# Sodium Hypobromite Oxidation of Certain Cycloalkanones

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#### Received April 18, 1957

The hypohalite oxidation of methyl ketones to carboxylic acids is a well-recognized useful synthetic procedure.<sup>1,2</sup> More recently higher alkylaryl and alkylheterocyclic ketones have been converted to carboxylic acids in good yields by the use of alkaline hypohalite solutions.<sup>3,4</sup> The present work reports the hypohalite oxidation of cyclohexanone and cyclopentanone.

Cyclohexanone was smoothly converted to adipic acid by three equivalents of sodium hypobromite solution at room temperature. The attack of sodium hypobromite on cyclopentanone was considerably more vigorous however, and when the reaction was allowed to proceed at  $30-35^{\circ}$ , a very small amount of succinic acid was isolated. When conducted at 5–10° a fair yield of glutaric acid along with a smaller amount of succinic acid was isolated. With cyclopentanone the consumption of sodium hypobromite was more than the three moles required according to the stoichiometry as described by Levine and Stephens<sup>4</sup> as evidenced by the disappearance of oxidizing reagent during the course of addition of cyclopentanone.

#### EXPERIMENTAL

Oxidation of cyclohexanone. A sodium hypobromite solution was prepared according to the directions of Levine and Stephens<sup>4</sup> from 88.0 g. (2.2 moles) of sodium hydroxide and 28 ml. (0.55 mole) of bromine in 300 ml. of water. The solution was allowed to warm to 20° and was stirred rapidly while 14.7 g. (0.15 mole) of cyclohexanone was added over a 15-min. period with ice-bath cooling to maintain the temperature at 20-25°. After all the ketone had been added the solution was stirred 2 hr. longer at room temperature. The mixture was then acidified with concentrated hydrochloric acid, whereupon adipic acid precipitated. The slurry was cooled to 5° and filtered. The adipic acid was washed with ice water and dried at 75-80°. The yield of adipic acid, m.p. 150-152°, amounted to 17.3 g. (82%).

Oxidation of cyclopentanone. Cyclopentanone was added dropwise to a sodium hypobromite solution prepared from 88.0 g. of sodium hydroxide and 28 ml. of bromine in 300 ml. of water. In spite of ice-bath cooling, when the addition was started at  $20^\circ$ , the temperature rose to  $30-35^\circ$ . After 10.6 g. of cyclopentanone had been added during 15 min., the solution became colorless and gave a negative test with starch-potassium iodide test paper. The mixture was stirred 15 min. longer, acidified with hydrochloric acid, and evaporated to dryness in vacuum. The residue was extracted thoroughly with ether, and the ether solution was dried and evaporated. Trituration with ether-benzene induced crystallization, and after recrystallization from water there was obtained 2.5 g. of succinic acid, m.p. 186–188°. The mother liquor from trituration with ether-benzene was examined for glutaric acid but none could be isolated.

When the reaction mixture was maintained at  $5-10^{\circ}$  and the cyclopentanone (12.6 g.) added dropwise over a 0.5-hr. period, 1.7 g. of succinic acid and 8.8 g. of glutaric acid were obtained.

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# Inertness of Tetrachlorofulvenes in the Diels-Alder Reaction

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#### Received April 18, 1957

Recently the preparation of tetrachlorofulvenes was disclosed but no mention was made of their being tried in a diene synthesis.<sup>1</sup> It seemed to us that these compounds would be ideal in kinetic studies of the Diels-Alder reaction. Therefore, 1,2,3,4-tetrachloro-6-phenylfulvene (I, R = H) and four of its derivatives (I, R = NO<sub>2</sub>, Cl, N(CH<sub>3</sub>)<sub>2</sub>, and OCH<sub>3</sub>) were prepared.



The fulvenes in preliminary tests gave no evidence of reaction with maleic anhydride in benzene and finally were heated in molten maleic anhydride at  $117^{\circ}$  for a week. At the end of this time cooling gave colored crystals of the fulvenes in the maleic anhydride and no adduct could be isolated.

When 6-(9-anthryl)-1,2,3,4-tetrachlorofulvene (II) was prepared, treatment with maleic anhydride



lead to only a mono adduct. The product still had the color typical of a fulvene and its spectrum indicated the maleic anhydride had reacted with the anthracene moiety.

The color of 1,2,3,4-tetrachloro-6-(2-furyl)fulvene pentadiene did not fade when heated at 100° with maleic anhydride for a week. In addition p-[6-(1,2,-

<sup>(1)</sup> R. C. Fuson and B. A. Bull, Chem. Revs., 15, 275 (1934).

<sup>(2)</sup> M. S. Newman and H. L. Holmes, Org. Syntheses, Coll. Vol. II, 428 (1943).

<sup>(3)</sup> M. W. Farrar and R. Levine, J. Am. Chem. Soc., 71, 1496 (1949).

<sup>(4)</sup> R. Levine and J. A. Stephens, J. Am. Chem. Soc., 72, 1642 (1950).

<sup>(1)</sup> E. T. McBee, R. K. Meyers, and C. F. Baranauckas, J. Am. Chem. Soc., 77, 87 (1955).

NOTES

3,4-tetrachloro fulvenyl)]phenyl *p*-maleimidobenzoate (III) was prepared.



This compound has a maleimido group which has been shown to be an active dieneophile. If the fulvene portion were a reactive diene, one would expect this compound to give a polymer via the Diels-Alder reaction, but the compound was found to be quite stable.

Compound III was dissolved in vinyl acetate and a trace of benzoyl peroxide was added. Heating gave a red polymer and no unchanged III could be isolated. The color of the polymer showed that the fulvene portion was not involved in any polymerization, but since the starting fulvene could not be recovered, copolymerization through the maleimido group with the vinyl acetate was indicated. This suggests variously colored N-substituted maleimides could be used to prepare colored plastics instead of mixing in dyes or pigments.

The inertness of the tetrachlorofulvenes in the Diels-Alder reaction is unexpected since 1,2,3,4-tetrachlorcyclopentadiene reacts with maleic anhydride<sup>1</sup> as does hexachlorocyclopentadiene.<sup>2</sup> Therefore, the negative inductive effect of the halogens does not seem by itself to preclude reaction of the fulvene. Steric hindrance of the aromatic group at the 6 position in these tetrachlorofulvenes is less than that in 6,6-diphenylfulvene which reacts with maleic anhydride.<sup>8</sup> Possibly the negative chlorine atoms and conjugation through the exo double bond have increased resonance stabilization enough to prevent the Diels-Alder reaction.

An attempt to hydrogenate the exo double bond in 1,2,3,4-tetrachloro-6-(p-anisyl)fulvene to give a more reactive diene resulted in the uptake of seven equivalents of hydrogen and the formation of hydrogen chloride. The product had an odor similar to anethole and was not investigated further.

## EXPERIMENTAL

Tetrachlorofulvenes. Hexachlorocyclopentadiene was reduced to 1,2,3,4-tetrachlorocyclopentadiene according to previously published directions. This was condensed with furfural, anisaldehyde, benzaldehyde, p-chloro-, p-dimethylamino-, and p-hydroxybenzaldehyde to give known fulvenes.<sup>1</sup>

When a 2.45 g. sample of 1,2,3,4-tetrachlorocyclopentadiene was condensed with 1.81 g. of *p*-nitrobenzaldehyde, 1.73 g. of 6-(*p*-nitrophenyl)-1,2,3,4-tetrachlorofulvene was obtained. Recrystallization from absolute ethanol gave intensely red needles, with a blue opalescence, m.p. 196.5-197°.

Anal. Calcd. for C<sub>12</sub>H<sub>6</sub>Cl<sub>4</sub>NO<sub>2</sub>: C, 42.74, H, 1.50. Found: C, 42.62; H, 1.69.

From 2.33 g. of 9-anthraldehyde and 2.31 g. of 1,2,3,4tetrachlorocyclopentadiene was obtained 2.42 g. of dark red crystals melting at 185-190°. Recrystallization from absolute ethanol gave red prisms of II, m.p. 193-195°.

Anal. Caled. for C<sub>20</sub>H<sub>10</sub>Cl<sub>4</sub>: C, 61.26: H, 2.57. Found: C, 61.07: H, 2.67.

p-Maleimidobenzoyl chloride. p-Maleimidobenzoic acid<sup>4</sup> (5 g.) when refluxed with thionyl chloride (16 ml.) for 4 hr. gave a quantitative yield (5.79 g.) of light yellow acid chloride. After purification by treatment with Darco in benzene, recrystallization from benzene and petroleum ether and sublimation *in vacuo* at 145–155° colorless crystals melting at 165.5–167° were obtained.

Anal. Caled. for C<sub>11</sub>H<sub>6</sub>ClNO<sub>3</sub>: C, 56.07; H, 2.57. Found: C, 56.11; H, 2.48.

Methyl p-maleimidobenzoate. Heating one gram of the acid chloride in methanol for 15 hr. gave 0.40 g. of ester, m.p. 129-133°. Recrystallization from methanol and decolorization with Darco gave white platelets, m. 133-135°.

Anal. Calcd. for C<sub>12</sub>H<sub>9</sub>NO<sub>4</sub>: C, 62.34; H, 3.92. Found: C, 62.24; H, 3.92.

This ester was also prepared by treating the silver salt of the acid with methyl iodide.

p-[6-(1,2,3,4-Tetrachlorofulvenyl)]phenyl p-maleimidobenzoate. A solution of 1.06 g. of 6-(p-hydroxyphenyl)-1,2,3,4tetrachlorofulvene and 1.10 g. of p-maleimidobenzoyl chloride in 15 ml. of benzene were heated under a reflux condenser for 15 hr. Cooling and diluting with petroleum ether (b.p. 60-70°) gave 1.01 g. of red solid, m.p. 245-249°. The analytical sample was obtained by recrystallization from benzene and melted at 249-250.5°.

Anal. Caled. for  $C_{23}H_{11}Cl_4NO_4$ : C, 54.46; H, 2.18. Found: C, 54.56; H, 2.22.

Diels-Alder reactions. The molar extinction coefficient of 1,2,3,4-tetrachloro-6-(*p*-chlorophenyl)-fulvene in dry benzene was found to be 120 at 540 m $\mu$  by using solutions  $3.28 \times 10^{-3}$  to  $8.21 \times 10^{-3}$  molar. When a benzene solution  $5.47 \times 10^{-3}$  molar in fulvene and  $4.51 \times 10^{-2}$  molar in maleic anhydride was heated at 61°, no change in the optical density was found after 15 hr. Similarly when material in sealed tubes was heated at 117°, no change in the optical density was found after 5 days.

When 0.11 g. samples of the fulvenes were dissolved in 3.49 g. of maleic anhydride and heated at  $117^{\circ}$  for a week, the fulvene color did not change. Heating with water and filtering the residue gave only unchanged starting material in all cases.

A homogeneous solution of 0.56 g. of Compound II and 0.31 g. of maleic anhydride in 10 ml. of benzene was heated under a reflux condenser for one day. The orange solid which precipitated was collected by filtration, washed with benzene and dried, yield 0.35 g., m.p. 238-240.5°. One recrystallization from benzene gave light orange platelets, m.p. 239-241° (turning dark red).

Anal. Calcd. for C<sub>24</sub>H<sub>12</sub>Cl<sub>4</sub>O<sub>3</sub>: C, 58.78; H, 2.46. Found: C, 59.11; H, 2.50. Sap. Equiv. Calcd.: 245. Found, 242.

The ultraviolet spectrum of II and its maleic anhydride derivative indicated reaction had occurred with the anthracene ring rather than with the fulvene moiety.<sup>6</sup>

Copolymerization of vinyl acetate with p-[6-(1,2,3,4-tetrachlorofulvenyl)]phenyl p-maleimidobenzoate. A solution of 1.50 ml. of vinyl acetate, 0.0174 g. of p-6-(1,2,3,4-tetrachlorofulvenyl)phenyl p-maleimidobenzoate (3.431  $\times$  10<sup>-5</sup> mole), 3 granules of benzoyl peroxide and 6 ml. of acetone was sealed in a Pyrex test tube. The tube was heated at 87.9° for 98 hr. The tube was cooled and the red solution poured into water. The resulting red semi-solid was isolated from the aqueous solution by decantation. This material was completely soluble in both acetone and ethanol. When an ethanol solution was concentrated and chilled to  $-40^{\circ}$ ,

(5) P. Argabright, Ph.D. Thesis, University of Colorado

<sup>(2)</sup> E. A. Prill, J. Am. Chem. Soc., 69, 62 (1947).

<sup>(3)</sup> O. Diels, K. Alder, and P. Pries, Ber., 62, 2081 (1929).

<sup>(4)</sup> H. Barnstorff, Ph.D. Thesis, University of Colorado.

no unreacted fulvene could be isolated. Other attempts to isolate the starting fulvene also were unsuccessful.

Acknowledgment. The research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18(600)-648. The hexachlorocyclopentadiene was a gift of the Shell Chemical Company. The analyses were performed by Galbraith Laboratories.

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# Preparation of o-Phenylenebis(dichloroarsine) and o-Phenylenebis(dimethylarsine)

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### Received April 18, 1957

Kalb<sup>1</sup> failed to convert *o*-benzenediarsonic acid by the action of concentrated hydrochloric acid and sulfur dioxide into o-phenylenebis(dichloroarsine), obtaining 1,3-dichloro-1,3-dihydrobenzofurarsan instead. This observation was also made by Hamilton and Ludeman.<sup>2</sup> Chatt and Mann<sup>3</sup> converted 1,3-dichloro-1,3-dihydrobenzofurarsan into o-phenylenebis(dichloroarsine) by the action of thionyl chloride. However, Goldsworthy and associates<sup>4</sup> converted *p*-benzenediarsonic acid into p-phenylenebis(dichloroarsine) in a single step by the action of alcoholic hydrogen chloride and sulfur dioxide. In our hands, by means of the modified procedures as detailed below, o-phenylenebis-(dichloroarsine) has been prepared in 65% yield in a single step from o-benzenediarsonic acid, and ophenylenebis(dimethylarsine) in 88% yield from the bis(dichloroarsine). The yields obtained are significantly higher by the simplified procedures than those previously reported.

#### EXPERIMENTAL

o-Benzenediarsonic acid. o-Benzenediarsonic acid was prepared by treating diazotized arsanilic acid with sodium arsenite solution according to the method of Kalb.<sup>1</sup> The yield of air-dried acid containing one molecule of water of crystallization (did not melt at 360°) was 56.2%.

o-Phenylenebis(dichloroarsine). A solution of 178.4 g. (0.5187 mole) of the above o-benzenediarsonic acid in 3000 ml. of concentrated hydrochloric acid (37.25%) containing 2.0 g. of potassium iodide was treated with a brisk stream of sulfur dioxide until precipitation ceased (35 min.). The orange-colored solid was removed by filtration and pressed as dry as possible on a sintered glass filter (435.8 g.). The

moist, oily solid was treated with 400 ml. of carbon disulfide whereby some material dissolved, and two liquid layers were obtained. The aqueous layer was separated and discarded. Evaporation of the remaining carbon disulfide solution on a water bath and subsequent cooling yielded crystals. Recrystallization from carbon disulfide yielded colorless crystals of pure o-phenylenebis(dichloroarsine) (123.45 g. or 64.7%) melting at 96°.

Anal. Calcd. for  $C_6H_4As_2Cl_4$ : C, 19.59; H, 1.10; Cl, 38.57. Found: C, 19.44; H, 1.15; Cl, 38.61.

o-Phenylenebis(dimethylarsine). o-Phenylenebis(dimethylarsine) was prepared by a modification of the method of Chatt and Mann.<sup>3</sup> A Grignard solution was prepared in a 3-l. flask from 48.15 g. (1.98 atoms) of magnesium turnings, 281.05 g. (1.98 moles) of dry methyl iodide, and 500 ml. of sodium-dried ether. With rapid stirring and ice cooling in an argon atmosphere, a solution of 121.4 g. (0.330 mole) of o-phenylenebis(dichloroarsine) in 570 ml. of dry ether was added (1 hr.). After stirring at room temperature for another hour, a solution of 413.0 g. of ammonium chloride in 1150 ml. water was added with ice-cooling (40 min.). The organic layer was separated, then the inorganic layer was extracted with 300 ml. of ether and rejected. After drying the combined organic solutions with sodium sulfate under argon, the ether was removed by fractional distillation. The residual liquid was fractionated at reduced pressure, bleeding in argon, collecting the fraction boiling at 153-158° at 20 mm. The yield was 82.75 g. (87.6%) of pale yellow liquid, o-phenylenebis(dimethylarsine), having the following physical properties: f.p.,  $-12^{\circ}$  (sharp); and  $n_{D}^{20}$ , 1.6204. The substance is rapidly oxidized by air, and must be stored under argon.

Chatt and Mann<sup>3</sup> obtained a yield of 26%, and mentioned only the b.p. of the product (156° at 20 mm.).

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# Cyclization of an Unsaturated Benzyl Ether to a Hydrofuran

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### Received April 18, 1957

The work reported in this communication is the outgrowth of another problem and owes its genesis to the failure of the amino ketone  $I^1$  to react with the methyl Grignard reagent. That this inertness probably is not due to steric factors was made evident by the normal reaction of II with this reagent. Some ketone was always recovered from the reaction mixture however. On refluxing with acetic anhydride-pyridine the tertiary alcohol from II lost the elements of water to give the dihydro compound III, the structural assignment being based on the following consideration: The ultraviolet absorption had too small an extinction coefficient for ring conjugated absorption, eliminating the possibility of a double bond shift. From the results of previous work on the relative stabilities of the endo- vs. the exodouble bond the exo-methylene structure can tenta-

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<sup>(2)</sup> C. Hamilton and C. Ludeman, J. Am. Chem. Soc., 52, 3284 (1930).

<sup>(3)</sup> J. Chatt and F. Mann, J. Chem. Soc., 610 (1939).

<sup>(4)</sup> L. Goldsworthy, W. Hook, J. John, S. Plant, J. Rushton, and L. Smith, J. Chem. Soc., 2208 (1948).

<sup>(1)</sup> E. L. May and J. G. Murphy, J. Org. Chem., 20, 257 (1955).