alcohol to a xylene (1 l.) dispersion containing 19.6 g. (0.85 atom) of sodium. A solution of 68.0 g. (0.370 mole) of IX in 200 ml. of xylene was added (30 hr.) to the dispersion by use of the high-dilution assembly described above. The entire operation was conducted in an atmosphere of nitrogen. The reflux temperature was maintained at 125–135° by continuous distillation of lower boiling materials. Reflux was continued for 1 hr. after addition was complete and the mixture was then processed as were the acyloin mixtures described above. Distillation of the product was accompanied by gas evolution and all material distilling below 225° (0.2 mm.) was collected. Redistillation through a short path system afforded 9.00 g. (13.2%) of 2-carbethoxy-4-hydroxycyclohexanone (VII), b.p. 115–120° (0.2 mm.). A certain degree of superheating was unavoidable due to the nature of the system and, as described above, the use of more conventional systems permitting liquid-vapor equilibration resulted in prohibitive polymerization. The infrared spectrum of this material was identical with that described above.

The reaction of X with excess phenylhydrazine in alcohol solution gave a red derivative identical with that (XII) formed from 2-carbethoxy-1,4-cyclohexanedione, m.p. and mixed m.p., 243.0–243.5°. The mother liquors were cooled to 0° whereupon a second derivative crystallized. Recrystallization from water gave colorless needles, m.p. 216–217° (after apparently losing solvent at 70–75°). A sample dried at 100° (0.2 mm.) lost 50% of its weight during drying.

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.2. Found: C, 67.90; H, 6.36; N, 12.3.

That this derivative is the pyrazolone rather than the phenylhydrazone-lactone was established by examination of its infrared spectrum. It exhibited, in addition to absorption at 2.9 μ attributable to hydroxyl, a band in the 6.05–6.30 μ region, characteristic of pyrazolone derivatives and due to carbonyl absorption. An attempted preparation of the 3,5-dinitrobenzoate of X yielded only ethyl 3,5-dinitrobenzoate, identified by mixed melting point and white solid which was extremely slightly soluble in common solvents and considered to be polymeric.

Reaction of 1,4-cyclohexanedione with phenylhydrazine. 1,4-Cyclohexanedione (1.1 g.) was prepared by the acid hydrolysis of 2.0 g. of 4,4-ethylenedioxycyclohexanone (VI). The crude product was used without purification. It gave a 91% yield of the bisphenylhydrazone, m.p. 148–149° (lit.[23] 150°), during a reaction time of 1 hr. in an alcoholic solution containing excess phenylhydrazine. Longer reaction times did not afford any other product.

Reaction of 4-hydroxycyclohexanone with phenylhydrazine. 4-Hydroxycyclohexanone was prepared from VI. A solution of 3.00 g. of VI in 15 ml. of methanol was reduced by the portion-wise addition of 0.38 g. of sodium borohydride. Acidification followed by isolation by ether extraction gave 1.01 g. of crude product. A solution comprised of 0.60 g. of this material and 1.62 g. of phenylhydrazone in 10 ml. of acetic acid was warmed on the steam bath. Solid began to crystallize almost immediately (presumably the normal derivative) and an additional 15 ml. of acetic acid and 5 ml. of ethanol were added. After 3 hr. under reflux, the dark red solution was concentrated under reduced pressure to *ca.* 6 ml. and diluted with sufficient water to produce clouding. Cooling and scratching induced crystallization. The mixture was filtered and the semi-solid washed with cold ether. Crystallization from methanol-water gave 0.31 g. of tan solid, m.p. 144–146°. Further crystallization from ethyl acetate-petroleum ether (60–68°) gave pure 4-hydroxy-2,3,4,5-tetrahydrocarbazole (XIII), m.p. 148.5–149.5°.

Anal. Calcd. for $C_{12}H_{13}ON$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.81; H, 7.09; N, 7.51.

A mixed melting point of this substance with the bisphenylhydrazone of 1,4-cyclohexanedione (m.p. 150°) was depressed to 120°. The infrared spectrum exhibited strong absorption at 3.0 μ (NH, OH). The ultraviolet absorption spectrum showed λ_{max} 227 mμ, ϵ 40,200, λ_{max} 282 mμ, ϵ 6,740, and λ_{max} 290 mμ, ϵ 6,270. These values are very close to those recorded for 3-indoleacetic acid.[24]

Acknowledgment. We are grateful to Research Corporation for the financial support of this work.

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[CONTRIBUTION FROM THE CHEMICALS AND PLASTICS DIVISION, QUARTERMASTER RESEARCH AND DEVELOPMENT CENTER]

DDT Synergists. The Synthesis and Properties of Some 2,2-Difluoro-1,1-diarylethanols and 2-Fluoro-1,1-diarylethenes

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A number of 2,2-difluoro-1,1-diarylethanols have been prepared by treatment of ethyl difluoroacetate with aryl Grignard reagents. These alcohols were reduced to the corresponding ethanes, which, in turn, were dehydrofluorinated to yield a series of 2-fluoro-1,1-diarylethenes. Some preliminary results of a study of the insecticidal power and of the synergistic activity of these compounds with DDT are reported.

In connection with studies on synergism of DDT, we undertook the preparation of a number of diarylethanols containing fluorine in the ethane moiety. While this program was in progress, Kaluszyner and coworkers[2,3] reported the preparation of a number of 2,2,2-trifluoro-1,1-diarylethanols from the reaction of aryl Grignard reagents with ethyl trifluoroacetate. This paper summarizes the results obtained in this laboratory from the treat-

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TABLE I

2,2-DIFLUORO-1,1-DIARYLETHANOLS $Ar_2C(OH)CHF_2$

Ar	B.P., °C.	Mm.	Yield, %	Formula	Color with Concd. H_2SO_4	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl[a]	110–111	0.15	64	$C_{14}H_{12}F_2O$	Orange	71.78	72.1	5.17	5.1
p-Fluorophenyl[b]	99–100	0.05	43	$C_{14}H_{10}F_4O$	Red-orange	62.23	62.5	3.73	3.7
p-Chlorophenyl[c]	130–136	0.20	53	$C_{14}H_{10}Cl_2F_2O$	Cherry-red	55.47	55.63	3.33	3.47[d]
p-Bromophenyl[e]	153–164	0.17	40[f]	$C_{14}H_{10}Br_2F_2O$	Red	42.88	42.9	2.57	2.4[g]

[a] n_D^{25} 1.5593. [b] n_D^{24} 1.5276. [c] n_D^{20} 1.5780. [d] Calcd.: Cl, 23.40. Found: Cl, 23.94. [e] $n_D^{26.5}$ 1.6039. The compound crystallized in the form of thick prisms after standing six months, m.p. 54.5–56.0°. [f] A large amount of tarry residue was obtained on distillation of the crude material. [g] Calcd.: Br, 40.77. Found: Br, 40.5.

TABLE II

2,2-DIFLUORO-1,1-DIARYLETHYL ACETATES $Ar_2C(OCOCH_3)CHF_2$

Ar	M.P., °C.	Recryst. Solvent	Yield, %	Formula	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl	51.0–52.0	Methanol	80	$C_{16}H_{14}F_2O_2$	69.55	69.6	5.11	5.1
p-Fluorophenyl[a]	...	...	89	$C_{16}H_{12}F_4O_2$	61.53	61.8	3.87	3.9
p-Chlorophenyl	86.0–86.8	Pet. ether	82	$C_{16}H_{12}Cl_2F_2O_2$	55.67	55.8	3.50	3.3
p-Bromophenyl	80.0–80.5	Methanol-water	86	$C_{16}H_{12}Br_2F_2O_2$	44.25	44.3	2.79	2.9[b]

[a] Resisted all attempts to induce crystallization; isolated as very viscous oil by molecular distillation at 80° and 0.1 mm., n_D^{25} 1.5158. [b] Calcd.: Br, 36.80. Found: Br, 36.8.

ment of ethyl difluoroacetate with various arylmagnesium bromides.

Phenylmagnesium bromide and its derivatives carrying either chlorine, bromine, or fluorine in the *p*-position reacted readily at 0° with ethyl difluoroacetate to yield the expected 2,2-difluoro-1,1-diarylethanols, $Ar_2C(OH)CHF_2$. As Table I shows, the yields of the ethanols varied from 40 to 64%, depending upon the substituent in the aromatic ring. The yields were lowered when the reaction was carried out at room temperature or above. All of the tertiary alcohols were isolated as colorless or faintly straw-colored, high-boiling, viscous oils; only the *p*-bromo compound crystallized. The ethanols gave characteristic colors with concentrated sulfuric acid and displayed the typical O-H stretching band at 3590 cm.$^{-1}$ in the infrared (carbon tetrachloride solution). The alcohols were further characterized by conversion to the acetates (Table II).

The ethanols were reduced to the corresponding ethanes in good yield (Table III) by heating under reflux for ten days with phosphorus and iodine in aqueous acetic acid.[4] It was interesting to note that the ethanes, unlike the ethanols, were rather mobile oils and all of them, except for 2,2-difluoro-1,1-bis-(*p*-fluorophenyl)ethane, crystallized readily. The ethanes, as expected, gave no coloration with concentrated sulfuric acid and their infrared spectra showed complete absence of hydroxyl.

The ethanes were converted smoothly to the corresponding 2-fluoro-1,1-diarylethenes (Table IV) when refluxed with 2% ethanolic potassium hydroxide. The clean-cut nature of this dehydrofluorination is interesting in view of the report[3] that treatment of 2,2,2-trifluoro-1,1-diarylethanes with ethanolic potassium hydroxide or sodium ethoxide results in alcoholysis of the trifluoromethyl group. All of the ethenes displayed very intense absorption in the infrared at 1630 cm.$^{-1}$ (carbon tetrachloride solution), indicative of the presence of $>C=C<$ conjugated with an aromatic ring.[5] Furthermore, these compounds gave positive tests with bromine in carbon tetrachloride and with potassium permanganate in water-acetone solution, whereas the ethane progenitors were completely unreactive toward these diagnostic reagents.

Dimroth and Bockemüller had previously described[6] the preparation of 2-fluoro-1,1-diphenylethene and claimed this compound was a solid melting at 93.5°. Our preparation, in contrast, is a mobile oil at room temperature and, moreover, as Table IV reveals, all of the *p*-halo substituted derivatives melt below 93.5°. These investigators prepared their sample of this ethene by dehydrofluorinating with ethanolic potassium hydroxide 1,2-difluoro-1,1-diphenylethane, which was claimed to have been formed by treating 1,1-diphenylethene with a mixture of lead tetraacetate and hydrogen fluoride in chloroform. The isolation of desoxybenzoin as a by-product from the latter reaction suggests that possibly the structure believed by Dimroth and Bockemüller to be 2-fluoro-1,1-di-

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TABLE III

2,2-DIFLUORO-1,1-DIARYLETHANES Ar_2CHCHF_2

Ar	M.P., °C.	Recryst. Solvent	Yield, %	B.P., °C.	Mm.	Formula	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl	38.5–39.5	Ethanol	91	85	0.15	$C_{14}H_{12}F_2$	77.05	76.8	5.54	5.5
p-Fluorophenyl[a]	...	...	90	79–80	1.5[b]	$C_{14}H_{10}F_4$	66.14	66.6	3.97	4.0
p-Chlorophenyl	37.5–38.5	Methanol-water	90	110–118	0.08	$C_{14}H_{10}Cl_2F_2$	58.56	58.8	3.51	3.5[c]
p-Bromophenyl	42.0–42.8	Methanol	89	...	...	$C_{14}H_{10}Br_2F_2$	44.70	44.80	2.68	2.8[d]

[a] Could not be obtained crystalline. [b] n_D^{24} 1.5179. [c] Calcd.: Cl, 24.69. Found: Cl, 24.8. [d] Calcd.: Br, 42.48. Found: Br, 42.5.

TABLE IV

2-FLUORO-1,1-DIARYLETHENES $Ar_2C{=}CHF$

Ar	M.P., °C.	B.P., °C.	Mm.	Recryst. Solvent	Yield, %	Formula	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl[a]	...	77	0.05	...	91	$C_{14}H_{11}F$	84.82	85.1	5.59	5.7
p-Fluorophenyl	32–33	81–82	1.0[b]	Methanol	93	$C_{14}H_9F_3$	71.79	71.9	3.87	4.0
p-Chlorophenyl	78.0–79.5	...	...	Methanol	85	$C_{14}H_9Cl_2F$	62.91	62.9	3.39	3.4[c]
p-Bromophenyl	84.2–85.2	...	...	Methanol	85	$C_{14}H_9Br_2F$	47.20	47.0	2.55	2.4[d]

[a] Crystallizes in refrigerator, n_D^{24} 1.5872. [b] $n_D^{24.5}$ 1.5481. [c] Calcd.: Cl, 26.53. Found: Cl, 26.4. Calcd.: F, 7.11. Found: F, 6.96. [d] Calcd.: Br, 44.86. Found: Br, 44.7.

phenylethene is actually an isomer prepared by the dehydrofluorination of an unexpected rearranged product. Further support of the validity of our structure, in addition to the evidence cited above, was obtained by oxidizing the compound by chromic anhydride in acetic acid to benzophenone, isolated, in excellent yield, as the 2,4-dinitrophenylhydrazone.

EXPERIMENTAL[7]

The preparation of *2,2-difluoro-1,1-diphenylethanol* illustrates the general procedure used in obtaining the substituted ethanols. Freshly purified ethyl difluoroacetate (20.0 g., 0.16 mole), diluted with an equal volume of ether, was added with stirring in the course of 1 hr. to the ice-cold Grignard reagent prepared from 10.7 g. (0.44 g.-atom) of magnesium turnings and 69.0 g. (0.44 mole) of bromobenzene in 100 ml. of ether. Stirring and cooling in the ice-bath were maintained for 2 hr. after completion of the addition of the ester. The reaction mixture, after standing at room temperature overnight, was treated, while stirring and cooling, with saturated ammonium chloride, prepared by shaking 40 g. of the salt with 100 ml. of water. The yellow suspension was filtered with suction through a sintered-glass funnel, the filter cake was washed with ether, and the combined ethereal extract washed twice with water before being dried over sodium sulfate. Evaporation of the ether yielded a dark orange oil which was diluted with an equal volume of methanol and refrigerated at −35° for 2 days in order to allow the traces of biphenyl to crystallize. Filtration of the mixture followed by steam distillation of the filtrate (2 l. of distillate was collected and discarded) gave a product which was essentially free of starting material and derived products. The oily residue was dissolved in ether and dried over sodium sulfate. Removal of the solvent and distillation of the residue afforded 24.0 g. (64%) of the product, b.p. 110–111° at 0.15 mm., as a colorless oil.

The *2,2-difluoro-1,1-diarylethyl acetates* were prepared either by heating the alcohol with acetic anhydride in the presence of catalytic amounts of concentrated sulfuric acid[8] or by allowing the alcohol to stand at room temperature for several hours with a mixture of acetic acid-trifluoroacetic anhydride.[9] The products, isolated in the usual way, showed the characteristic carbonyl absorption band at 1750 cm.$^{-1}$ in carbon tetrachloride solution.

Reduction to *2,2-difluoro-1,1-diarylethanes* was effected by heating 8.0–10.0 g. of the appropriate alcohol under reflux for 10 days with a mixture of 3.5 g. of red phosphorus, 1.27 g. of iodine, 50 ml. of glacial acetic acid, and 1.0 ml. of water. The cooled reaction mixture was filtered with suction directly into a separatory funnel containing 300 ml. of 2.5% sodium bisulfite. The oily suspension was neutralized by adding portions of solid sodium bicarbonate with intermittent shaking and was then extracted with ether. The ether extract was dried over sodium sulfate after being washed with water. Removal of the ether and distillation of the residue *in vacuo* yielded a colorless, mobile oil, which spontaneously crystallized, except in the case of the *p*-fluoro compound.

General procedure for the preparation of 2-fluoro-1,1-diarylethenes. The substituted ethane (2.2 g.) was heated under reflux for 2.5 hr. with 60 ml. of 2% ethanolic potassium hydroxide. The solvent was removed under reduced pressure and the residue extracted with several portions of ether. The combined ethereal extract was washed with water and dried over magnesium sulfate. Removal of the ether afforded a colorless oil which was distilled at diminished pressure. Of this series, only 2-fluoro-1,1-diphenylethene could not be obtained crystalline at room temperature.

Oxidation of 2-fluoro-1,1-diphenylethene. A 281-mg. quantity of this compound was heated under reflux for 3 hr. with a mixture of 550 mg. of chromium trioxide, 15 ml. of glacial acetic acid, and 3 drops of water. The green solution was

(7) Melting points are corrected and boiling points are uncorrected. Infrared measurements were made using a Baird double beam recording spectrophotometer equipped with a sodium chloride prism. The majority of the elemental analyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass.

(8) L. F. Fieser, *Experiments in Organic Chemistry*, 2nd. ed., D. C. Heath and Company, Boston, 1941, p. 397.

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poured onto cracked ice, 30 ml. of water was added, and the mixture was extracted twice with 50-ml. portions of ether. The combined extract was washed successively with water, 10% potassium carbonate (20 ml.), and water. After drying over sodium sulfate and evaporation of the ether the residue was dissolved in 8 ml. of ethanol and treated with 2,4-dinitrophenylhydrazine. Recrystallization of the precipitate from glacial acetic acid gave orange needles, m.p. 239–240° (recorded[10] m.p. 238–239°). A mixed melting point with an authentic specimen of benzophenone 2,4-dinitrophenylhydrazone showed no depression. The infrared spectra of the two samples (chloroform solution) were totally superimposable.

Biological results. In tests with house flies, the ethanes carrying *p*-chloro- and *p*-bromo-substituents were the most active insecticides of the entire series of compounds; the corresponding ethanols were somewhat less active. None of the acetates and ethenes displayed significant insecticidal activity.

On the other hand, the *p*-chloro- and *p*-bromo-substituted ethanes, ethanols, and acetates proved to be excellent synergists for DDT in tests with DDT-resistant house flies. The synergistic activity of these compounds surpassed that of 1,1-bis(*p*-chlorophenyl)ethanol (DMC), one of the most effective DDT synergists.[11] The ethenes were less effective. A detailed report of this study will be published elsewhere.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL COMPANY]

Cupric Acetate Catalyzed Monocyanoethylation of Aromatic Amines

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Cupric acetate monohydrate has been shown to be a highly effective new catalyst for the monocyanoethylation of a variety of aromatic amines. Unlike other cyanoethylation catalysts, its action is not appreciably inhibited by the presence of *ortho*- or *N*-substituents on the amines to be cyanoethylated. Also, its use leads to improved yields and shorter reaction times than obtained with conventional catalysts.

Cyanoethylation of 17 aromatic amines with cupric acetate catalyst is reported, and some observations are made on the relative influence of steric and electronic effects of the substituent groups upon the mechanism of the reaction, the reaction conditions required, and yields and nature of the products obtained.

The reaction of acrylonitrile with compounds containing active hydrogen atoms has been widely investigated.[1,2] While primary and secondary aliphatic amines react readily with acrylonitrile in the absence of catalysts to give high yields of 3-aminopropionitriles, some heterocyclic amines (carbazole, indole, pyrrole) react only in the presence of basic catalysts.[1] Aniline, however, does not react with acrylonitrile in the absence of catalysts,[3] and early investigators reported that aniline does not undergo cyanoethylation even in the presence of basic catalysts.[3,4] The cyanoethylation of a variety of aromatic amines is reported, however, to proceed readily with acid catalysts, particularly acetic acid.[4,5,6] It has also been shown that copper salts, particularly cuprous chloride, have a beneficial effect when employed in conjunction with acetic acid.[6,7,8] Also reported is cyanoethylation of aromatic amines in the presence of acetic anhydride,[9] aniline salts,[10] and by the exchange reaction of an aromatic amine hydrochloride with 3-diethylaminopropionitrile.[11]

This last reaction has been considered to occur *via* an S_N2 reaction involving attack of the arylamino nitrogen upon the β-carbon of the cyanoethyl group rather than an S_N1 elimination-addition reaction.[11c]

Pietra[12] has recently disclosed that good yields

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