Communications to the Editor

Chem. Pharm. Bull.
32(10)4220—4222(1984)

REACTION OF 5,13-DI-TERT-BUTYL-8,16-DIMETHYL[2.2]METACYCLOPHAN-1-ENE WITH DICHLOROCARBENE

Masashi Tashiro,*[,a] Kazumasa Kobayashi,[a] Takehiko Yamato,[a] Kunitoshi Yoshihira,[b]
Kayoko Kawazoe,[c] Sadao Sato[c] and Chihiro Tamura[c]

Research Institute of Industrial Science and Department of
Molecular Science and Technology, Graduate School of
Engineering Science, Kyushu University,[a]
6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816,
National Institute of Hygienic Science,[b] 1-18-1 Kamiyoga,
Setagaya-ku, Tokyo 158, and
Analytical and Metabolic Research Laboratories, Sankyo Co., Ltd.,[c]
1-2-58 Hiromachi, Shinagawa-ku, Tokyo 140, Japan

Treatment of 5,13-di-tert-butyl-8,16-dimethyl[2.2]metacyclophan-1-ene with 50% KOH in a mixture of chloroform and benzene in the presence of tetrabutylammonium chloride as a phase transfer catalyst afforded a heptafluvenophanene and a cycloheptatrienophanene in 17% and 22% yields.

KEYWORDS —— dichlorocarbene; [2.2]metacyclophanene; seven member ring; phase transfer catalyst; heptafluvenophanene; cycloheptatrienophanene

It is well known that dichlorocarbene reacts with various olefines to afford the corresponding dichlorocyclopropane derivatives;$^{1)}$ Weyerstahl and Blame reported that reaction of methylnaphthalenes and toluene with dichlorocarbene in the presence of phase transfer catalyst afforded cycloheptatriene derivatives in low yields.$^{2)}$ However, there is no information on the reaction of the title compound 1, which has an olefinic bond and methylarene moieties, with dichlorocarbene.

We report here on the chemical behavior of **1** with dichlorocarbene in the presence or absence of a phase transfer catalyst. Treatment of **1** with 50% KOH aq. solution in a mixture of chloroform and benzene in the presence of tetrabutylammonium chloride as a phase transfer catalyst at 5°C according to Weyerstahl's procedure afforded heptafulvenophanene **2**$^{3)}$ and cycloheptatrienophanene **3**$^{4)}$ in 17% and 22% yield, respectively, but not dichlorocyclopropane derivative **4**. It was also found that similar treatment of **2** afforded **3**. This result suggests that **2** is an intermediate in the formation of **3**.

The molecular structure of 3 was determined by X-ray analysis.

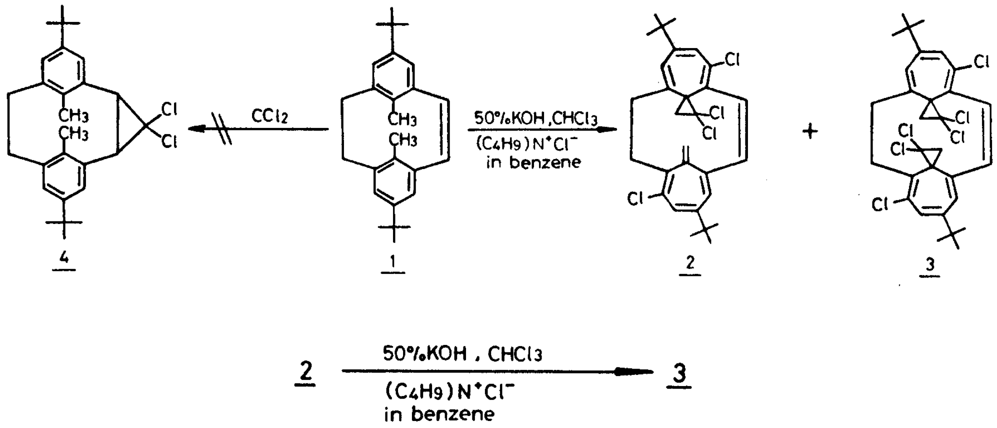

Chart 1

Crystal data: monoclinic, $P2_1/c$, a = 11.852 (5), b = 7.343 (1), c = 18.459 (5) Å and β = 109.75 (2)°, V = 1512.0 $Å^3$, ρc = 1.33 $g.cm^{-3}$, and Z = 2. Bond angles and bond lengths of 3 are shown in Figure 2.

The structure of 2 was assumed from the above chemical conversion and its spectral data.[3)] It is expected from the above result that dichlorocarbene might react with 8,16-dimethyl[2.2]metacyclophan-1-ene (5) and 5,13-di-tert-butyl-8,16-dimethyl[2.2]metacyclophane (6) to give the corresponding cycloheptatrienophane and related compounds.

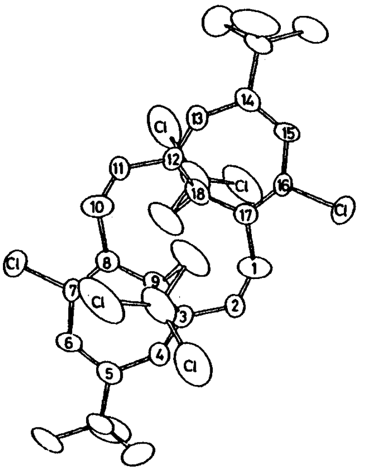

Figure 1.
ORTEP Drawing of 3

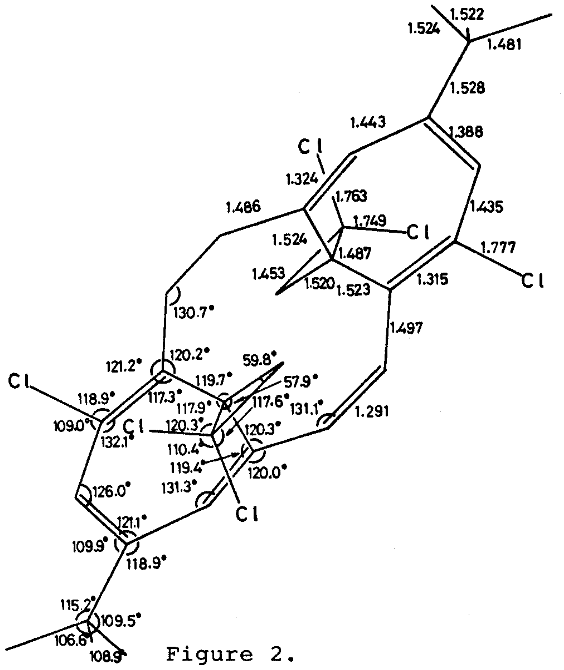

Figure 2.
Bond Angles and Bond Lengths of 3

However, similar treatment of 5 afforded a small amount of a mixture of complex products with a large amount of recovery of 5. The reaction of 6 with dichlorocarbene gave very poor yield (0.86%) of the expected 7[5)] with a large amount

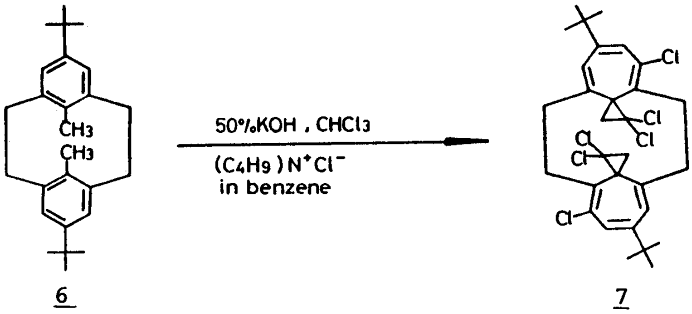

Chart 2

of tarry materials. The structure of 7 was assumed considering its spectral data[5] in comparison with those of 3.

The above results suggest that the tert-butyl groups and C-C double bond of 1 accelerated the reaction with dichlorocarbene.

REFERENCES

1. R. A. Mass, Chap. 2 in "Carbenes" ed by M. Jones, Jr. and R. A. Moss, John Willy and Sons, Inc., New York, 1973.
2. P. Weyerstahl and G. Blume, Tetrahedron, 28, 5281 (1972).
3. Compound 2: reddish brown plates (MeOH); mp 202-204°C; IR (KBr): 2960, 1623, 1542, 1465, 1364, 1223, 1200, 1140, 1075, 1052, 1032, 1020, 1000, 981, 965, 955, 865, 843, 782, 745, 688 cm^{-1}; UV (cyclohexane) λmax 217 nm (log ε 4.26, sh), 252 (4.19, sh), 294 (3.93, sh), 415 (4.03); ^{1}H-NMR (CCl_4) δ: 5.43, 5.52 (each 1H, each d, J = 1.5 Hz, exocyclic methylene protons); MS m/e: 520, 522, 524 (M^+). Anal. Calcd for $C_{29}H_{32}Cl_4$: C, 66.68; H, 6.17. Found: C, 66.68; H, 6.16.
4. Compound 3: pale yellow needles (MeOH); mp 196-197°C; IR (KBr): 2960, 1610, 1590, 1475, 1450, 1410, 1390, 1370, 1260, 1240, 1120, 1090, 1070, 1010, 940, 890, 850, 760, 730, 700, 660 cm^{-1}; UV (cyclohexane) λmax 218 nm (log ε 4.39), 272 (4.31), 350 (3.88, sh); ^{1}H-NMR (CCl_4) δ: 1.24 (18H, s), 1.48 (2H, d, J = 8 Hz), 1.58 (2H, d, J = 8 Hz), 1.62-1.76 (2H, m), 3.10-3.24 (2H, m), 6.09 (2H, s), 6.42 (2H, d, J = 1.5 Hz), 6.64 (2H, d, J = 1.5 Hz); ^{13}C-NMR ($CDCl_3$) δ: 30.411 (q), 32.349 (t), 32.701 (t), 36.341 (s), 39.218 (s), 64.111 (s), 126.462 (d), 130.511 (s), 130.980 (d), 133.626 (s), 133.799 (d), 134.799 (s), 149.007 (s); MS m/e: 602, 604, 606, 608 (M^+). Anal. Calcd for $C_{30}H_{32}Cl_6$: C, 59.53; H, 5.33. Found: C, 59.50; H, 5.42.
5. Compound 7: pale yellow prisms (MeOH); mp 218-221°C; IR (KBr): 2960, 2920, 2860, 1615, 1582, 1475, 1460, 1440, 1387, 1370, 1260, 1100, 1067, 1030, 1010, 975, 925, 910, 862, 840, 800, 755, 730, 708 cm^{-1}; UV (cyclohexane) λmax 213 nm (log ε 4.32), 237 (4.33), 283 (3.70); ^{1}H-NMR ($CDCl_3$) δ: 1.20 (18H, s), 1.56, 1.66 (each 2H, each d, J = 8 Hz), 1.80-3.16 (8H, m), 6.35 (2H, d, J = 1.0 Hz), 6.51 (2H, d, J = 1.0 Hz); MS m/e: 604, 606, 608, 610 (M^+). Anal. Calcd for $C_{30}H_{34}Cl_6$: C, 59.33; H, 5.64. Found: C, 59.41; H, 5.71.

(Received August 10, 1984)