Reaction of dibromocarbene with aromatic ethers

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The reaction of dibromocarbene with 1-methoxynaphthalene, 2-methoxynaphthalene, and anisole is discussed. Bromotropones were isolated in good yields in the case of 1- and 2-methoxynaphthalenes. Anisole, on treatment with bromoform and potassium *t*-butoxide gave 4-bromotropone, whereas, on heating with phenyl(tribromomethyl)mercury, *p*-anisic acid and 4,4'-dimethoxybenzophenone were the main products.

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Parham and Reiff (1) have reported that dichlorocarbene reacts with indenes to give cyclopropyl adducts which subsequently afford chloronaphthalenes in high yields by ring expansion and elimination of hydrogen chloride. Birch and Graves (2) have shown that 2,5-dihydro-anisole affords tropone and substituted tropones with dichlorocarbene. Parham *et al.* (3) have also reported the formation of chlorobenztropones from 1- and 2-methoxynaphthalenes.

Seyferth *et al.* (4–6) have extensively studied the reaction of phenyl(trihalomethyl)mercury with a large number of carbene acceptors. The yields obtained were good and the neutral conditions could be maintained, since on heating phenyl(trihalomethyl)mercury compounds in benzene, phenylmercury halide is formed.

Using this method as a source of carbene, a number of aromatic ethers were studied in the hope of isolating bromotropones, which, on subsequent hydrolysis, would lead to the corresponding tropolones.

1-Methoxynaphthalene on heating with phenyl(tribromomethyl)mercury in dry benzene afforded 7-bromo-2,3-benztropone (1, 33%). The ketone was characterized by conversion to the corresponding dinitrophenylhydrazone and by comparison of its infrared (i.r.) and ultraviolet (u.v.) spectra to those of known 7-chloro-2,3-benztropone. The reaction of 2-methoxynaphthalene was effected in the same manner as above. In addition to recovered ether (80%), there was obtained a bromotropone (2) in 37%yield. The ketone was characterized by conversion to the corresponding oxime and by its i.r. and u.v. spectra.

Bromotropones proved resistant to acid hydrolysis and were recovered essentially unchanged after reaction with aqueous hydro-



chloric acid at $120-140^{\circ}$ and concentrated sulfuric acid at $0-15^{\circ}$. Similarly, no useful products could be isolated with aqueous potassium hydroxide at 100° .

Anisole showed no reactivity towards dichlorocarbene derived from chloroform and a base (7). Similarly, anisole was recovered unchanged on heating with sodium trichloroacetate in diglyme and with phenyl(trichloromethyl)mercury in benzene; however, reaction of anisole with bromoform and potassium *t*-butoxide gave 4-bromotropone in low yield. Reaction of anisole with phenyl(tribromomethyl)mercury in benzene at 80° gave none of the tropone but instead, *p*-anisic acid (4) and 4,4'-dimethoxybenzophenone (5) along with a host of other products.

The formation of 4-bromotropone (3) probably involves a similar mechanism to that



involved in the formation of 7-chloro-2,3-benztropone (3) from 1-methoxynaphthalene, i.e. addition of the carbene to the aromatic ring followed by a nucleophilic displacement of a bromide ion, subsequent to a nucleophilic attack on the methyl group.

The formation of p-anisic acid (4) is difficult to explain. Seyferth and Burlitch (8) have isolated, besides other products, cyclohexyl bromide from a reaction of cyclohexane and phenyl(bromodichloromethyl)mercury, which suggests the possibility of a radical mechanism (9). On that basis the following mechanism may be suggested:



Alternatively, *p*-anisic acid may be formed by an ionic mechanism as shown in Schemes 1 and 2.





The isolation of diphenylmercury, haloforms, and metallic mercury in such reactions by various research groups $(6, 10)^1$ supports the above mechanisms.



The formation of 4,4'-dimethoxybenzophenone may be rationalized by Scheme 3.



The above mechanism postulates the formation of $\mathbf{6}$ as shown in Scheme 2. This may ionize to give an electrophile which would react with anisole to give $\mathbf{8}$ followed by hydrolysis to the observed product.

Experimental

Reaction of 1-Methoxynaphthalene

A solution of 1-methoxynaphthalene (7 g) and phenyl-(tribromomethyl)mercury (8 g) was refluxed with stirring in dry benzene (100 ml) under nitrogen for 2.5 h. The mixture was cooled, filtered, and the residue washed several times with benzene. The filtrate and the washings were combined and distilled *in vacuo* to remove the solvent and the unreacted starting ether (3.5 g). The residue was extracted with boiling petroleum ether (b.p. $40-60^\circ$) until no unreacted 1-methoxynaphthalene was recovered and then with 1:1 petroleum ether (b.p. $40-60^\circ$) - benzene mixture to give dirty yellow crystals of 7bromo-2,3-benztropone (1) m.p. $94-102^\circ$. Recrystallization of this product from petroleum ether (b.p. $60-80^\circ$) after sublimation gave white crystals, m.p. $108-109^\circ$ (1 g,

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¹S. D. Saraf. Unpublished results.

Anal. Calcd. for C₁₁H₇BrO: C, 56.17; H, 3.0; Br, 34.0. Found: C, 56.17; H, 2.9; Br, 34.3.

33%). Ultraviolet spectrum (95% ethanol): E_{max} 226 mµ

The dinitrophenylhydrazone was prepared in the usual manner and recrystallized from ethyl acetate as red needles, m.p. 232-233°.

Anal. Calcd. for C17H12N4O4Br: C, 49.15; H, 2.65; Br, 19.3; N, 13.5. Found: C, 49.10; H, 2.90; Br, 19.2; N, 13.5.

Reaction of 2-Methoxynaphthalene

The reaction of 2-methoxynaphthalene (10 g) with phenyl(tribromomethyl)mercury (10 g) in dry benzene (200 ml) was carried out as described above for 1methoxynaphthalene. Work-up in the usual manner, followed by chromatography on neutral alumina, gave 2-methoxynaphthalene (8 g) and 2-bromo-4,5-benztropone (2). The ketone was purified by vacuum sublimation followed by crystallization from petroleum ether (b.p. 60-80°) to give white needles, m.p. 142-143° (1.1 g, 37 %). Ultraviolet spectrum (95% ethanol): Emax 237 mµ (loge 4.4), E_{max} 276 mµ (log_e 4.6), E_{max} 341 mµ (log_e 3.6), E_{max} 358 mµ (log_e 3.3). Infrared spectrum (Nujol): included bands at 1632, 1607, 1558, and 1550 cm⁻¹

Anal. Calcd. for C11H7BrO: C, 56.17; H, 3.0; Br, 34.0. Found: C, 56.2; H, 3.2; Br, 33.5.

The oxime of 2 was prepared in the usual manner and crystallized from ethanol-water. Light yellow needles were obtained which melted at 201-202°.

Anal. Calcd. for C₁₁H₈NBrO: C, 52.3; H, 3.3; N, 5.8; Br, 31.5. Found: C, 52.3; H, 3.2; N, 5.6; Br, 32.0.

Reaction of Anisole with Dibromocarbene

Method A

A stirred solution of anisole (10 g) and potassium *t*-butoxide (20 g) in dry benzene was cooled to -10° and bromoform (15 ml) added dropwise. After 2 h at room temperature, the mixture was filtered, anisole (8 g) recovered by distillation, and the residue was chromatographed on neutral alumina. It was eluted with etherbenzene mixture (1:2) to give a brown solid (132 mg). Repeated crystallizations of this product gave 4-bromotropone (3) as colorless needles, m.p. 111-112° (lit. (11) m.p. 112-113°). Ultraviolet spectrum (95% ethanol): E_{max} 230 mµ(log_e 4.12) E_{max} 308 mµ (log_e 3.72)

Anal. Calcd. for C7H5BrO: C, 45.4; H, 2.7. Found: C, 45.6; H, 3.0.

Method B

A stirred solution of freshly distilled anisole (30 g) and phenyl(tribromomethyl)mercury (35 g) in dry benzene (200 ml) was heated at 80° under nitrogen for 2.5 h and the reaction mixture was worked up in the usual manner. Unreacted anisole was distilled and the residue was extracted with boiling petroleum ether (b.p. 40-60°). This extract deposited a solid, which was crystallized from aqueous ethanol to give p-anisic acid (110 mg), yield 2%, m.p. 182-184°, undepressed on admixture with an authentic specimen (lit. (12) m.p. 182–183°).

The filtrate was concentrated and chromatographed on neutral alumina with petroleum ether (b.p. 40-60°). The first fraction from the column gave a light-yellow liquid (a, 3.2 g). Further elution with benzene gave two solids (b, 445 mg) and (c, 100 mg).

Fraction a

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Thin-layer chromatography showed it to be a mixture of ten compounds but repeated chromatography on alumina resulted in the isolation of only one compound (25 mg) which crystallized from ethanol as colorless needles, m.p. 95-96°. Ultraviolet spectrum (95% ethanol): E_{max} 225 and 312 mµ. The product could not be identified. Fractional distillation of the rest failed to separate the products.

Fraction b

This fraction was rechromatographed on alumina with benzene. The product 4,4'-dimethoxybenzophenone crystallized from petroleum ether (b.p. 60-80°) as long colorless needles, m.p. 145-146.5°, undepressed on admixture with an authentic specimen (lit, (13) m.p. 145-146.5°).

Fraction c

This fraction was rechromatographed on alumina to give a colorless solid, m.p. 151-152.5°, ultraviolet spectrum (95% ethanol): E_{max} 272 and 279 mµ. The molecular weight (Rast) was 226 and an analysis gave: C, 78.6; H, 6.8; OCH₃, 27.6. The product could not be identified.

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