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# STEREOSELECTIVITY OF CARBENE INTERMEDIATES—II

## PHENYLBROMOCARBENE[1,2]

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**Abstract**—1-Phenyl-1-bromocyclopropanes have been prepared via reaction of benzal bromide, potassium *t*-butoxide, and olefins. Trimethylethylene and *cis*-butene react so as to yield mainly that cyclopropane in which bromine is *cis* to the larger number of methyl groups. Rates of addition of the reactive intermediate (relative to *iso*-butene) have been determined for the several olefins.

Our interest in phenylchlorocarbene[3] also led us to study the butoxide-caused decomposition of benzal bromide.[2] Our concern was heightened by reports that the stereoselectivity of phenylchlorocarbene had been determined.[4] Knowing that steric hindrance is an important factor in carbene stereoselectivity,[1] and believing that carbene substituent polarizability is also significant, comparison of the stereoselectivities of phenylchloro and phenylbromo species became one goal of our investigation. Another objective was comparison of dichloro, dibromo and phenylbromocarbenes in their abilities to discriminate between olefins.[5]

## RESULTS

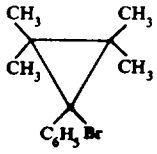
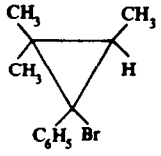
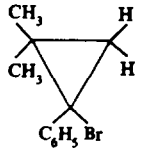
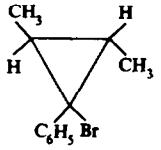
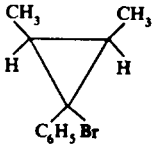
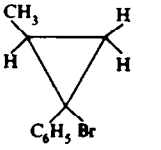
*Synthesis of* 1-*phenyl*-1-*bromocyclopropanes.* Although the intermediacy of phenylbromocarbene had been postulated in order to account for the formation of 1-phenyl-1-bromoethylenes via basic decomposition of benzal bromide in the presence of diazolakanes,[7] addition of the postulated carbene to olefins appeared uninvestigated.

Good to fair yields of 1-phenyl-1-bromocyclopropanes were obtained. Data pertaining to the new compounds are collected in Table 1.

Product identities were established by elemental analyses, and by consonant IR and NMR spectra. In addition, treatment of III with butyllithium followed by hydrolysis, afforded 1-phenyl-2,2-dimethylcyclopropane, identical (NMR) to authentic

[1] Paper I: R. A. Moss, *J. Org. Chem.* **30**, 3261 (1965).
[2] A portion of this work has been communicated: R. A. Moss and R. Gerstl, *Tetrahedron Letters*, No. 39, 3445 (1965).
[3] R. A. Moss, *J. Org. Chem.* **27**, 2683 (1962).
[4] Private communication from G. L. Closs, March, 1965. G. L. Closs and J. J. Coyle, *J. Org. Chem. in press.* We thank Prof. Closs for a copy of this manuscript. See, also, J. E. Hodgkins, J. D. Woodyard and D. L. Stephenson, *J. Amer. Chem. Soc.* **86**, 4080 (1964).
[5] In the foregoing, the term "carbene" is used only in a generic sense, and is not meant to carry structural implications. Further discussion will appear below; elsewhere "carbene" includes "true carbene" and "carbenoid."[6]
[6] G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.* **86**, 4042 (1964). (A definition of "carbenoid" appears in this article.)
[7] H. Reimlinger, *Chem. Ber.* **97**, 339 (1964); *Angew. Chem.*, Int. Ed. **1**, 156 (1962).

Table 1. 1-Phenyl-1-bromocyclopropanes

| Adduct | Olefin | Structure | B.p. (m.p.)[a] | Yield, %[b] | Analyses | |
|---|---|---|---|---|---|---|
| | | | | | Required | Found |
| I | Tetramethylethylene |  | (76–77°) | 53 | %C, 61·65<br>%H, 6·77<br>%Br, 31·58 | 61·40<br>6·79<br>31·83 |
| II | Trimethylethylene[c] |  | 82°/0·55 mm | 51 | 60·24<br>6·33<br>33·43 | 60·14[d]<br>6·33<br>32·58 |
| III | *iso*-Butene |  | 48°/0·02 mm | 73 | 58·66<br>5·82<br>35·52 | 58·41<br>5·55<br>35·58 |
| IV | *trans*-Butene |  | 50°/0·01 mm | 62 | 58·66<br>5·82<br>35·52 | 57·72[d]<br>6·00<br>36·20 |
| V | *cis*-Butene[c] |  | 56°/0·13 mm | 73 | 58·66<br>5·82<br>35·52 | 59·00<br>5·98<br>35·11 |
| VI | Propene[c] |  | 61°/0·6 mm | 40 | 56·89<br>5·25<br>37·86 | 56·78<br>5·38<br>37·90 |

[a] Uncorrected. [b] Of purified product. [c] Mixture of geometric isomers; see below. [d] Best of several analyses. Analytical difficulties are known in phenylchloro analogs, see ref. 8.

material.[6] Similar treatment of V afforded a mixture of *syn* and *anti*-1-phenyl-*cis*-2,3-dimethylcyclopropanes, each identical (NMR) to authentic material.[6]

Because the phenylbromocyclopropanes proved unstable to several gas chromatographic conditions, NMR assumed especially great importance. With its aid, we were able to establish isomer compositions in II and V, and also to quantitatively assay two-component mixtures of adducts I–V.

*NMR Spectra of 1-phenyl-1-bromocyclopropanes.* The alkyl regions of the NMR spectra of adducts II, III, IV and V are reproduced in Figs 1, 2, 3 and 4, respectively. All adducts in Table 1 also exhibited multiplets in the aryl region.

[8] S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.* **81**, 2586 (1959).

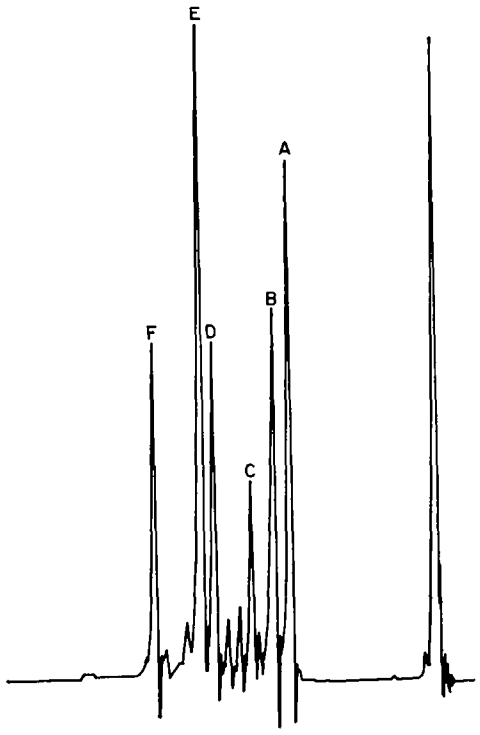



FIG. 1.

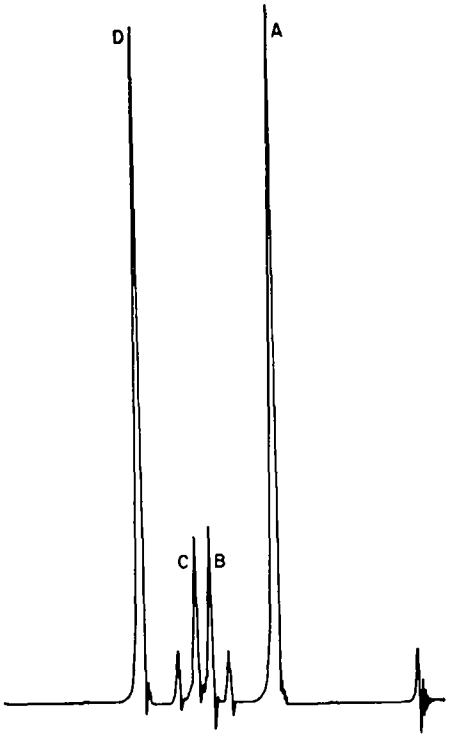



FIG. 2.

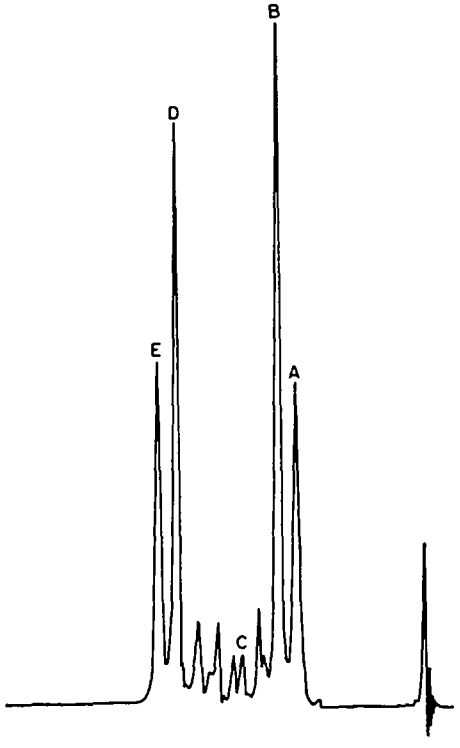



FIG. 3.

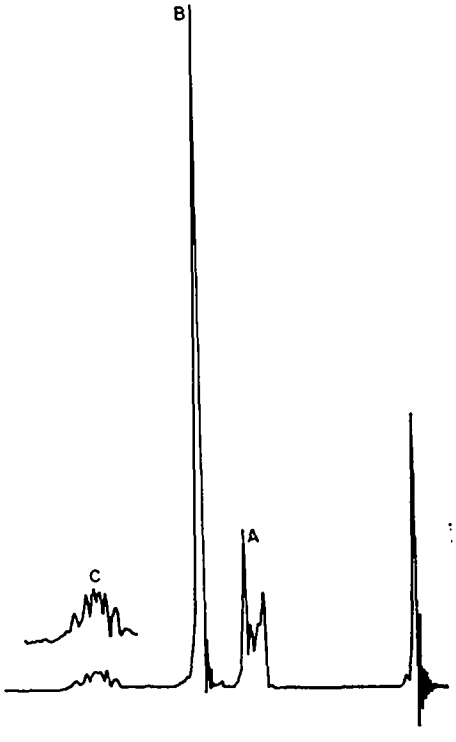



FIG. 4.

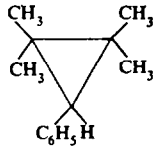
These multiplets (centered *ca.* 7·3 ppm downfield from internal TMS; solvent $CCl_4$) always had proper integral weights, relative to alkyl absorptions. Alkyl absorptions to be specifically discussed (here, and in the experimental section) are designated by letter in the figures, and chemical shifts of these absorptions appear in Table 2. Also included are the two absorptions of I.

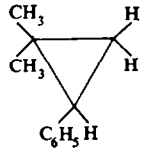
TABLE 2. NMR SPECTRA OF 1-PHENYL-1-BROMOCYCLOPROPANES, CHEMICAL SHIFTS OF SELECTED PEAKS, ALKYL REGION[a]

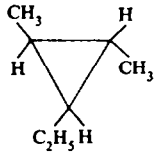
| Compd | Fig. | Absorption A | B | C | D | E | F |
|---|---|---|---|---|---|---|---|
| I | — | 63 | 85 | — | — | — | — |
| II | 1 | 50 | 56 | 65 | 75 | 79 | 94 |
| III | 2 | 49 | 68 | 78 | 93 | — | — |
| IV | 3 | 48 | 54 | 63 | 85 | 91 | — |
| V | 4 | 51–61 | 73 | 100–115 | — | — | — |

[a] In c/s downfield from internal TMS, solvent $CCl_4$.

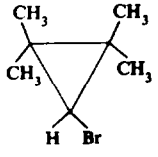
In *phenylcyclopropanes*, methyl groups *syn* to phenyl are shielded relative to methyl groups *anti* to phenyl.[1,6] This differential shielding, a consequence of phenyl anistropy, and dependent on conformational factors,[6,9] leads to chemical shift differences ($\delta$ *syn*-methyl-$\delta$ *anti*-methyl) of 0·31 ppm for IH, of 0·43 ppm for IIIH, and of 0·37 ppm for IVH.[6] In the corresponding bromocyclopropanes, *syn* and *anti* methyl

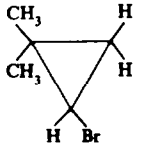

IH

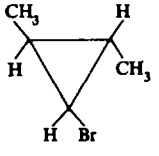

IIIH


IVH

groups are subjected to a smaller differential anisotropy. Thus, chemical shift differences of 0·04 ppm for I Br; of 0·14 ppm for IIIBr and of (less than) 0·2 ppm for IVBr, have been recorded.[10]


I Br


III Br


IV Br

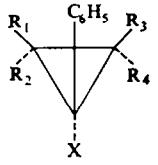
In 1-phenyl-1-bromocyclopropanes, therefore, the principal origin of differential alkyl group shielding probably resides in phenyl anisotropy. Effects of the halogen, however, are not insignificant. Thus, speaking of the phenylchlorocyclopropanes, Closs has said that the chlorine atom "appears to amplify the effect of the phenyl ring."[4] If, in the phenylbromocyclopropanes, the high-field resonances are assigned to methyl groups *syn* to phenyl, and the low-field resonances to methyl groups *anti* to

[9] G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.* **87**, 3265 (1965).
[10] G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.* **87**, 4270 (1965).

phenyl, the NMR spectra can be analysed as in Table 3. Comparison with results for phenylchlorocyclopropanes,[4] and for phenylcyclopropanes,[6] is satisfactory.

When applied to adducts II and V, which are mixtures of isomeric cyclopropanes, a similar analysis allows assignment of absorptions in the composite spectra, Fig. 1 and 4.

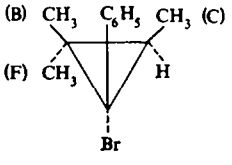
TABLE 3. CHEMICAL SHIFTS OF METHYL GROUPS IN SOME 1-PHENYL-1-X-CYCLOPROPANES[a]



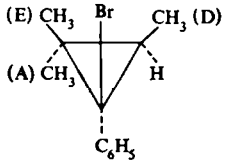

| $R_i$ | X = Br[b] | X = Cl[c] | X = H[d] |
|---|---|---|---|
| $R_1 = R_3 = CH_3$ | 8·95 | 8·97 | 9·08[e] |
| $R_2 = R_4 = CH_3$ | 8·58 | 8·63 | 8·77 |
| $R_1 = CH_3$ ($R_3$ = H) | 9·18 | 9·17 | 9·23 |
| $R_2 = CH_3$ ($R_4$ = H) | 8·45 | 8·50 | 8·80 |
| $R_1 = CH_3$ ($R_3$ = H) | 9·15 | 9·2 | 9·22 |
| $R_4 = CH_3$ ($R_2$ = H) | 8·54 | 8·6 | 8·85 |

[a] In tau values, relative to internal TMS, solvent $CCl_4$. [b] This work.
[c] Ref. 4. [d] Ref. 6. [e] This compound was prepared for us by Mr. J. Funk.

In II (Fig. 1), A and F are assigned as indicated, and tentative assignments are suggested for the other methyl absorptions.




II–*syn*–φ




II–*anti*–φ

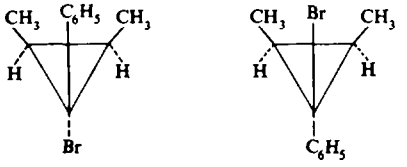
These assignments are supported by the following observations: (1) The assignments are in accord with *a priori* expectations that II-*syn*-$\phi$ should exhibit two high-field methyl signals and a low-field *singlet*; whereas II-*anti*-$\phi$ should exhibit a high-field *singlet* and two low-field methyl signals. (2) The isomer mixture was partially separated into its components by careful fractional distillation. NMR's of a series of 7 cuts clearly showed that peaks B, C and F belonged predominantly to one (higher-boiling) component, while peaks A, D and E belonged predominantly to the other (lower-boiling) component.[11] (3) The chemical shift of A, 50 c/s, is essentially identical to that of the equivalent methyl group of III, 49 c/s. Methyl group F, 94 c/s, also agrees with the analogous signal in III, 93 c/s. (4) Assigned absorptions are in good

[11] Control experiments showed that the isomers were stable to distillation temperatures. The changing NMR's of successive fractions therefore reflected a true fractionation, rather than a selective pyrolysis.

agreement with the phenylchloro assignments.[4] Here the analog to A is found at 54 c/s; the analog to F at 90 c/s. (5) If 5/3 the integral weight of A is subtracted from the integral weight of the aryl protons, the remainder, within 2%, is found to be 5/3 of the integral weight of F.

The last observation is particularly important, for it suggests that peaks A and F are true representatives of three protons in II-*anti*-$\phi$ and II-*syn*-$\phi$, respectively. The stereoselectivity of the addition producing the isomers, II, is therefore given by the integral weights A/F.

In a similar manner, adduct mixture, V, can be analysed. With reference to Fig. 4,




multiplet A is assigned to the methyl groups of V-*syn*-$\phi$, and multiplet C is assigned to the cyclopropyl protons of this isomer. Absorption B is assigned to all protons of V-*anti*-$\phi$.

Support of these assignments: (1) Fractional distillation revealed that A and C behaved as a unit (higher-boiling isomer), whereas B belonged to the other (lower-boiling) isomer.[11] (2) Spin-decoupled NMR spectra further substantiated that A and C are part of the same molecule. (3) Integral weights A/C = 3·04. Subtraction of 5/8 the integral weight of (A + C) from the integral weight of the aryl multiplet left a residue, 5/8 the integral weight of B. (4) Good agreement was observed between methyl chemical shifts in V and in phenylchloro analogs. Here, the anolog to A occurs at 55 c/s, the analog to B at 73 c/s.[4] (The odd observation that all alkyl protons in V-*anti*-$\phi$ afford a single sharp signal, finds analogy in 1-*anti*-phenyl-*cis*-2,3-dimethylcyclopropane, in which a similar effect is observed.[6] The *anti*-phenyl presumably adopts a conformation in which its plane bisects the ring.[9] In this conformation it deshields the *cis* ring hydrogens whose chemical shifts fortuitously become equal to those of the methyl groups.) The analysis indicates that the stereoselectivity of the addition producing the isomers, V, is given by the ratio B/(A + C.)

*Stereospecificity.*[12] NMR spectra of undistilled preparations of V (see Fig. 4) revealed that very little IV could have been present. Peak D of IV (Fig. 3) was noticable for its absence in spectra of V. Under our NMR conditions, the stereospecificity of the addition reaction is at least 95%, and probably close to 100%.[13]

*Stereoselectivity.* From the integral ratio A/F (Fig. 1, Adduct II), determined on undistilled product,[14] the isomer distribution, II-*anti*-$\phi$/II-*syn*-$\phi$ was 1·28 (average of three syntheses, %a.d. = 3·9).

From the integral ratio B/(A + C) (Fig. 4, adduct V), determined on undistilled

[12] See W. Kirmse, *Carbene Chemistry* Chap. 12. Academic Press, New York (1964).

[13] Control NMR experiments indicated that 5% IV was easily detected in V.

[14] Results quoted below will demonstrate that undistilled adducts were not contaminated with materials absorbing in the alkyl region of the NMR. Furthermore, distillation, without fractionation, of the crude isomer mixture, afforded pure cyclopropanes with a very similar isomer ratio.

product,[14] the isomer distribution, V-*anti*-$\phi$/V-*syn*-$\phi$ was 1·35 (average of three syntheses, %a.d. = 0·74). With both trimethylethylene and *cis*-butene, then, the phenylbromocarbene species added so as to produce a small excess of that isomer in which the halogen was *syn* to the larger number of methyl groups.

*Relative rate experiments.* With pure adducts in hand, and having assigned the necessary absorptions in their NMR spectra, it was possible to quantitatively assay various two-component mixtures.[15] Competition experiments, i.e. experiments in which a mixture of two olefins, of known composition, was employed as carbene substrate, were then carried out. In all cases, NMR spectra of the resultant undistilled cyclopropane mixtures exhibited only those alkyl absorptions which might have arisen via superimposition of the spectra of the pure cyclopropanes. Further evidence on this point was desired.

TABLE 4. COMPETITION OF VARIOUS OLEFIN PAIRS FOR PHENYLBROMOCARBENE, *ca.* 25°

| olefin 1/olefin 2[a] | $k_1/k_2$ | %a.d.$_n$[b] |
|---|---|---|
| tetramethylethylene–*trans*-butene | 11·3 | $14\cdot_4$ |
| tetramethylethylene–trimethylethylene | 1·28 | $7\cdot0_3$ |
| tetramethylethylene–*iso*-butene | 1·65 | $13\cdot_7$ |
| tetramethylethylene–*cis*-butene | 5·79 | $1\cdot9_3$ |

[a] Each run involved a different ratio of olefins.

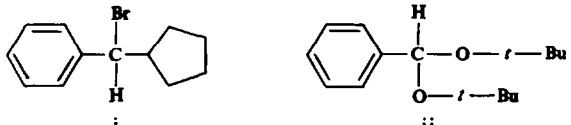
[b] % average deviation from the mean value; the subscript indicates the number of separate competitions performed.

The reaction of benzal bromide with potassium *t*-butoxide in cyclopentane led to a complex product mixture.[16] Many absorptions were observed in the alkyl region of the NMR of this material. When, however, benzal bromide was treated with potassium t-butoxide in a mixture of tetramethylethylene and *forty-fold excess cyclopentane*, the alkyl region of the crude product's NMR *showed only the two singlets associated with adduct I.* This result implied strongly that decomposition of benzal bromide in pure olefin led to crude product in which the *only* component absorbing in the alkyl region of the NMR was a cyclopropane.

NMR analyses of crude product mixtures obtained from olefin competition experiments carried out in the standard manner, yielded the data collected in Table 4.

[15] Details of analyses will be found in the experimental section.

[16] We have not characterized these products. Nevertheless, NMR spectral data of the crude product mixture, and of fractions obtained during its distillation, suggested that two minor components were "insertion" product, i, and benzaldehyde-*t*-butyl acetal, ii. (Product ii has been prepared by




i ii

Westheimer via reaction of benzal chloride and potassium *t*-butoxide in *t*-butanol.[17] The published NMR data are in accord with our observations.) The major product(s) of the reaction were high boiling, and exhibited only aryl protons in the NMR.

[17] J. J. Cawley and F. H. Westheimer, *Chem. & Ind.* 656 (1960).

Although reproducibility was not much better than 15% in two cases, greater accuracy was suggested for these numbers by cross-check experiments. Thus, from the data in Table 4, it was possible to predict relative rate ratios for trimethylethylene–*cis*-butene, and *trans*-butene–iso-butene competitions. In both cases, predicted and observed data agreed to 1% or better.

Finally, control experiments established quantitative stability of prepared cyclopropane mixtures to reaction conditions.

## DISCUSSION

In several cases, it has recently proven necessary to abandon observation of olefin cyclopropanation as a diagnostic for carbene intermediacy in α-elimination reactions. Thus, various α-halometallics (carbenoids[6]) may react directly with olefin to afford cyclopropanes, bypassing prior elimination of metal halide and formation of a true carbene.[1,6,10,18,19]

Lithium carbenoids may be more apt to bypass carbene formation than other α-halometallics. Thus, although lithium trichloromethide, and not dichlorocarbene is probably the reactive intermediate in α-elimination involving bromotrichloromethane and alkyllithiums,[18,20,21] the classic KOH or NaOH catalysed hydrolysis of chloroform,[22] as well as the thermal decompositions of phenylmercuricbromodichloromethide and of sodium trichloroacetate[23] *may* proceed via dichlorocarbene. It is *conceivable*, therefore that attack of potassium t-butoxide on bromoform or chloroform does produce true dihalocarbenes. A similar statement can be made about attack of potassium t-butoxide on benzal chloride or bromide. In the following, we will compare the dibromo, dichloro, phenylbromo and phenylchloro species, generated via potassium t-butoxide and haloform or benzal halide. Although the nature of the reactive intermediate is presently unknown, the similar reaction conditions probably validate comparison of reactive intermediate selectivities.

*Stereoselectivity.* Addition of unsymmetrically substituted carbenes to olefins which have neither a center of symmetry, nor a twofold rotational axis defined by the carbon–carbon double bond, affords isomeric cyclopropanes. Among monosubstituted carbenes and carbenoids, *syn* stereoselectivity (formation *mainly* of that cyclopropane with the carbene substituent *cis* to the largest number of ring alkyl groups) is generally observed.[1] Predominant *anti* selectivity is observed for carbalkoxy and various aryloxy and alkoxy species.[24] Since both phenyl[6] and chlorocarbenoid[10] exhibit *syn* stereoselectivity, it is of interest to determine the stereoselectivity of phenylchlorocarbene. This has been done by Closs,[4] who reports that chloro-*syn* addition predominates over phenyl-*syn* addition whether the "carbene" is produced via an α-halolithium precursor or via benzal chloride and potassium *t*-butoxide.[25] Data

[18] W. T. Miller and D. M. Whalen, *J. Amer. Chem. Soc.* **86**, 2089 (1964).

[19] E. P. Blanchard and H. E. Simmons, *J. Amer. Chem. Soc.* **86**, 1337 (1964); H. E. Simmons, E. P. Blanchard and R. D. Smith, *ibid.*, **86**, 1347 (1964).

[20] D. F. Hoeg, D. I. Lusk and A. L. Crumbliss, *J. Amer. Chem. Soc.* **87**, 4147 (1965).

[21] See also, G. Köbrich, K. Flory and H. R. Merkle, *Tetrahedron Letters* No. 15, 973 (1965), and other articles in this series.

[22] W. J. le Noble, *J. Amer. Chem. Soc.* **87**, 2434 (1965).

[23] D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.* **86**, 2730 (1964).

[24] See the relevant discussions in W. Kirmse, *op. cit.*, Ref. 12.

[25] It is of interest that neither phenylcarbene[6] nor chlorocarbene,[10] when produced from diazo precursors, display appreciable stereoselectivity.

TABLE 5. STEREOSELECTIVITY OF "PHENYLHALOCARBENES" FROM BENZAL HALIDES AND POTASSIUM *t*-BUTOXIDE

| Olefin | Halo-*syn* Addition/Phenyl-*syn* Addition | |
|---|---|---|
| | Phenylbromocarbene[a] | Phenylchlorocarbene[b] |
| *cis*-butene | 1·35 | 3·0 |
| trimethylethylene | 1·28 | 1·5 |

[a] This work, *ca.* 25°. [b] Ref. 4, 60–75°.

for the latter method, and for comparable results of this investigation, appear in Table 5.

Previous results have suggested that a delicate balance of steric and electrostatic interactions between olefin and carbene substitutients determines the stereoselectivity of addition.[1,4,6] Strong London interaction of a polarizable carbene substituent and the olefinic alkyl groups (which, relative to ground state, have become somewhat positive in the transition state) presumably favors *syn* addition. An effect of this kind seems especially well illustrated by Schöllkopf's reports that although "phenoxycarbene" displays mainly *anti* stereoselectivity, phenylthio and phenylseleno species display *syn* stereoselectivity.[26]

TABLE 6. RELATIVE ADDITION RATES

| Olefin | Cl—$\ddot{C}$—Cl[a] | Br—$\ddot{C}$—Br[b] | $\phi$—$\ddot{C}$—Br[c] |
|---|---|---|---|
| tetramethylethylene | 6·6 | 3·5 | 1·6 |
| trimethylethylene | 2·9 | 3·2 | 1·3[d] |
| *iso*-butene | 1·00 | 1·00 | 1·00 |
| *cis*-butene | — | — | 0·29[d] |
| *trans*-butene | — | — | 0·15 |

[a] Ref. 28, −20 to −10°. [b] Ref. 29, *ca.* 0° in *t*-butanol solvent. [c] This work, *ca.* 25°. [d] Composite of both isomers.

With regard to phenylhalocarbenes, though bromine is presumably more polarizable than chlorine, it is also larger.[27] The data in Table 5 might be interpreted as suggesting that adverse steric effects of replacing chlorine with bromine outweigh the favorable increase in halogen polarizability, with regard to the *syn* directive ability of halogen in phenylhalocarbene species.

*Relative Addition Rates.* Relative addition rates for dichloro, dibromo, and phenylbromo species, all produced via potassium *t*-butoxide, are collected in Table 6.

The data indicate that the phenylbromo species is quite similar to the dibromo species, in that the usual "electrophilic" sequence is only just apparent with the more

[26] U. Schöllkopf and J. Paust, *Chem. Ber.* **98**, 2221 (1965), and earlier papers in this series, particularly; U. Schöllkopf and H. Küppers, *Tetrahedron Letters* No. 2, 105 (1963); U. Schöllkopf and G. J. Lehmann, *ibid.* No. 4, 165 (1962).

[27] The size differential has been cited by Doering in comparing relative addition rates of dichloro and dibromo carbenes.[28]

[28] W. v. E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.* **80**, 5274 (1958).

[29] P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.* **78**, 5430 (1956).

substituted olefins. These species are both considerably more selective with di- and monosubstituted olefins.[29] Presumably, the decreasing value of tetramethylethylene/*iso*-butene, (6·6, 3·5 and 1·6) is a reflection of increasing steric hindrance to carbene addition[28] in the sequence dichloro, dibromo and phenylbromo. Once again, note should be taken of the limitations inherent in estimating "carbene stability" from "electrophilicity" in the olefin-addition reaction.

## EXPERIMENTAL[30]

### *Reagents*

Benzal bromide (Aldrich) and potassium *t*-butoxide (*t*-BuOK) (MSA) were used without further purification. (The bromide showed no carbonyl absorption in the IR.) Olefins were all rated 99% or better: tetramethylethylene (Phillips), trimethylethylene (Aldrich), *trans*-butene, *cis*-butene and *iso*-butene (Matheson).

### 1-*Phenyl*-1-*bromocyclopropanes*

All the adducts summarized in Table 1 were synthesized with identical procedures by shaking benzal bromide with 1·2 equiv. *t*-BuOK and 10–12 equiv. olefin, in a sealed tube, at *ca.* 25°, for 50–70 hr. Adduct III is presented as an example. A $\frac{3}{4}$" by 18" Carius combustion tube, fitted with a screw-top (Teflon gasket seal), was cooled to −70° and charged with 40 g (0·71 moles) *iso*-butene. *t*-BuOK, 7·8 g (0·07 moles), followed by benzal bromide, 12·7 g (0·05 moles), was added. The tube was sealed, warmed to room temp, and shaken for 68 hr at *ca.* 25°.

The tube was opened, after re-cooling, and its contents diluted with 100 ml of ether. The ethereal solution was washed successively with its own volume of water, 1N HCl, water, 10% $NaHCO_3$ aq, and water. After drying ($Na_2SO_4$), ether was stripped, and the residue distilled over a Micro-Vigreux column. A total of 8·3 g (73%) of clear liquid, b.p. 48–49°/0·02 torr, was collected; 1-phenyl-1-bromo-2,2-dimethylcyclopropane.

A 0·53 g sample of this material was dissolved in 30 ml anhydrous $Et_2O$. The soln was cooled to 0° and, under $N_2$, 6 ml of 2N butyllithium, in pentane, was added over 10 min. After stirring for 2 hr, the reaction mixture was diluted with 30 ml of water. The ethereal phase was dried, filtered and stripped. The residue was chromatographed on a Wilkens A-90P instrument, silicone grease column at 150°. The principal high-boiling component was trapped; its NMR was identical to that of authentic 1,1-dimethylphenylcyclopropane.[6]

### *Competition experiments*

The same procedure as was used for the syntheses was employed here, except that the two olefins selected for competition replaced the single olefin employed in synthesis. When one olefin was a gas, under standard conditions of temp and press, small corrections were made to account for loss into the dead volume of the sealed tube at 25°.

In general, competitions were not run to completion; work-up was carried out after 24 hr. Controls showed that variation of the time factor, presence of excess base, and excess bromide did not change observed product ratios or isomer ratios.

Relative rates were calculated from the standard expression: $k_1/k_2 = P_1/P_2 \times O_2/O_1$, where the $P_i$ quotient represents the cyclopropane product ratio and the $O_i$ quotient represents the mole ratio of starting olefins. Olefin was present in 12-fold excess over bromide. Results appear in Table 4.

Product ratios were determined by NMR on undistilled products. Details of analysis for each competition follow.

*Tetramethylethylene*-iso-*butene.* The absorption at 63 c/s of I (6 protons/molecule) was integrated with respect to the absorption at 49 c/s of III (peak A, Fig. 2, 3 protons/molecule). In pure III, an absorption occurred at 63 c/s which was 0·071 the weight of the 49 c/s methyl absorption. A correction was therefore applied to the 63 c/s absorption of the product mixture, so as to count only the

[30] Microanalyses were obtained from Micro-Tech Laboratory, Skokie, Ill. IR spectra were recorded with a Beckman IR-5A instrument; NMR spectra were recorded with a Varian A-60 instrument. All m.ps and b.ps are uncorrected.

absorption due to I. Three prepared test mixtures of I and III were thus analysed with % errors of 4·2, 6·0, and 0·0%.

*Tetramethylethylene.*–trans-*butene.* A plot was made of the integral ratio of the 63 c/s absorption of I and the 54 c/s absorption of IV (peak B, Fig. 3) against actual mole ratio of the adducts in several prepared mixtures. (An absorption of IV, peak C, 0·14 the weight of the 54 c/s absorption was covered by the 63 c/s absorption of I, and was therefore subtracted from the 63 c/s absorption of the mixture.) A straight line was obtained: mole ratio (I/IV) = 0·34 × peak ratio (I/IV). Two test mixtures were prepared and, using the calibration curve, their mole ratios were determined with errors of 5% and 1%.

*Tetramethylethylene–trimethylethylene.* A plot was made of the integral ratio of the 85 c/s absorption of I and the 94 c/s absorption of II (peak F, Fig. 1) against actual mole ratio of the adducts in several prepared mixtures. (An absorption of II, 0·12 the weight of the 94 c/s absorption was covered by the 85 c/s absorption of I and was therefore subtracted from the 85 c/s absorption of the mixture.) A straight line was obtained: mole ratio (I/II) = 0·18 × peak ratio (I/II). The calibration curve was checked with further test mixtures, and then applied to actual competitions. In determining the calibration, pure II isomer mixture was used, which had the experimentally observed *syn–anti* composition.

*Tetramethylethylene*–cis-*butene.* The 85 c/s absorption of I (6 protons/molecule) was integrated with respect to the 73 c/s absorption of V (peak B, Fig. 4). Since the latter absorption represented all alkyl protons of V-*anti*-$\phi$, and since the isomer ratio in V was known, product ratios (I/V) were easily obtained. A prepared mixture was analysed with 2% error.

*Cross-check experiments.* From the relative rates gathered in Table 4, it was possible to derive relative rates for the cross-check competitions, *trans*-butene–*iso*-butene, and *cis*-butene–trimethylethylene. Starting, in each case, with known olefin mole ratios and derived relative rates, the product ratios to be expected in each cross-check competition could be predicted. Prepared product mixtures, of predicted composition, were compared with the actual competition product mixtures via NMR. Various ratios of peak integrals of prepared and actual product mixtures, for both cross-checks, displayed agreement to 1% or better.

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