chromatography of benzpyrene and its derivatives. The procedure described in this note,[4] which is the result of the examination of a large number of solvent systems, shows promise in dealing with these compounds as well as with other polycyclic hydrocarbons. It has already been found useful in examining reaction mixtures obtained from benzpyrene by the action of various reagents, and may be applicable to the detection of 3,4-benzpyrene in smokes and fogs.

The results obtained with a number of benzpyrene derivatives and other polycyclic hydrocarbons are indicated in Table I. Considerable variation in the absolute R_F values was observed from run to run; similar variations were noted in paper chromatography of oxygenated steroids in analogous solvent systems.[4] However, the relative order of the different compounds was the same in different runs; a known spot of benzpyrene was used as a control, and was readily detected by its characteristic fluorescence. It will be noted that with the hexane–dimethylformamide system the more polar the compounds, the lower the R_F values which were observed.

TABLE I

AVERAGE R_F VALUES OF 3,4-BENZPYRENE, SOME OF ITS DERIVATIVES AND SOME OTHER POLYCYCLIC AROMATIC HYDROCARBONS USING THE HEXANE–DIMETHYLFORMAMIDE SOLVENT SYSTEM

Compounds	No. of runs (av.)	Av. of R_F values	Color under ultraviolet light
3,4-Benzpyrene	10	0.54	Blue
Benzpyrene derivatives			
10-Ethyl	4	.80	Blue
10-Acetyl	4	.26	Green
α-Hydroxy-10-ethyl	4	.07	Blue
4′-Hydroxy-1′,2′,3′,4′-tetrahydro	3	.14	Greenish-blue
4′-Keto-1′,2′,3′,4′-tetrahydro	2	.37	Greenish-blue
Anthracene	4	.84	Blue
Naphthacene	3	.51	Orange
Chrysene	4	.72	Dark blue
Pyrene	5	.62	Green
Fluoranthene	4	.82	Green
20-Methylchlolanthrene	3	.89	Blue
1,2-Benzanthracene	3	.66	Blue
1,2,5,6-Dibenzanthracene	3	.54[a]	Blue

[a] Considerable tailing occurs.

Experimental

The polycyclic hydrocarbons were purified by chromatography and by conversion to trinitrobenzene complexes. The benzpyrene derivatives were synthesized mainly by known procedures; some new procedures are noted below.

10-(α-Hydroxyethyl)-benzpyrene.—10-Acetylbenzpyrene[5] (0.10 g.) in 50 cc. of dry benzene was added dropwise to 50 cc. of dry ether, containing 2 cc. of approximately 1.0 *M* ethereal lithium aluminum hydride. The mixture was refluxed for 2.5 hr., cooled, and water was added to decompose excess reagent, followed by dilute hydrochloric acid. The organic layer was separated, washed with water and bicarbonate, was then dried and the solvent was removed. The yellow solid remaining was chromatographed on alumina from benzene solution. A small amount of the starting ketone was eluted with benzene, and the product was eluted by 1:1 chloroform–ethyl acetate; the product, fine yellow needles, m.p. 150–156°, yielded 0.07 g. (73%), m.p. 163–166°, after two crystallizations from benzene.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.19; H, 5.45. Found: C, 89.23; H, 5.34.

The reported[5b] m.p. is 153–154°.

10-Ethylbenzpyrene (IV).—10-Acetylbenzpyrene (350 mg.) in 25 cc. of triethylene glycol was heated with 0.3 cc. of 85% hydrazine hydrate and 0.25 g. of potassium hydroxide at 140–160° for 1.5 hr. The condenser was then removed, and the vapors were allowed to escape while the temperature was raised to 195–200°. The condenser was dried and replaced, and the solution was heated at 190–200° for 4.5 hr. The mixture was then poured into water, extracted three times with ether, the solvent dried and removed, the residue was taken up with 1:1 petroleum ether–benzene, and chromatographed on 5 g. of alumina. Elution with six fractions (300 cc. each) of the same solvent gave, after crystallization from benzene, 280 mg. (89%) of material melting at 115–116°. The compound was obtained by Windaus[5a] in poor yield melting at 112°.

Paper Chromatography.—A 4″ × 18″ strip of Whatman No. 1 filter paper was completely saturated with redistilled N,N-dimethylformamide,[6] then dried by hanging in the air for 1 hr. During this time, about 1 μg. of the sample, in benzene solution, was applied to a marked spot 2″ from the lower end of the paper, using a micro-pipet. A stream of nitrogen was used to dry the spot.

The developing chamber, which consisted of a Pyrex jar covered with a glass plate, was lined with filter paper which was kept saturated with the developing solvent. The paper strip was equilibrated in the chamber overnight before being developed by the ascending technique with hexane saturated with N,N-dimethylformamide. All experiments were conducted in the dark to prevent photodecomposition of the samples, the position of the spots being checked by observation under ultraviolet light.

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[4] *Cf.* A. Zaffaroni, R. B. Burton and E. H. Keutmann, *Science*, **111**, 6 (1950); *J. Biol. Chem.*, **188**, 763 (1951).

[5] A. Windaus and K. Raichle, *Ann.*, **537**, 157 (1938); (b) L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **61**, 1565 (1939).

[6] We are indebted to the Electrochemical Department of duPont for this material.

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Free Radical Additions Involving Fluorine Compounds. III. The Addition of Bromochlorodifluoromethane to Olefins[1,2]

BY PAUL TARRANT AND ALAN M. LOVELACE

RECEIVED SEPTEMBER 13, 1954

An earlier paper in this series[3] reported that dibromodifluoromethane reacted with various hydrocarbon olefins to give one-to-one addition products; however, the presence of chlorine atoms near the double bond of the olefin prevented the addition from occurring. In order to determine whether steric effects were responsible for the lack of reactivity in this instance, a study was made of the reaction of bromochlorodifluoromethane with various olefins. It was found that the reaction took place readily with olefins which reacted with CF_2Br_2, *e.g.*, $CH_2{=}CF_2$, $CH_2{=}CHCH_3$, $CH_2{=}C(CH_3)_2$ and $CH_3CH{=}CHCH_3$, and the corresponding addition products containing the chlorodifluoromethyl group were obtained in comparable yields. It is therefore interesting to note that the substitution of one of the bromine atoms of di-

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[2] We wish to thank the Dow Chemical Co., Midland, Mich., for furnishing us a generous quantity of bromochlorodifluoromethane.

[3] P. Tarrant and A. M. Lovelace, THIS JOURNAL, **76**, 3466 (1954).

TABLE I

THE PROPERTIES OF THE ADDITION PRODUCTS OF OLEFINS AND BROMOCHLORODIFLUOROMETHANE

Olefin	Addition product	Conv., %	B.p., °C.	B.p., Mm.	$n^{25}D$	d^{25}_4	MR_D Calcd.	MR_D Found	Ag equiv. Calcd.	Ag equiv. Found
$CH_2{=}CHCH_3$	$CF_2ClCH_2CHBrCH_3$	42	55–56	55	1.4194	1.5784	33.30	33.19	103.7	104.2
$CH_3CH{=}CHCH_3$	$CF_2ClC(CH_3)HCHBrCH_3$	73.4	62	49	1.4321	1.5322	37.82	37.43	110.7	110.3
$CH_2{=}C(CH_3)_2$	$CF_2ClCH_2CBr(CH_3)_2$	22	69	86	1.4281	1.4960	37.82	37.87	110.7	113.0
$CH_2{=}CF_2$	$CF_2ClCH_2CF_2Br$	35	79	760	1.3669	1.7890	26.68	28.67	96.0	97.1

bromodifluoromethane by chlorine does not appreciably retard the peroxide-catalyzed reaction with olefins as does a similar substitution by fluorine.

Previous work in this Laboratory has shown that bromotrichloromethane forms an addition product with 1-chloropropene,[4] whereas dibromodifluoromethane does not. The difference in behavior of the two methane derivatives presumably may be due either to steric effects or to a decrease of reactivity of the CF_2Br_2 to reaction with certain radicals. However, since the chlorodifluoromethyl radical is smaller than the trichloromethyl radical, it is clear that the size of the attacking radical is not the cause for the failure of the reaction with 1-chloropropene. It is thus reasonable to assume that the failure of CF_2Br_2 to react with chloroolefins is also not due to steric factors but is probably caused by the inability of the chlorine-containing radical formed, $CF_2BrCHCl\dot{C}HCH_3$ from 1-chloropropene, to continue the chain reaction by removing a bromine atom from the methane derivative.

The addition of bromochlorodifluoromethane to olefins follows the same course as bromotrichloromethane. The carbon-to-bromine bond is broken and the chlorodifluoromethyl radical adds to the methylene end of terminal double bonds. For example, bromochlorodifluoromethane reacted with 2-methylpropene to give $CF_2ClCH_2CBr(CH_3)_2$, for reduction of the one-to-one addition product with zinc and acid gave 1-chloro-1,1-difluoro-3-methylbutane.[5] Further proof is afforded by the reduction of the propylene-adduct to 1-chloro-1,1-difluorobutane.[6] On the basis of the products which are formed, the resulting chlorodifluoromethyl radical adds to an olefinic bond in the same manner as other radicals such as $CCl_3\cdot$, $CF_2Br\cdot$, etc., and the reaction is propagated by the reaction of the secondary radical, such as $CF_2ClCH_2\underset{\bullet}{C}HCH_3$ from propylene, with a molecule of CF_2BrCl. The properties of the addition products are given in Table I.

The addition products from bromochlorodifluoromethane and the olefins are somewhat different in chemical reactivity from the corresponding adducts of dibromodifluoromethane. For instance, it is possible to remove hydrogen bromide from the 2-methylpropene–bromochlorodifluoromethane adduct to give 1-chloro-1,1-difluoro-3-methyl-2-butene,[5] whereas it was not possible to stop the dehydrohalogenation of the corresponding adduct of dibromodifluoromethane until both bromine atoms were removed and 1,1-difluoro-3-methyl-1,3-butadiene was formed.[2]

The removal of hydrogen bromide from the propylene adduct gave 1-chloro-1,1-difluoro-2-butene. It is of some interest to note that the infrared absorption due to the carbon-to-carbon double bond in this olefin occurred at 5.93 μ while the double bond adsorption of the isomeric 4-chloro-4,4-difluoro-1-butene was at 6.08 μ.

The CF_2ClBr–olefin adducts react with zinc and hydrochloric acid to give compounds retaining the chlorodifluoromethyl group. For example, the propylene adduct gave $CF_2ClCH_2CH_2CH_3$ and material believed to have the structure $CF_2ClCH_2CH(CH_3)CH(CH_3)CH_2CF_2Cl$. The reaction of the dibromodifluoromethane adduct under similar conditions give cyclopropane derivatives containing no bromine.[7]

From these differences in reactivity between the adducts from CF_2Br_2 and CF_2BrCl it is evident that the difluorochloro group is much more resistant to chemical attack than the difluorobromo group.

The two-step reaction for the preparation of $CF_2ClCH_2CH(CH_3)_2$ starting with CF_2ClBr and 2-methylpropene offers a better method than the one previously reported which requires the use of 2-chloropropane and 1,1-dichloroethylene.[5]

Experimental[8]

3-Bromo-1-chloro-1,1-difluorobutane.—A 1.4-l. stainless steel autoclave was cooled in Dry Ice, and bromochlorofluoromethane (926 g., 5.6 moles), propylene (83 g., 2.0 moles) and benzoyl peroxide (20 g., 0.08 mole) were added. The clave was sealed, rocked and heated at 100° for four hours. The volatile material was removed leaving 262 g. of residue. Distillation of this material yielded 170 g. of 3-bromo-1-chloro-1,1-difluorobutane with properties shown in Table I. The structure of this compound was established by its reduction to the known 1-chloro-1,1-difluorobutane.

3-Bromo-1-chloro-1,1-difluoro-3-methylbutane.—Heating bromochlorodifluoromethane (911 g., 5.52 moles) with 2-methylpropene (102 g., 1.8 moles) in the presence of benzoyl peroxide (20 g., 0.08 mole) for four hours at 80° as described above gave 200 g. of high-boiling residue. Distillation gave 95 g. of the one-to-one addition product which has the structure $CF_2ClCH_2CBr(CH_3)_2$ since treatment with base gave the known $CF_2ClCH{=}C(CH_3)_2$. The low yield is attributed to a leak in the pressure reactor.

3-Bromo-1-chloro-1,1-difluoro-2-methylbutane.—Substituting 2-butene (86 g., 1.5 moles) for the isobutylene in the experiment above gave 243 g. of $CF_2ClCH(CH_3)CHBrCH_3$. Because of the symmetry of the olefin, only one product is possible since it has been established that the adducts of bromochlorodifluoromethane contain the chlorodifluoromethyl group.

1-Bromo-3-chloro-1,1,3,3-tetrafluoropropane.—A 1.4-l. stainless steel autoclave was charged with bromochlorodifluoromethane (315 g., 1.9 moles), 1,1-difluoroethylene (16 g., 0.25 mole) and benzoyl peroxide (5 g., 0.02 mole) and sealed. The reactants were agitated and heated for four hours at 100°. The one-to-one addition product was isolated by distillation. The yield of 35% corresponds favor-

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(4) M. L. Van Natta, M.S. Thesis, University of Florida, 1952.

(5) P. Tarrant, J. Attaway and A. M. Lovelace, THIS JOURNAL, 76, 2343 (1954).

(6) A. L. Henne and J. B. Hinkamp, *ibid.*, 67, 1197 (1945).

(7) A. M. Lovelace, Ph.D. Dissertation, University of Florida, June, 1954.

(8) Analyses by Peninsular ChemResearch, Inc., Gainesville, Florida.

ably to the 28% yield of $CF_2BrCH_2CF_2Br$ obtained by adding CF_2Br_2 to 1,1-difluoroethylene.[7]

The Attempted Addition of Bromochlorodifluoromethane to 1-Chloropropene.—The autoclave, charged with the methane derivative (920 g., 5.6 moles), 1-chloropropene (152 g., 20 moles) and benzoyl peroxide (20 g., 0.08 mole), was rocked and heated four hours at 100°. No material boiling higher than the chloropropene was obtained and 918 g. of bromochlorodifluoromethane was recovered.

1-Chloro-1,1-difluorobutane.—A mixture of 3-bromo-1-chloro-1,1-difluorobutane (115 g.), zinc dust (113 g.) and hydrochloric acid (600 ml. of 1.5 molar) was refluxed for several hours. Distillation of the organic product gave two fractions. The first (11 g.) consisted of 1-chloro-1,1-difluorobutane, b.p. 55.5°, $n^{25}{}_D$ 1.3476. The higher boiling material (18 g.), b.p. 81.2°, $n^{25}{}_D$ 1.3660, $d^{25}{}_4$ 1.0647, is believed to be the coupled product $CF_2ClCH_2CH(CH_3)CH(CH_3)CH_2CF_2Cl$.

Anal. Calcd. for $C_8H_{12}Cl_2F_4$: Cl, 27.8. Found: Cl, 27.9.

1-Chloro-1,1-difluoro-3-methylbutane.—A mixture of 3-bromo-1-chloro-1,1-difluoro-3-methylbutane (93 g.), zinc dust (30 g.) and hydrochloric acid (170 ml. of 1.5 molar) was refluxed for six hours. The organic layer was separated and distilled. The reduced compound (34 g.), b.p. 74.5–75.5°, $n^{25}{}_D$ 1.3665, $d^{25}{}_4$ 1.064, was obtained in a 65% yield and 10 g. of unreacted starting material was recovered.

1-Chloro-1,1-difluoro-2-methylbutane.—Refluxing the 2-butene adduct (100 g.) with zinc dust (130 g.) and hydrochloric acid (200 ml. of 1.5 molar) gave a 30% yield of $CF_2ClCH(CH_3)CH_2CH_3$. A center fraction of the distilled material had the following properties: b.p. 74.5–75°, $n^{25}{}_D$ 1.3636, $d^{25}{}_4$ 1.0487.

Anal. Calcd. for $C_5H_9ClF_2$: Cl, 24.9. Found: Cl, 24.6.

1-Chloro-1,1-difluoro-2-butene.—1,1-Difluoro-1-chloro-3-bromobutane (165 g.) was added dropwise to potassium hydroxide (84 g.) dissolved in isopropyl alcohol (250 cc.) in a liter flask equipped with stirrer, addition funnel and six-inch column with variable take-off head. Reflux was maintained at 75°. The material was removed, washed, dried and fractionated. One fraction of 47 g. was obtained with the following constants: b.p. 59.5–60°, $n^{25}{}_D$ 1.3656, $d^{25}{}_4$ 1.1100; MR_D calcd. for $C_4H_5F_2Cl$: 25.07, found 25.17; chlorine analysis calcd. for $C_4H_5F_2Cl$: 28.1, found 26.42. The yield was 46% of the theoretical.

1-Chloro-1,1-difluoro-3-methyl-2-butene.—In the apparatus described above was placed 200 cc. of methanol and potassium hydroxide (28 g.). To this refluxing mixture was added 1,1-difluoro-1-chloro-3-bromo-3-methylbutane (80 g.) dropwise. The olefin resulting was removed, dried and fractionated. The yield of $CF_2ClCH{=}C(CH_3)_2$, b.p. 10–11° (28 mm.) was 78% (39 g.).

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Kolbe Electrolysis of *dl*-α-Bromopropionate in Water

BY G. W. THIESSEN AND R. MILLER[1]

RECEIVED JULY 8, 1954

The electrolysis of potassium *dl*-α-bromopropionate in concentrated aqueous solution yields ethylidene bromide, plus some unidentified material. This is a surprising result. If the general acid R·COOH be converted to a salt and electrolyzed with a smooth platinum anode, the typical products are R·R· (R minus H), R·COO·R, and R·So, So being a radical derived from the solvent anion.[2] Ethylidene bromide is none of these; nor is it the (R minus Br) which might be expected by analogy to (R minus H). Instead it is (R plus Br).

The extra Br gained by R must have come from another R, directly or indirectly. Although the solvent after electrolysis shows much bromide ion, the direct transfer seems likelier, for these reasons: (a) there is practically no H transfer between solvent and R in the electrolysis of acetate to methane[3]; (b) in the electrolysis of acetate to methane at low current densities, the H gained by R comes from another methyl, not the solvent[4]; and (c) in the electrolysis of propionate to ethylene, which is (R minus H), the hydrogen is lost from the β-carbon.[5] Hydrogen (electropositive) lost thus would correspond to bromine (electronegative) lost from the α-carbon.

In presence of excess bromide ions, the efficiency of the electrolysis becomes low, apparently due to the preferential discharge of bromide. This was discovered in an attempt to conserve the potassium ion by replenishing free acid as the electrolysis proceeded; the process was impracticable. This is held as an additional argument against the extra acquired bromine atom being derived from an ion in the solvent. As a further argument in the same direction, the oily yield appears in the first few minutes of electrolysis, before hydrolytic or reductive development of bromide ion in the solvent could have proceeded far.

Experimental

Thirty ml. (51 g., 0.33 g.-mole) of Eastman Kodak Co. *dl*-α-bromopionic acid was mixed, with cooling, with 42 ml. of distilled water and 21 ml. of aqueous saturated (room temperature) potassium hydroxide solution. The anode used was Pt wire approx. 0.17 cm.² surface and the cathode Pt foil, about 1.4 cm.² surface. The temperature in the cell was held to 40° or less by external cooling, the mean current density about 1.2 amp./cm.² at anode and the total throughput, about 0.4 faraday. No diaphragm was used. Excessive temperature or throughput yields free bromine; excess free acid hinders separation of the yield.

The electrolyte soon becomes cloudy and deposits about 3 g. of heavy amber oil. Gases evolve simultaneously, being mostly hydrogen and carbon dioxide in about equal amounts; a few per cent. of oxygen may appear, with traces at most of carbon monoxide and unsaturates. The yield from several electrolyses is united to form a working crude sample. Washing with cold concd. sulfuric acid yields a portion more dense than the acid, which boils in the neighborhood of 105° with some decomposition to produce HBr. Its density is 2.03, $n^{25}{}_D$ 1.515, 84.9% Br; for ethylidene bromide, the b.p. is 108–110°, density 2.05, $n^{25}{}_D$ 1.513, 85.1% Br. No satisfactory derivative for ethylidene bromide was found recorded.

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[1] Assistance from the Research Corporation is gratefully acknowledged.

[2] G. Thiessen, *Trans. Ill. Acad. Sci.*, **43**, 77 (1950).

[3] H. Erlenmeyer and W. Schoenauer, *Helv. Chim. Acta*, **20**, 222 (1937).

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[5] W. Schanzer and P. Kruis, *ibid.*, **A191**, 301 (1942).

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Phenylsilanetriol

BY LESLIE J. TYLER

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Previous investigators[1,2] have made use of the hydrolysis of alkoxysilanes with distilled water to prepare the corresponding hydroxy compounds. These mild conditions allow the isolation of un-

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[1] J. F. Hyde, THIS JOURNAL, **75**, 2166 (1953).

[2] S. W. Kantor, *ibid.*, **75**, 2712 (1953).