For 4-bromonitrobenzene, only the final data are recorded here:

Solvent	Temp., °C.	α_{ϵ_0}	β	P_∞	R_D	P_0	μ
Benzene	30	3.96	0.511	186.2	40.7	145.5	2.68 ± 0.02
α-Methylnaphthalene	30	4.64	.413	164.3	40.7	123.6	2.47 ± .02

Summary

The dipole moments of three polycyclic spirans have been measured. The high moment found for the intensely colored (III) bears out the assumption that a zwitterionic structure (IIIB) contributes considerably to the actual state of this molecule. The slightly colored, thermochromic (II) has a comparatively small moment of the same order of magnitude as that of the colorless, non-thermochromic (I). As this moment does not increase appreciably with the temperature, parallel to the appearance of color, it is suggested that color may be due not only to zwitterionic structures (IB), (IIB), (IIIB), but also to non-zwitterionic, non-spiranic, quinoid forms such as (IIC).

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

RECEIVED NOVEMBER 26, 1949

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

Aryltrichloromethylcarbinols

BY ERNST D. BERGMANN, DAVID GINSBURG AND DAVID LAVIE[1]

In a previous paper,[2] the condensation of ketones and branched-chain aliphatic aldehydes with chloroform has been investigated, using potassium hydroxide as the condensing agent, in conjunction with acetals as the reaction medium. This reaction has now been extended into the series of benzaldehyde and its substitution products (Table I).

Several workers[3,4,5,6] have previously condensed *benzaldehyde* with chloroform in the presence of small quantities of powdered potassium hydroxide; Howard[4] obtained a yield of 16% of phenyltrichloromethylcarbinol when he used 18% of the molar quantity of potassium hydroxide. Evidently, his experiments were carried out under the assumption that alkali serves as a catalyst—while experience has shown that not a free trichloromethylcarbinol is formed in this type of reaction, but its potassio derivative. The influence of increased quantities of the hydroxide on the conversion was therefore investigated. An amount of 36% of the theory of potassium hydroxide gave, indeed, a yield of 30%, the remainder of the reactants being recovered. Increase of the alkali to the theoretical amount, however, gave only a yield of 41.3%, because of a side reaction which became marked under these conditions, leading to benzoic acid, 11% of the latter being isolated. The use of acetaldehyde-dibutylacetal as reaction medium was not advantageous, 25% of the chlorinated alcohol and 27.8% of benzoic acid being formed when one mole of potassium hydroxide was employed. In the case of 4- and 2-nitrobenzaldehyde, no condensation product was isolated at all, the only reaction taking place being the Cannizzaro condensation: the nitrobenzoic acids and nitrobenzyl alcohols were isolated. 2-Phenylbenzaldehyde behaved likewise.

In view of the negligible effect of the presence of acetals on the condensation between benzaldehyde and chloroform, the systematic study of the reaction between the latter and the substituted benzaldehydes which are listed in Table I was carried out without solvent but, in all cases, one mole of powdered potassium hydroxide was used for each mole of aldehyde. All aldehydes gave the expected reaction and, as far as they are concerned, no significant differences in the influence of methyl, chloro and methoxy groups, respectively, is visible, nor does the position of the substituent (*o*, *m*, *p*) have a marked effect. In particular, substituents in the ortho position do not appear to cause an effect describable as steric hindrance. In the reaction with 3-chlorobenzaldehyde, a substantial amount of 3-chlorobenzoic acid was observed, which accounts for the low yield of (3-chlorophenyl)-trichloromethylcarbinol (12%). In all other cases in Table I, the amount of acid formed (*i. e.*, the extent to which Cannizzaro reaction occurred) was relatively small.

All the carbinols were slowly-crystallizing liquids, but their acetates were well-defined, crystalline solids.

It has been shown recently[7] that substances of the type $RCHOHCCl_3$ can be transformed into α-alkoxy-acids according to the equation

$$RCHOHCCl_3 + R'OH \xrightarrow{KOH} RCH(OR')COOK$$

---

[1] Some of the experimental work described in this paper forms part of a thesis presented by D. Lavie to the Hebrew University in partial fulfilment of the requirements for the degree of Ph.D.

[2] Ch. Weizmann, E. Bergmann and Sulzbacher, THIS JOURNAL, **70**, 1189 (1948).

[3] Jocicz, *Chem. Zentr.*, **68**, I, 1013 (1897).

[4] Howard, *et al.*, THIS JOURNAL, **47**, 455 (1925); **57**, 376, 2317 (1935).

[5] Rapson, Saunder and Steward, *J. Chem. Soc.*, 74 (1944).

[6] von Leuthold, French Patent 791,172 (*C. A.*, **30**, 3157 (1936)).

[7] Ch. Weizmann, Sulzbacher and E. Bergmann, THIS JOURNAL, **70**, 1153 (1948).

TABLE I

ARYLTRICHLOROMETHYLCARBINOLS FROM CHLOROFORM AND SUBSTITUTED BENZALDEHYDES

	Carbinol					Analyses of acetate, %					
						Carbon		Hydrogen		Chlorine	
Substituent	Yield, %	Formula	B. p. °C.	Mm.	Acetate m. p., °C.	calcd.	found	calcd.	found	calcd.	found
2-Me	28	$C_9H_9OCl_3$	157–160	33	67–68	46.9	46.7	3.9	3.6	37.8	37.8
3-Me	37	$C_9H_9OCl_3$	162–167	30	69	46.9	46.5	3.9	4.2	37.8	37.5
4-Me^a	67	$C_9H_9OCl_3$	173–174	30	108.5–109					37.8	38.1
2-OMe^b	36	$C_9H_9O_2Cl_3$	193–198	20	56–57	44.4	44.5	3.7	3.8	35.8	35.5
3-OMe	66	$C_9H_9O_2Cl_3$	150–155	3	75–76	44.4	44.5	3.7	4.1	35.8	35.7
4-OMe^c	47	$C_9H_9O_2Cl_3$	160–163	24	81.5–82	44.4	44.0	3.7	3.6	35.8	35.6
2-Cl	25	$C_8H_6OCl_4$	176–177	30	89–90	39.7	40.4	2.6	3.0	47.0	46.6
3-Cl	12^d	$C_8H_6OCl_4$	165–170	30	59–60.5	39.7	40.0	2.6	2.8	47.0	46.9
4-Cl^e	35	$C_8H_6OCl_4$	180–183	23	124.5–125					47.0	46.8

[a] Dinesmann, *Compt. rend.*, **141**, 201 (1905) (*Chem. Zentr.*, **76**, II, 753 (1905)); from chloral and toluene (b. p. 154–156° (13 mm.); acetate, m. p. 107–108°). [b] See Lebedew (*Chem. Zentr.*, **71**, II, 326 (1900)); yield, 40%; b. p. 174° (12 mm.); acetate, m. p. 58°. [c] Dinesmann, ref. *a*, from chloral and anisole (b. p. 184–186°, (16 mm.); acetate, m. p. 79–81°). [d] A considerable quantity of 3-chlorobenzoic acid was isolated. [e] von Leuthold, French Patent 791,172 (*C. A.*, **30**, 3157 (1936)); from chloral and chlorobenzene.

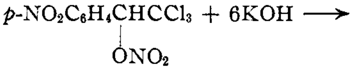
As the O-alkyl-mandelic acids, which would thus become available, are susbstances of possible pharmacological interest, some of the aryltrichloromethylcarbinols were converted into the corresponding substituted α-ethoxy- and α-butoxyphenylacetic acids, by treatment with ethanolic or butanolic potassium hydroxide solution, respectively. It was noted that 4-methoxy-α-butoxy- and 2-methoxy-α-ethoxyphenylacetic acid could not be distilled *in vacuo* without decomposition (Table II).

TABLE II

R	B. p., °C.	Mm.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
(a) Substituted α-*ethoxy*-phenylacetic acids $RC_6H_4CH(OC_2H_5)COOH$ from aryltrichloromethylcarbinols, $RC_6H_4CHOHCCl_3$							
4-Me	125–127	0.1	$C_{11}H_{14}O_3$	68.0	67.8	7.2	7.4
2-Cl	138–150	3	$C_{10}H_{11}O_3Cl$	56.0	56.4	5.1	5.6^a
3-OMe	155–160	0.5	$C_{11}H_{14}O_4$	62.9	63.0	6.7	6.5
4-OMe	166–170	1.5	$C_{11}H_{14}O_4$	62.9	62.8	6.7	6.2
H	140–145	3	$C_{10}H_{12}O_3$	66.7	66.4	6.7	6.6
(b) Substituted α-*butoxy*-phenylacetic acids $RC_6H_4CH(OC_4H_9)COOH$ from aryltrichloromethylcarbinols, $RC_6H_4CHOHCCl_3$							
4-Me	115–120	0.1^b	$C_{13}H_{18}O_3$	70.3	70.2	8.1	8.5
2-Cl	130–140	3	$C_{12}H_{15}O_3Cl$	59.0	59.0	6.2	6.6^c
2-OMe	125–130	0.6	$C_{13}H_{18}O_4$	65.5	64.8	7.5	7.8
3-OMe	165–170	3	$C_{13}H_{18}O_4$	65.5	64.9	7.5	7.5
H	115–120	0.1	$C_{12}H_{16}O$	69.2	68.8	7.7	7.9

[a] Calcd.: Cl, 16.5. Found: Cl, 16.9. [b] M. p. 155°. [c] Calcd.: Cl, 14.7. Found: Cl, 14.5.

In order to obtain (4-nitrophenyl)-trichloromethylcarbinol which failed to form from 4-nitrobenzaldehyde and chloroform, the nitration of phenyltrichloromethylcarbinol was studied. Depending upon the conditions of nitration, either a 76% yield of the desired product or a 39% yield of its nitric acid ester[8] $C_8H_5N_2O_5Cl_3$, were obtained. The former was also characterized as its acetyl derivative. The proof of the structure of the ester could not be based upon its hydrolysis which failed; however, the following observations constitute satisfactory evidence: oxidation with chromic acid gave 4-nitrobenzoic acid, so that the second NO_2-group must have entered the side-chain. Treatment with an excess of potassium hydroxide led to potassium 4-nitrobenzoate, potassium nitrite and potassium chloride, presumably according to the scheme[9]



$$p\text{-}NO_2C_6H_4\underset{\displaystyle ONO_2}{\underset{|}{C}}HCCl_3 + 6KOH \longrightarrow$$

$$p\text{-}NO_2C_6H_4COOK + KNO_2 + 3KCl + HCOOK + 3H_2O$$

In accordance with the observations of Weizmann, Sulzbacher and Bergmann,[7] the nitration product of phenyltrichloromethylcarbinol, upon treatment with methanolic potassium hydroxide, was converted into α-methoxy-4-nitro-phenylacetic acid in 81% yield.

Experimental[10]

Phenyltrichloromethylcarbinol.—(a) To a well-stirred mixture of benzaldehyde (106 g.) and chloroform (200 g.), powdered fused potassium hydroxide (61.5 g.) was added with ice-cooling. When the exothermic reaction subsided, stirring was continued for thirty minutes, the product poured into an excess of water containing 50 g. of concentrated sulfuric acid, and extracted twice with chloroform. The combined chloroform extracts were washed with sodium carbonate solution (which dissolved 14 g. of benzoic acid), dried and distilled; b. p. 158–160° (26 mm.); yield, 93.8 g. (41.3%); refractive index $n^{20}D$ 1.5673.

(b) A mixture of potassium hydroxide (61.5 g.) and acetaldehydedibutylacetal (250 cc.) was heated at 150° for fifteen minutes with stirring and slowly cooled to ice temperature. To the fine suspension so obtained, was added a mixture of benzaldehyde (106 g.) and chloroform (130 g.). The reaction produced a thick magma, which was decomposed with ice water. From this extract, benzoic acid (34 g.) was precipitated by acidification. From the organic layer, the carbinol (56.5 g.) was obtained by distillation (25%).

(4-Nitrophenyl)-trichloromethylcarbinol.—To an ice-cold mixture of phenyltrichloromethylcarbinol (55 g.) and concentrated sulfuric acid (25 cc.), was added slowly a

---

[8] Similar substances have been isolated by Fieser, *et al.*, THIS JOURNAL, **68**, 2248, 2249, 2252 (1946).

[9] Potassium *nitrite* has also been observed in the alkaline hydrolysis of the *nitric acid* esters of glycol and glycerol (Nef, *Ann.*, **309**, 184 (1899); Carlson, *Ber.*, **40**, 4192 (1907); Beilstein, Vol. I, p. 516; Berl and Delpy, *Ber.*, **43**, 1421 (1910)).

[10] All melting and boiling points are uncorrected.

mixture of nitric acid (27.5 g., d. 1.36) and concentrated sulfuric acid (20 cc.). The temperature rose to 15–20°, and a reddish oil separated on the surface (which at lower temperatures became so viscous as to interfere with the stirring). The mixture was poured onto ice and extracted with ether. The latter was washed with sodium carbonate solution, separated and dried, and the residue distilled in *vacuo;* at 155–158° (0.1 mm.), 50 g. (76%) of a yellow oil was obtained which crystallized upon standing (preferably after seeding). From carbon tetrachloride and petroleum ether, the product crystallized in colorless prisms, m. p. 93–94°. *Anal.* Calcd. for $C_8H_6O_3NCl_3$: C, 35.5; H, 2.2; N, 5.2. Found: C, 36.0; H, 2.7; N, 5.4.

Oxidation (of 2 g.) in boiling glacial acetic acid (35 cc.) with chromic acid (3 g.) gave 4-nitrobenzoic acid, m. p. 240°. Admixture with an authentic sample showed no depression.

The **acetyl derivative** was obtained from the carbinol (2 g.) and boiling acetic anhydride (5 cc.). The crystals precipitating spontaneously were recrystallized from alcohol; white prisms, m. p. 154.5°; yield, 87%. *Anal.* Calcd. for $C_{10}H_8O_4NCl_3$: C, 38.4; H, 2.5; N, 4.5. Found: C, 38.1; H, 2.5; N, 4.8.

(**4-Nitrophenyl**)**-trichloromethylcarbinol Nitrate.**—Nitration of phenyltrichloromethylcarbinol (25 g.) with fuming nitric acid (85 cc.) at a temperature not exceeding 0°, gave a homogeneous solution which was poured onto crushed ice. The semi-solid product was triturated successively with water, sodium carbonate solution and methanol (10 cc.). It was thus converted into 15 g. of crystals which were recrystallized from ethyl or butyl alcohol, forming platelets of m. p. 137.5–138°; yield 38.5%. *Anal.* Calcd. for $C_8H_5O_5N_2Cl_3$: C, 30.5; H, 1.6; N, 8.8. Found: C, 31.0; H, 1.6; N, 9.2. **Oxidation** as above gave 4-nitrobenzoic acid. **Alkaline degradation**: The solutions of the substance (1.57 g.) and of potassium hydroxide (1.55 g.) each in butyl alcohol (30 cc.) were mixed and boiled for three hours. After cooling, the salt mixture (1.98 g.) was filtered off which contained 0.57 g. of potassium 4-nitrobenzoate (0.47 g. of the free acid), 0.42 g. of potassium nitrite and 0.99 g. of potassium chloride. From the filtrate a further crop of 0.22 g. of 4-nitrobenzoic acid was isolated by extraction with water and acidification. The equation given above for the degradation reaction requires the formation of 0.85 g. of nitrobenzoic acid (found, 81%), 0.42 g. of potassium nitrite and 1.11 g. of potassium chloride (found, 90%).

Reaction of Chloroform and 4-Nitrobenzaldehyde.—When potassium hydroxide (3.0 g.) was added to a mixture of chloroform (9 g.) and 4-nitrobenzaldehyde (7.5 g.), a precipitate was formed which dissolved in water and gave, upon acidification, 4-nitrobenzoic acid. The filtered chloroform solution was evaporated and left a residue which crystallized spontaneously. The crystals had the m. p. of 4-nitrobenzyl alcohol (93°).[11]

Reaction of Chloroform and 2-Nitrobenzaldehyde.—2-Nitrobenzaldehyde (7.5 g.) and chloroform (6 g.) were condensed in the manner described above, using potassium hydroxide (4.25 g.) as condensing agent and acetaldehydedibutylacetal (12.5 cc.) as reaction medium. The precipitate which formed was collected, and its aqueous solution acidified. It proved to be the potassium salt of 2-nitrobenzoic acid (m. p. 147.5°). Distillation of the filtrate yielded a fraction of b. p. 140° (3 mm.) which crystallized upon trituration with ice-cold methanol. From aqueous methanol, the substance formed needles which, according to their melting point, were 2-nitrobenzyl alcohol (m. p. 74°).[12]

In the **condensation between chloroform and 2-phenylbenzaldehyde,**[13] 2-phenylbenzoic acid[14] and 2-phenylbenzyl alcohol[15] were formed. The latter boiled at 176–180° (30 mm.). *Anal.* Calcd. for $C_{13}H_{12}O$: C, 84.8; H, 6.5. Found: C, 85.1; H, 6.3.

The other experiments are summarized in Table I.

4-Nitro-α-methoxyphenylacetic Acid.—A solution of (4-nitrophenyl)-trichloromethylcarbinol (2.7 g.) in methanol (10 cc.) was added to a solution of potassium hydroxide (2.8 g.) in methanol (20 cc.) and the mixture heated under reflux for two and one-half hours. The potassium chloride formed (2.1 g. = 95%) was filtered off and the filtrate evaporated to dryness and acidified. The product was taken up in ether and crystallized spontaneously after distillation *in vacuo* (b. p. 195° (5 mm.)). After recrystallization from benzene, it melted at 112°; yield, 1.7 g. (81%). *Anal.* Calcd. for $C_9H_9O_5N$: C, 51.2; H, 4.2; N, 6.6; OCH_3, 14.7. Found: C, 51.2; H, 4.5; N, 7.1; OCH_3, 14.5.

The analogous reactions, carried out with the other aryltrichloromethylcarbinols, are summarized in Table II.

Summary

1. The condensation of chloroform with ten benzaldehydes to aryltrichloromethylcarbinols under the influence of potassium hydroxide has been investigated. 2- and 4-nitrobenzaldehyde and 2-phenylbenzaldehyde undergo exclusively, 3-chlorobenzaldehyde largely, Cannizzaro reaction.

2. Nitration of phenyltrichloromethylcarbinol gives the 4-nitro derivative or its nitrate, according to conditions.

3. The aryltrichloromethylcarbinols are converted into α-ethoxy- and α-butoxy-phenylacetic acids by treatment with ethanolic and butanolic potassium hydroxide solution, respectively.

DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, ISRAEL

RECEIVED FEBRUARY 15, 1950

---

[11] Beilstein and Kuhlberg, *Ann.*, **147**, 340 (1868).

[12] Jaffé, *Z. physiol. Chem.*, **2**, 55 (1878).

[13] Fanto, *Monatsh.*, **19**, 586 (1876).

[14] Beilstein, Vol. IX, p. 670.

[15] v. Braun and Manz, *Ann.*, **468**, 274 (1929); b. p. 174° (13 mm.).