J. Chem. Research (S),
1999, 348–349
J. Chem. Research (M),
1999, 1501–1509

Revisiting the Reactions of Phenyl(trihalomethyl)mercury with Tetraphenylcyclone (TPCP)

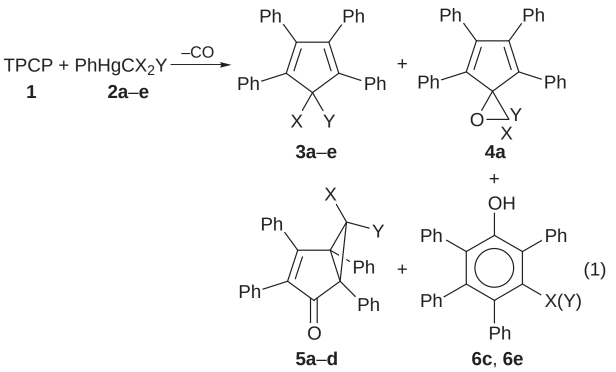
Hongxing Wang,[a] Wenxiang Gu,[b] Gaoju Zhang,[a] Zhenwei Huan[a] and Jin-Pei Cheng*[a]

[a] *Department of Chemistry, Nankai University, Tianjin 300071, China*
[b] *Department of Applied Chemistry, South China Agriculture University, Guangzhou 510642, China*

Unexpectedly high yields of deoxygenation products from the title reactions are observed and rationalized.

Previous studies on the reactions of halocarbenes with carbonyl groups have revealed that ketones usually give much lower yields of CO as deoxygenation product as compared to aldehydes because of the greater steric hindrance in the proposed carbonyl ylide intermediate in the former case.[8] In contrast, we found a CO yield up to 50% in the reactions of TPCP with phenyl(trihalomethyl)mercury,[10] the precursors of dihalocarbenes. This finding promoted us to re-examine the title reactions.

The reactions of five mercurials with TPCP are shown in eqn. (1) and the product distributions are given in Table 1.



Besides a relatively minor amount of C=C bond adduct **5** and the rearranged product **6** of **5**, the major products derived were **3** and **4**: both were thought to result from the carbonyl ylide intermediate (**c** in Scheme 4). A high yield of CO is clear for all these reactions.

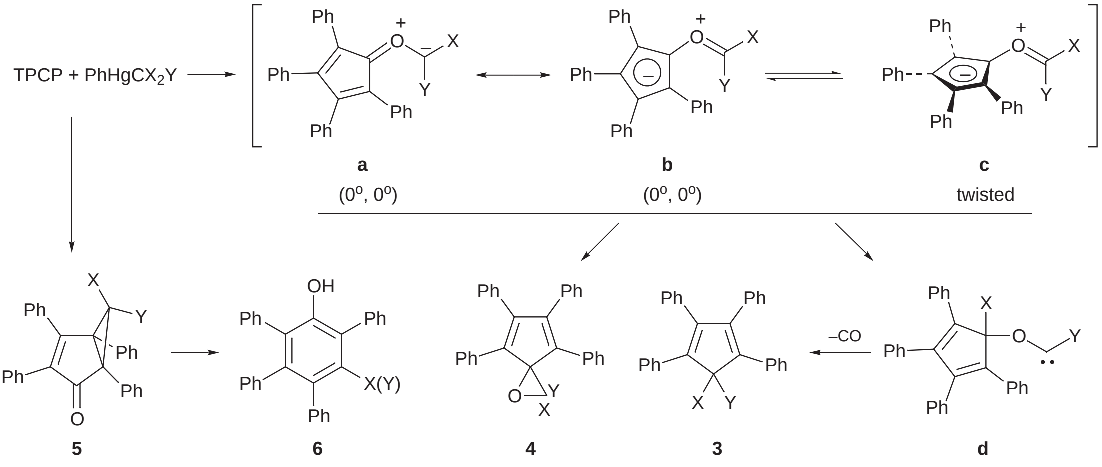
Table 1 Product distribution and yields of CO in the reactions of phenyl(trihalomethyl) mercury with TPCP

Carbene	**3**[a] (%)	**4**[a] (%)	**5*** (%)	**6**[a] (%)	CO[b] (%)
2a (X=Y=Cl)	**3a** (45.0)	**4a** (36.3)	**5a** (17.9)		47.1
2b (X=Cl, Y=Br)	**3b** (40.0)		**5b** (38.0)		49.6
2c (X=Y=Br)	**3c** (41.0)		**5c** (14.6)	**6c** (31.3)	50.9
2d (X=F, Y=Cl)	**3d** (45.0)		**5d** (39.0)		48.1
2e (X=F, Y=Br)	**3e** (35.0)			**6e** (21.0)	51.5

[a] Isolated yield. [b] An average of three or more runs.

Although controversies on the reaction mechanisms regarding the formation of the products such as **3** and **4** exist,[8,9,18] the close pattern of product distribution observed for the five reactions studied in this work (Table 1) and the failure to isolate a 1,4- (or 1,6-) cycloadduct in the similar reactions of cycloheptatrienones (**8a** and **8b**), cyclopentadienone,[21] 1,2-diphenylindenone (**7**), and TPCP all seem to disfavor the 1,4-cycloaddition mechanism.[18] The proposed mechanism is shown in Scheme 4, which explains all the experimental observations in both the reactions *via* a 'push-pull' stabilized carbonyl ylide intermediate and the reaction on the C=C bond.

The isolated oxirane **4** in one case also provided supporting evidence for the ylide mechanism according to an earlier report in the literature.[23]



Scheme 4

---

* To receive any correspondence (*e-mail*: jpcheng@sun.nankai.edu.cn).

Techniques used: ^{1}H NMR, IR, MS

References: 26 Tables: 2

Figures: 1

Schemes: 4

Received, 19th January 1999; Accepted 23rd February 1999
Paper E/9/00516A

References cited in this synopsis

8 (*a*) C. W. Martin, P. R. Lurd, E. Rapp and J. A. Landgrebe, *J. Org. Chem.,* 1978, **43**, 1071; (*b*) J. F. Gish and J. A. Landgrebe, *ibid*., 1985, **50**, 2050.

9 H. Hart and T. Raggon, *Tetrahedron Lett.,* 1983, **24**, 4891.

10 (*a*) Z. W. Huan, Y. M. Pan, X. S. Qu and Z. H. Gao, *Chem. J. Chin. Univ.,* 1989, **10**, 41; (*b*) Y. M. Pan, Z. W. Huan and X. S. Qu, *Acta Chim. Sin.,* 1990, **48**, 920.

18 (*a*) C. W. Jefford, J. Mareda, J.-C. E. Gehret, N. T. Kabengele, W. D. Graham and U. Burger, *J. Am. Chem. Soc.,* 1976, **98**, 2585; (*b*) C. W. Jefford, V. de los Heros and U. Burger, *Tetrahedron Lett.,* 1976, 703; (*c*) C. W. Jefford, W. D. Graham and U. Burger, *ibid*., 1975, 4717; (*d*) L. A. M. Turkenburg, W. H. de Wolf and F. Bickelhaupt, *ibid*., 1982, 769; (*e*) P. M. Kwantes and G. W. Klumpp, *ibid*., 1976, 707.

19 R. A. Mos and Jr. M. Jones, in *Reactive Intermediate*, John Wiley and Sons, New York, 1978, vol. 1, pp. 92–95, vol. 2, pp. 83–86.

21 M. S. Baird, D. G Lindsay and C. B. Reese, *J. Chem. Soc. C,* 1969, 1173.

23 M. Lipson, B. C. Noll and K. S. Peters, *J. Org. Chem.,* 1997, **62**, 2409 and references therein.