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# PHENYLBROMOCYCLOPROPANES: PROBABLE GENERATION OF PHENYLBROMOCARBENE

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Several years ago, one of us reported that reasonable yields of gem-phenylchlorocyclopropanes could be obtained via the action of potassium t-butoxide on benzal chloride in the presence of olefin, presumably via the intermediacy of phenylchlorocarbene (1). At that time, we indicated that this reaction did not proceed well at ambient or lesser temperatures, and was not suited to cyclopropanation of low-boiling olefins (2). Recently, others have confirmed these observations, setting 50° as the lower temperature limit for cyclopropanation with benzal chloride and potassium t-butoxide (3).

As bromoform is known to be more susceptible to basic hydrolysis than chloroform (4), we suspected that the hitherto unknown phenylbromocarbene ought to be easily obtainable, under mild thermal conditions, via the action of potassium t-butoxide on benzal bromide.

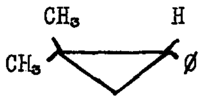
Indeed, olefins are converted to phenylbromocyclopropanes in this manner. Reaction conditions, yields and boiling points of purified products are collected in Table I.

As indicated in Table I, reaction conditions were quite simple. Work-up includes dilution with ether, washing (water, 1N HCl, 10% $NaHCO_3$ (5), water), followed by drying, removal of solvent, and finally distillation or recrystallization. (The latter procedure is quite wasteful; *e.g.*, crude yield of I was 74%.)

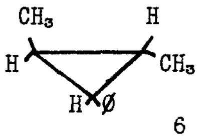
Cyclopropane structures are assigned on the strength of elemental analysis and spectral data, particularly NMR, Table II.

The NMR of **2** is quite complex, indicating the presence of the expected isomeric cyclopropanes. It is, however, in general accord with the cyclopropane structure.

As final structural proof, cyclopropanes **3** and **4** were each debrominated *via* exchange with butyllithium, in ether, at 0°, followed by hydrolysis. VPC on a QF-1 column yielded, in each case, one major high-boiling constituent, identical in NMR properties with authentic samples of the expected reduction products, **5** and **6**, respectively (6).



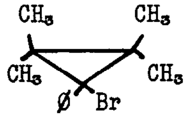
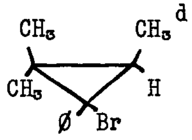
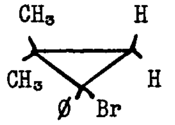
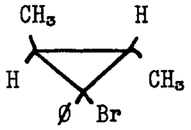
**5**



**6**

## TABLE I

### 1-Phenyl-1-bromocyclopropanes

| No. | Olefin | Product | Conditions[a] | B.P.[b] (m.p.) | Yield,[c] % |
|---|---|---|---|---|---|
| 1 | Tetramethyl-ethylene |  | 1 | (76-77°) | 53 |
| 2 | Trimethyl-ethylene |  [d] | 1 | 82°/0.55 mm. | 51 |
| 3 | iso-Butene |  | 2 | 48°/0.02 mm. | 73 |
| 4 | trans-Butene |  | 2 | 50°/0.01 mm. | 62 |

[a] Condition 1: benzal bromide slowly added to stirred suspension of 1.2 equiv. butoxide in refluxing olefin. Reaction time 6 hr. Purify by recrystallization and sublimation or distillation. Condition 2: benzal bromide and 1.2 equiv. butoxide sealed into glass tube with excess olefin, and agitated for ca. 65 hr. at room temperature.* Purified by distillation.

[b] Uncorrected.

[c] Determined on purified products whose spectral properties were identical with analytical samples. Satisfactory C, H, Br analyses were obtained for adducts 1 and 3.*

[d] The mixture of geometric isomers was not separated.

TABLE II

NMR Data for Phenylbromocyclopropanes

| | Resonance Position (Area) Character[a] | | |
|---|---|---|---|
| Cyclopropane | Aryl | Methyl | Cyclopropyl |
| 1 | 434(5.0)S[b] | 85(5.8)S; 62(6.0)S | ------------ |
| 3 | 436(5.3)M | 93(3.0)S; 49(3.0)S | 78, 68 (2.1)[c] |
| 4 | 437(5.0)M | 88D; 51D[d] | 113-48[d] |

[a] Varian A-60. Measured as dilute solutions in $CCl_4$. Resonance positions in cps downfield from internal TMS. S = singlet, D = doublet, M = multiplet.

[b] Broad.

[c] Chemical shifts of protons of an AB quartet. $J_{AB}$ = 6 cps.

[d] The alkyl region is complex, extending from 113-48 cps. Methyl protons appear as doublets. J = 6 cps. The total integrated area, relative to the aryl multiplet, is 7.7.

Although formation of cyclopropanes is not conclusive evidence for carbene intermediacy (6), it is reasonable to assume, subject to further investigation, that the present reaction involves phenylbromocarbene.

At any rate, cyclopropanation with benzal bromide, as expected, is more facile than the analogous reaction with benzal chloride. Not only can good yields of adducts be obtained at ambient temperature but, though treatment of benzal chloride in tetramethylethylene at 0° gives no isolable cyclopropane after 3.5 hr. (1), similar treatment of benzal bromide leads to recovery of 65% starting material and isolation of 54% 1, based on missing benzal bromide.

We are currently investigating the stereochemical and kinetic selectivity of the reactive intermediate.

## Acknowledgment

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## References

1. R. A. Moss, *J. Org. Chem.* **27**, 2683 (1962). See, also, S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.* **81**, 2586 (1959); and R. Breslow, R. Haynie and J. Mirra, *ibid.* **81**, 247 (1959).
2. Using sealed-tube conditions, such cyclopropanations have recently been accomplished by G. L. Closs and J. J. Coyle. Private communication from G. L. C.
3. J. E. Hodgkins, J. D. Woodyard and D. L. Stephenson, *J. Amer. Chem. Soc.* **86**, 4080 (1964).
4. J. Hine, *Divalent Carbon*, pp. 38ff. Ronald Press Co., New York (1964).
5. Benzoic acid is present in product, but not starting material. If not removed, it co-distills with adducts.
6. G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.* **86**, 4042 (1964).

   Analytical results for *2* and *4* were not as good: *Calcd.* for *2*, $C_{12}H_{15}Br$: %C = 60.3, %H = 6.32, %Br = 33.4; *Found*: 61.1, 6.47, 32.7. *Calcd.* for *4*, $C_{11}H_{13}Br$: 58.7, 5.82, 35.5; *Found*: 57.8, 6.00, 36.2. These values are the best of several sets. Redistillation, as well as treatment with small quantities of butoxide in refluxing hexane, followed by redistillation significantly altered neither spectra nor analyses. Analytical difficulties in chloro analogs are known (McElvain, *op. cit.*). In view of the additional evidence adduced above, structures *2* and *4* do not seem in doubt.