproducibility was, with one exception (7%), inside 5%. Data are gathered in Tables II and III.

Table II

syn/anti Preference. Addition of *p*-Tolyl Carbenoid to 1-Alkylethylenes at −10°

R	Iodide–pentane[a]	Bromide–pentane[a]	Bromide–ether[b]
CH_3	...	...	3.1[c]
C_2H_5	2.7	2.6[d]	2.1[e]
i-C_3H_7	1.9	1.9	1.4
t-C_4H_9	0.42	0.72	0.45

[a] Butyllithium (2 *N*) in pentane in reaction 1. [b] Methyllithium (2 *N*) in ether (from methyl bromide). [c] Determined at −50°, single value. [d] See ref. 2. [e] See ref. 17.

Table III

Rates of *p*-Tolyl Carbenoid Addition to 1-Alkylethylenes (Relative to *trans*-Butene) at −10°

R	Iodide–pentane[a]	Bromide–pentane[a]	Bromide–ether[b]
C_2H_5	0.68	0.90[c]	0.55[d]
i-C_3H_7	0.35	0.39	0.28
t-C_4H_9	0.12	0.15	0.14[e]

[a] Butyllithium (2 *N*) in pentane in reaction. [b] Methyllithium (2 *N*) in ether (from methyl bromide). [c] See ref. 2. [d] See ref. 17. [e] Single value.

(9) See ref. 2 for a full discussion of this effect.

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 155 ff.

(11) K. Crowley, *J. Am. Chem. Soc.*, **86**, 5692 (1964); J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.*, **87**, 3532 (1965).

Because of the known solvent effect on *syn/anti* preference,[2] these data, and relative rate data, were determined in both pure hydrocarbon and mixed ether–olefin solvent for bromide precursor. Though only small quantities of ether are introduced with the base, *e.g.*, 2 ml. of ether/20 ml. of olefin, the solvent effect has reached its limit.[2]

If the relative addition rates are partitioned so as to reflect *syn/anti* preference,[2] the data can be presented as in Table IV.

TABLE IV

RATES OF *p*-TOLYL CARBENOID ADDITION TO 1-ALKYLETHYLENES, INCORPORATING *syn/anti* PREFERENCE (RELATIVE TO *trans*-BUTENE) AT −10°[a]

	syn addition			*anti* addition		
R	Iodide–pentane	Bromide–pentane	Bromide–ether	Iodide–pentane	Bromide–pentane	Bromide–ether
C_2H_5	0.99	1.3	0.75	0.37	0.50	0.35
i-C_3H_7	0.46	0.51	0.33	0.24	0.27	0.23
t-C_4H_9	0.071	0.13	0.086	0.17	0.17	0.19

[a] All rates were normalized to *trans*-butene by a factor of 2.

Discussion

***syn* Stereoselectivity. Synthesis of Arylcyclopropanes.**—Of the common monosubstituted carbenes and carbenoids, carbalkoxy, alkoxy, and aryloxy (though with some exceptions) exhibit *anti* stereoselectivity.[12] On the other hand, arylthio,[12] arylseleno,[12] chloro[12] (with one recently reported exception[13]), and, as noted at the outset, aryl and alkyl carbenes and carbenoids[14] exhibit *syn* stereoselectivity.

Since *syn*- and *anti*-arylalkylcyclopropanes are readily separable *via* preparative v.p.c., and since *anti*-arylcyclopropanes are, *via* base-catalyzed isomerization, readily available from their *syn* isomers, those synthetic conditions which maximize *syn* addition are of particular interest. A goal of the present investigation was determination of those conditions. Parameters to be considered were precursor of the reactive intermediate, substitution of the aryl ring, solvent, and, of course, structure of the olefinic substrate.

It has previously been shown that *syn* preference holds whether the carbenic species is produced *via* aryldiazomethane photolysis or *via* the action of alkyllithium on a benzal bromide.[2] *syn* stereoselectivity, over-all yield, and general simplicity are optimal in the latter method, making it the method of choice.[15]

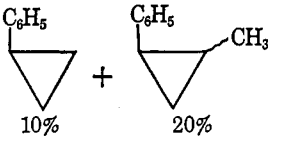
Benzal bromide precursors also appear to be better than alternative benzal halides. Benzal iodides, while affording arylcyclopropanes, are uninviting precursors because of the difficultly available halide, while benzal chlorides lead to arylchlorocarbenes.[16]

It has also been shown that aryl substituents markedly effect *syn* stereoselectivity, preference being highest for *p*-methoxy and lowest for phenyl carbenoid itself.[2] Olefin structure and carbenoid leaving group (including solvent) remain to be defined. With regard to the former, Table II clearly indicates that *syn/anti* for either solvent system and for either leaving group falls off as R becomes larger. The observation of preferential *anti* addition to *t*-butylethylene is the first well-defined observation of its kind for arylcarbenes or carbenoids. *anti* preference is independent of generative method.

Maximum *syn* preference for monoalkylethylenes is exhibited by propene. Replacement of olefinic hydrogen by a second *cis*-methyl group, *i.e.*, *cis*-butene, leads, at −10°, to *syn/anti* = 2.8.[2,17] The halue of 3.1 reported for propene (Table II) is not directly comparable, having been measured at −50°. It is therefore of some interest to note that a plot of log (*syn/anti*) *vs.* Taft E_s values[18] for ethyl, isopropyl, and *t*-butyl is excellently linear for bromide–pentane and bromide–ether and (acceptably so) for iodide–pentane data of Table II. The appropriate correlation predicts a value of 2.2 for *syn/anti* of propene at −10°. While much faith should not be placed in the predictive power of three-point correlations, it would appear that a second *cis* methyl group leads to at best a small increment in *syn/anti*. Introduction of a third alkyl substituent, trimethylethylene, leads to a large decrease in *syn/anti*.[2] Therefore, assuming that *cis*-dialkylethylenes exhibit a *syn/anti* trend similar to the monoalkylethylenes, the boundaries of olefin structure–*syn/anti* preference appear established.

With regard to carbenoid leaving group, both solvent and departing lithium halide must be considered. Table II indicates that, with lithium bromide as leaving group, *syn/anti* is always greater in hydrocarbon solvent (see below). Recently, several enhanced[5] and, in one case, complete[6] *syn* stereoselectivities involving carbenoid generation *via* methyllithium containing lithium iodide have been reported. We have found no enhancement of *syn/anti* with lithium iodide as opposed to lithium bromide leaving groups in hydrocarbon solvents. In fact of the three olefins examined the only significant change is in the opposite sense.[19] Though no striking "iodide effect" was uncovered, our data enable addition to the list of the *syn* stereoselective reactions of Dilling (eq. 2).[20] The 1-methyl-

$$CH_2Cl_2 + CH_3Li + C_6H_5CH{=}CH_2 \xrightarrow[LiI]{(C_2H_5)_2O}$$



(2)

2-phenylcyclopropane isolated is essentially homogeneous to v.p.c. on Apiezon L[20] and, in the n.m.r.,[21] exhibits alkyl, cyclopropyl, and benzylic proton signals superimposible with those of Ia, the *syn* adduct of

(12) See the relevant discussion in W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(13) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964).

(14) See below for an exception.

(15) Phenylcarbene species can be generated in other ways, *e.g.*, from benzyl chloride and *n*-butyllithium: G. L. Closs and L. E. Closs, *Tetrahedron Letters*, 26 (1960). Yields of addition products here and in other procedures are inferior.[12]

(16) R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962).

(17) R. A. Moss, Ph.D. Thesis, University of Chicago, 1963.

(18) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729, 3120 (1952).

(19) *syn/anti* for isopropylethylene with *p*-methylbenzal iodide and methyllithium in ether (prepared from either methyl bromide or methyl iodide) showed no pronounced change in *syn/anti* from the 1.4 bromide–ether value of Table II.

(20) W. L. Dilling, *J. Org. Chem.*, **29**, 960 (1964).

(21) We thank Dr. Dilling for a copy of his n.m.r. data. By analysis of this n.m.r., Dr. Dilling had established high probability for *syn* structure.

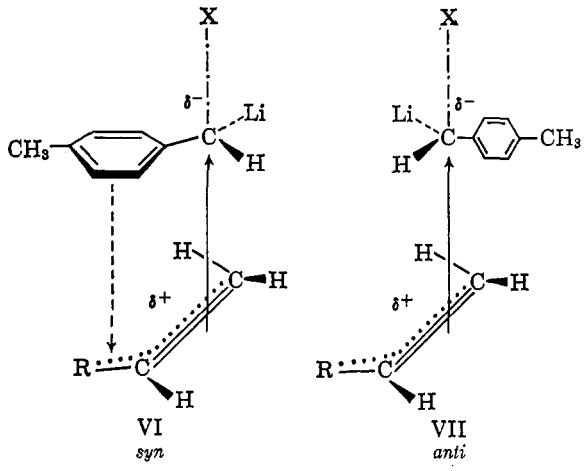
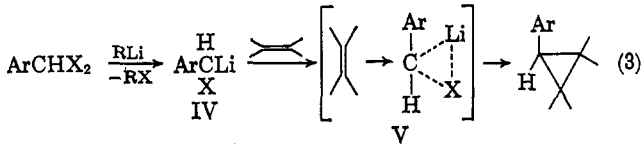


Figure 1.

propene and *p*-methylphenyl carbenoid.[22] Stereoselectivity in eq. 2 is therefore 95+%.[23]

***syn* Stereoselectivity. Steric Effects.**—Examination of Tables II, III, and IV makes appropriate several remarks about the origin of *syn* stereoselectivity. Reaction 1 could involve a free carbene, or the α-halolithium (IV) could react bimolecularly with olefin *via* a transition state (TS), V. Evidence supporting the



bimolecular pathway has recently been obtained.[2] The present data are certainly in agreement with the presence of lithium halide in the TS: the tables reveal selectivity differences dependent on whether the carbenoid precursor is a bromide or an iodide. In order to account for preferred *syn* addition in eq. 3, TS V has been projected in detail as in Figure 1.[2] In TS VI, electrostatic and London interactions between aryl π cloud and alkyl groups are presumed to lower the activation energy for *syn* addition relative to *anti* addition (TS VII).[24] While not demanding TS VI–VII, the present data are readily understandable in these terms. As olefinic alkyl groups increase in bulk, the *energetically preferred syn* addition mode (VI) becomes progressively less favorable with respect to *anti* addition (VII) in which only the hydrogen atom opposes the olefinic substituent. The result is a parallel fall-off in both *syn*/*anti* and over-all rate of carbenoid addition. These considerations seem clearly indicated in Table IV. Steric effects are seen to operate in *both syn* and *anti* addition modes over all three generative situations.[25] Rate decreases attending successive α methylation of propene are smaller in *anti* addition, perhaps because H–alkyl opposition in VII is less severe than aryl–alkyl opposition in VI.

An interesting comparison can be made of the selectivity of *p*-tolyl carbenoid and that of the Simmons–Smith reagent, a species known to react bimolecularly and to exhibit marked steric discrimination.[23,25d] The relative rate ratio for Simmons–Smith methylenation, at 35°, hexene-1 to *t*-butylethylene, is 2.6. The corresponding value for *p*-tolyl carbenoid, butene-1 to *t*-butylethylene (Table III, bromide–ether), is 3.9. (If this latter ratio is considered to be a composite of *syn* and *anti* addition, as in Table IV, the ratios are 8.7 and 1.8.) Allowing for differences in temperature and 1-alkene substrates, both species appear to display similar selectivities toward alkylethylenes.

In conclusion, it must be stressed that, while the present results are in agreement with the idea of simple steric effects operating in TS VI–VII, they by no means exclusively demand this model. The model is a simplification in which no account has been taken of detailed organolithium structure. α-Halolithium compounds may not be monomeric; their structures and reactivity may depend on the presence or absence of Lewis base solvents such as ether,[26] and even highly polarizable anions such as iodide.

Experimental Section[27]

Reagents.—*t*-Butylethylene was obtained from Columbia Organic Co. and was better than 99% pure as determined by v.p.c. and n.m.r. All other olefins were Matheson, pure grade. Methyllithium (2 *N*) in ether and *n*-butyllithium (2 *N*) in pentane were obtained from Lithium Corp. of America.

***p*-Methylbenzal bromide** was prepared according to published procedure[2]. N.m.r. in CCl_4 showed 447–418 m, (4.0), aryl; 381 s, (0.94), benzal; 139 s, (3.0), *p*-methyl.[28]

***p*-Methylbenzal Iodide.**—*p*-Methylphenyldiazomethane,[2] 2.4 g., was dissolved in 30 ml. of dry ether. The solution was cooled by an ice bath and stirred magnetically. A solution of 5 g. of iodine in 50 ml. of ether was added from a dropping funnel until the original red color had faded to light yellow. (About half of the iodine solution was required.) Addition was discontinued and the ethereal product solution was dried over anhydrous magnesium sulfate. The drying agent was removed and the solvent was stripped. The residual light orange oil solidified and was recrystallized from 6 ml. of pentane–ether, 5:1. A second recrystallization afforded 1.2 g. of tan crystals, m.p. 35–37°; the yield was 18.5%[29]. N.m.r. in CCl_4 showed 444–414 m (4.0), aryl; 368 s, (1.0), benzal; 140 s, (3.2), *p*-methyl.

Anal. Calcd. for $C_8H_8I_2$ (357.97): I, 70.90. Found: I, 73.38.

Synthesis of Arylalkylcyclopropanes. *syn*- and *anti*-1-*p*-Tolyl-2-*t*-Butylcyclopropane.—To 3.0 g. (11.4 mmoles) of *p*-methylbenzal bromide in 15 g. (178 mmoles) of *t*-butylethylene, under nitrogen and with vigorous stirring (magnetic stirrer), was slowly added 10 ml. of 2 *N* methyllithium in ether. The temperature was kept at 6 ± 2°. Aqueous quenching, ethereal extraction, drying, and stripping, followed by distillation over a micro Vigreaux column at *ca.* 62° (0.5 mm.), afforded 705 mg. of water white liquid, yield 28% (corrected for purity of distillate, see below).

(22) Data exist to show that removal of the *p*-methyl substituent in compounds similar to Ia cause essentially insignificant variations in alkyl, cyclopropyl, and benzylic n.m.r. signals.[2]

(23) Of interest is the fact that Simmons–Smith addition of ethylidene iodide to cyclohexene leads only to *exo*-7-methylnorcarane: H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964).

(24) Similar considerations have been presented for an entirely different kind of reaction: H. Kwart and T. Takeshita, *ibid.*, **84**, 2833 (1962); **86**, 4194 (1964), and references therein.

(25) Previous citations of steric effects in carbene–olefin reactions include (a) W. V. E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958); (b) G. L. Closs and G. M. Schwartz, *ibid.*, **82**, 5729 (1960); W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963); (d) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); (e) ref. 23.

(26) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964) and previous papers in this series.

(27) All melting points and boiling points are uncorrected. N.m.r. spectra were obtained on Varian A-60 equipment. Infrared spectra were taken on either Perkin-Elmer 421 or Beckman IR-5A instruments. These spectra were always in accord with expectations for each new product, and will not be discussed explicitly here, as more precise structural data is available from n.m.r.

(28) N.m.r. spectra are reported as signals, (integrals), and assignments.

(29) From the mother liquors and from other preparations, brown, low-melting solids could be obtained. Use of these materials in relative rate experiments did not give results appreciably different from those obtained with the crystalline material described here.

Recrystallization of the dark yellow residue from ether and again from carbon tetrachloride yielded white needles, identified as *trans*-4,4'-dimethylstilbene, m.p. 177–179° (lit.[30] m.p. 180°).

V.p.c. of the distillate on a 0.25 in. × 8 ft. column, 20% QF-1 on Gas-Chrom R (Aerograph, A-90-P; injector, 185°; column, 128°; He flow, 60 cc./min.) indicated that about 85% of this material consisted of two high-boiling components, retention times 39 and 47 min., respectively. A small impurity, manifested as a shoulder on the trace of the longer retention time product was presumably a bromide. Treatment of the distillate with 2 *N* ethanolic silver nitrate removed this impurity. The impurity could also be cleanly separated on capillary v.p.c. (see below). The high-boiling components were trapped separately and identified *via* n.m.r. spectroscopy (see Table I). The *syn* isomer had the shorter retention time.

Anal. Calcd. for $C_{14}H_{20}$ (188.31): C, 89.29; H, 10.70. Found: C, 89.34; H, 10.88.

Other cyclopropanes synthesized *via* reaction 1 above were prepared as just described, with the following exceptions. Addition to propene was carried out at −50°, and additions to isopropylethylene, 1-butene, and *trans*-butene were carried out at −10°. Because all other cyclopropanes had shorter retention times than the *t*-butyl isomers, the bromide impurity did not interfere with v.p.c. isolation. Boiling points, yields, and analyses are collected in Table V. The 1-aryl-2-ethylcyclopropanes and 1-aryl-2,3-*trans*-dimethylcyclopropane have been described previously.[2] All preparative v.p.c. was done on the QF-1 column described above. Under the indicated conditions, *syn*-cyclopropanes had shorter retention times than their *anti* isomers.

TABLE V

CYCLOPROPANES FROM 1-ALKENES AND *p*-METHYLBENZAL BROMIDE

Olefin	B.p., °C. (mm.)	Yield, %	Calcd., % C	Calcd., % H	Found, % C	Found, % H
Propene	37 (0.4)	37	90.35	9.65	90.41	9.89
Isopropylethylene	45–50 (0.5)	48	89.59	10.41	89.41	10.44
t-Butylethylene	62 (0.5)	28	89.29	10.70	89.34	10.88

(30) "Chemistry of Carbon Compounds," Vol. III[B], E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1956, p. 1145. The *trans* stereochemistry is supported by the strongly deshielded vinyl protons observable in the n.m.r. of this material, *ca.* τ 3; compare "High Resolution NMR Spectra Catalog," Vol. I, N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Ed., Varian Associates, Palo Alto, Calif., 1962, Spectra 305, 306.

Competition Experiments.—The procedure was similar to the synthetic procedure described above, except that mixtures of *trans*-butene and the requisite olefin were employed. All competitions were carried out with 0.4–0.5 g. of bromide or iodide starting material at −10°. Enough alkyllithium was added to achieve excess. *syn/anti* ratios and product ratios were determined on undistilled product by v.p.c. on a 150-ft. Apiezon L golay column (Barber-Colman, Series 5000 chromatograph). The flame ionization detector was calibrated with mixtures of purified cyclopropanes. Relative rates were derived from the standard expression: $K_2/K_1 = (P_1/P_2)(O_2/O_1)$, where P_1/P_2 is the cyclopropane product ratio and O_2/O_1 represents the mole ratio of starting olefins. Olefin was present in at least 20-fold excess.

Authenticity of observed v.p.c. product ratios was established by spectral examination of trapped products and by control experiments which established that spurious products were not contributing to v.p.c. traces at cyclopropane retention times. In addition, product ratios generally showed good agreement whether obtained from separation on QF-1 or Apiezon L capillary v.p.c.

Controls. Product Stability.—Mixtures of purified adducts (*t*-butyl series) showed no change in composition on rechromatography. *syn-anti* ratios of prepared mixtures were unaltered by treatment with excess alkyllithium reagents. Product ratios were also identical whether stoichiometrically sufficient, insufficient, or excess alkyllithium was employed.

Isomerization of *syn*- to *anti*-1-*p*-Tolyl-2-butylcyclopropane.—A mixture of *syn*- and *anti*-cyclopropanes, 35 mg., trapped from the QF-1 column, was sealed into an ampoule with 1.2 ml. of 2 *N* potassium *t*-butoxide in dimethyl sulfoxide. The ampoule was kept in an oil bath at 102° for 23 hr. The ampoule was broken into water (30 ml.), and the resulting liquid was extracted three times with 10-ml. portions of ether. Combined ether was dried and stripped. V.p.c. of the residue showed only one product, identical in retention time with *anti*-1-*p*-tolyl-2-*t*-butylcyclopropane. Trapping of this material and comparison of n.m.r. spectra verified this identity. Similar isomerization of pure *syn*-cyclopropane also led only to *anti* product. Isomerizations in the isopropyl adduct series, starting from pure *syn*-1-*p*-tolyl-2-isopropylcyclopropane, gave 90% *anti*-cyclopropane after 3 days. Equilibrium may not have been reached, however.

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Formation of Alkyl Halides from Acids by Decarboxylation with Lead(IV) Acetate and Halide Salts

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Halide salts induce the rapid decarboxylation of Pb^{IV} esters. Alkyl halides, particularly chlorides, are formed in excellent yields. This method of halodecarboxylation offers a convenient synthesis of alkyl halides from carboxylic acids. Unlike the classic Hunsdiecker reaction, it is applicable to secondary and tertiary acids. Cyclobutyl and neopentyl moieties are converted to the corresponding chlorides with no rearrangement. Decarboxylation by this method is strongly inhibited by oxygen. A free-radical mechanism is proposed which includes alkyl radicals and Pb^{III} species as intermediates. Halodecarboxylation with halide is compared with oxidative decarboxylation conducted with pyridine or acetate under comparable conditions. Similarities in the mechanisms of the two reactions are discussed with respect to electron transfer and ligand transfer in the propagation steps. Halodecarboxylation of Pb^{IV} esters with halide salts is also compared with the photochemically induced and thermal reactions with halogen (iodine).

Lead tetraacetate can be conveniently employed to effect decarboxylations of acids. The products of oxidation are generally alkenes and esters.[1] For example, α-methylbutyric acid is converted to a mixture of butenes and *sec*-butyl acetate and α-methylbutyrate.[2] Cyclohexanecarboxylic acid is oxidized to cyclohexene and cyclohexyl acetate and cyclohexanecarboxylate. Predominantly *exo*-norbornyl acetate has been ob-

(1) For leading references, see W. H. Starnes, *J. Am. Chem. Soc.*, **86**, 5603 (1964); R. Criegee, "Newer Methods of Preparative Organic Chemistry," Vol. 2, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1963, p. 368 ff; W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

(2) J. K. Kochi, *ibid.*, **87**, 1811 (1965).