petroleum ether gave plates, m.p. 71–72°, which liquified on exposure to air at room temperature. The substance showed λ_{max}^{EtOH} 210 mμ (ε = 11.52) and 349–350 mμ (ε = 6.00). Infrared absorption maxima were observed at 3500, 1690, and 1614 cm.$^{-1}$, indicating the presence of $>$NH, $>$CO and $>$C=C$<$ respectively. The substance is assigned the structure of ethyl 2-methyl-1,4-dihydronicotinate (IIIa).

Anal. Calc'd for $C_9H_{13}NO_2$: C, 64.7; H, 7.78; N, 8.39. Found: C, 64.81; H, 7.57; N, 8.56.

Compound IIIa gave a *red picrate* from ether solution which changed to yellow needles on repeated crystallization, m.p. 146°. The recrystallized material failed to depress the m.p. of known ethyl 2-methylnicotinate picrate. Redistillation of fraction (2) gave about 50% conversion to ethyl 2-methylnicotinate.

Fraction (3) exhibited a broad absorption band at 270–290 mμ and another band at 350 mμ, suggesting that this fraction is a mixture of IIIa and ethyl 2-methyl-1,4,5,6-tetrahydronicotinate.

Oxidation of ethyl 2-methyl-1,4-dihydronicotinate. The crude reaction product of condensation of acrolein with ethyl β-aminocrotonate, 48 g., was added to a mixture of 28 g. of conc'd sulfuric acid, 30 g. of conc'd nitric acid, and 90 g. of water. The mixture was cautiously warmed on a water-bath with occasional shaking; effervescence occurred for about 10 minutes. The resulting mixture was extracted with ether to remove a neutral substance, made basic, and again extracted with ether. Drying of the ether extract over sodium sulfate, removal of ether, and distillation of the residue gave 28.7 g. (61%) of ethyl 2-methylnicotinate, b.p. 107° (13 mm.), m.p. of *picrate* 146°, λ_{max}^{EtOH} 220 mμ (ε = 7.55) and 268 mμ (ε = 3.47).

Condensation of crotonaldehyde with ethyl β-aminocrotonate. Crotonaldehyde, 23 g. (0.33 mole), was condensed with 39 g. (0.30 mole) of ethyl β-aminocrotonate in 20 ml. of anhydrous ethanol containing 1 g. of piperidine by the procedure described above for the acrolein condensation. There was obtained 41 g. (75%) of ethyl 2,4-dimethyl-1,4-dihydronicotinate (IIIb), b.p. 115–130° (2 mm.). Recrystallization of this material from petroleum ether gave plates, m.p. 66°, which liquified on exposure to air at room temperature for 1 week. The recrystallized material showed λ_{max}^{EtOH} 210 mμ (ε = 13.40) and 330–331 mμ (ε = 7.74). Infrared absorption maxima were observed at 3500, 1683, and 1605 cm.$^{-1}$, indicating the presence of $>$NH, $>$CO and $>$C=C$<$ functions respectively.

Anal. Calc'd for $C_{10}H_{15}NO_2$: C, 66.3; H, 8.35; N, 7.73. Found: C, 66.36; H, 8.16; N, 7.74.

Ethyl 2,4-dimethyl-1,4-dihydronicotinate gave a *picrate* from ether solution as brown plates, m.p. 160° (decomp.).

Oxidation of IIIb by the procedure described above gave ethyl 2,4-dimethylnicotinate in 65% yield, λ_{max}^{EtOH} 263 mμ (ε = 2.55), m.p. of *picrate*, 175°.

Anal. Calc'd for $C_{16}H_{16}N_4O_9$: C, 47.1; H, 3.94; N, 13.73. Found: C, 47.87; H, 4.18; N, 14.03.

Treatment of IIIb with boiling ethanolic potassium hydroxide gave the potassium salt which on dry distillation with soda lime gave 2,4-lutidine, b.p. 165°. The *picrate*, m.p. 182–183°, failed to depress the m.p. of an authentic specimen.

Catalytic hydrogenation of ethyl 2-methyl-1,4-dihydronicotinate. Hydrogenation of 0.18 g. (0.0011 mole) of ethyl 2-methyl-1,4-dihydronicotinate in 20 ml. of methanol over 0.08 g. of 15% palladium on calcium carbonate catalyst led to absorption of 23 ml. of hydrogen (0.001 mole) in 20 minutes. Removal of catalyst and solvent and distillation of the residue gave ethyl 2-methyl-1,4,5,6-tetrahydronicotinate (Va), b.p. 115–120° (0.08 mm.), λ_{max}^{EtOH} 290 mμ (ε = 14.50).[2]

Catalytic hydrogenation of ethyl 2,4-dimethyl-1,4-dihydronicotinate. Hydrogenation of ethyl 2,4-dimethyl-1,4-dihydronicotinate as described above gave ethyl 2,4-dimethyl-1,4,5,6-tetrahydronicotinate, λ_{max}^{EtOH} 285 mμ (ε = 17.80), m.p. of *3,5-dinitrobenzoate*, 102–103°.

Anal. Calc'd for $C_{17}H_{19}N_3O_7$: C, 54.11; H, 5.08; N, 11.14. Found: C, 54.05 H, 4.50; N, 11.45.

Disproportionation of ethyl 2-methyldihydronicotinate. A mixture of 0.15 g. of ethyl 2-methyldihydronicotinate, 0.08 g. of a 15% palladium on calcium carbonate catalyst, and 15 ml. of methanol was shaken for 1 hour in a nitrogen atmosphere. Removal of the catalyst and solvent gave a base from which there was obtained a *picrate*, m.p. 146°, identical with that of ethyl 2-methylnicotinate. The ultraviolet absorption spectrum of this base showed maxima at 220 and 290 mμ and was identical with that of an equimolar mixture of IVa and Va.

Similar treatment of IIIb gave an equimolar mixture of IVb and Vb.

Acknowledgment. The author is indebted to Dr. E. Earl Royals who kindly read the manuscript and assisted in its arrangement with respect to English idiom and current Journal usage.

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Basic Alcoholysis of the Trifluoromethyl Group in 1,1,1-Trifluoro-2,2-diarylethanes

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Received March 8, 1956

Buxton, Stacey, and Tatlow[1] have recently summarized the state of our knowledge on the alkaline hydrolysis of trifluoromethyl groups in aliphatic compounds. Of special interest for the experiments reported here is the observation of these authors that α-trifluoromethylpropionic acid is hydrolyzed to methylmalonic acid while α-hydroxy-α-trifluoromethylpropionic acid remains unchanged, and the report[2] that 3,3,3-trifluoropropene is alcoholyzed to 3-ethoxy-3,3-difluoropropene. Also the diaryltrifluoromethylcarbinols[3] show this resistance to alkaline hydrolysis which appears to be connected with the presence of the hydroxyl in the immediate vicinity of the trifluoromethyl group. It seemed, therefore, of interest to study the basic alcoholysis of 1,1,1-trifluoro-2,2-diarylethanes, CF_3CHAr_2, with Ar = C_6H_4, p-ClC_6H_4, and p-BrC_6H_4.

Basic alcoholysis under anhydrous conditions converts these compounds into the corresponding esters Ar_2CHCO_2R. When alcoholic sodium hydroxide is used, the esters remain the predominant

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(1) Buxton, Stacey, and Tatlow, *J. Chem. Soc.*, 366 (1954).

(2) Henne, Smook, and Pelley, *J. Am. Chem. Soc.*, **72**, 4756 (1950).

(3) Kaluszyner, Reuter, and Bergmann, *J. Am. Chem. Soc.*, **77**, 4164 (1955).

TABLE I[a]

HYDROLYSIS PRODUCTS OF 1,1,1-TRIFLUORO-2,2-DIARYLETHANES, $(p\text{-X-}C_6H_4)_2CHCF_3$

X	Neutral product[b]	B.p. or M.p., °C.	Yield, %	Acid product[c]	M.p., °C.	Yield, %
F	$(FC_6H_4)_2CHCOOC_2H_5$	186/15 mm.	50	$(FC_6H_4)_2CHCOOH$	138	15
Cl	$(ClC_6H_4)_2CHCOOC_2H_5$	89	65	$(ClC_6H_4)_2CHCOOH$	165	18
Br	$(BrC_6H_4)_2CHCOOC_2H_5$[d]	102.5	70	$(BrC_6H_4)_2CHCOOH$		0

[a] All compounds in this Table have been reported by Voegtli and Laueger, *Helv. Chim. Acta*, **38**, 46 (1955). [b] Recrystallized from methyl acetate. [c] Recrystallized from benzene. [d] *Anal.* Calc'd for $C_{16}H_{14}Br_2O_2$: C, 48.4; H, 3.6. Found: C, 48.3; H, 4.1.

products; in this case they are accompanied by relatively small quantities of the salts of the corresponding acids Ar_2CHCO_2Na. Perhaps the saponification of the esters is retarded by steric hindrance.

When 1,1,1-trifluoro-2,2-bis(*p*-chlorophenyl)ethane was treated with exactly three moles of sodium ethoxide, a crystalline compound of m.p. 103° could be isolated from the resulting solution. The analysis and the positive reaction towards bromine indicated that the compound was the diethylacetal of di(*p*-chlorophenyl)ketene. Acid converts it into a 1:1 mixture of di(*p*-chlorophenyl)acetic acid and ethyl di(*p*-chlorophenyl)acetate, while humid air transforms it into the ester only. In this connection it is recalled that an attempt[4] to prepare diphenylketene diethylacetal produced the enolate of ethyl diphenylacetate.

It is assumed that the basic alcoholysis of the 1,1,1-trifluoro-2,2-diarylethanes involves the preliminary formation of an orthoester type compound such as $Ar_2CHC(OR)_3$ or $Ar_2CHCF(OR)_2$. The formation of such orthoesters from tri*chloro*methyl compounds has been reported before,[5] and it has also been shown[6] that the orthoesters of negatively substituted acids are apt to lose alcohol and to give ketene acetals.

The 1,1,1-trifluoro-2,2-diarylethanes were prepared by the method described before,[3] *viz.* by reduction of the corresponding diaryltrifluoromethylcarbinols. The *p,p'*-difluoro-compound so obtained is an oil, while Kirkwood[7] has assigned this formula to a crystalline compound (m.p. 79–80°) which he obtained by fluorination of 1,1,1-trichloro-2,2-di(*p*-fluorophenyl)ethane. An analogous discrepancy has been pointed out before[3] for the case of 1,1,1-trifluoro-2,2-di-(*p*-chlorophenyl)ethane, in which the correctness of the formula has been proven for the reduction product of di(*p*-chlorophenyl)trifluoromethylcarbinol by an independent synthesis. It can, therefore, be assumed that also the liquid reduction product of di(*p*-fluorophenyl)trifluoromethylcarbinol is the true corresponding ethane. It is devoid of insecticidal or synergistic properties, when tested by topical application to houseflies. Kirkwood[7] reports for his crystalline compound that it is not an insecticide (tested with *Drosophila melanogaster*), whilst Riemschneider,[8] without describing the source of his compound or its properties, claims that 1,1,1-trifluoro-2,2-di(*p*-fluorophenyl)-ethane is ten times as active as D.D.T.

EXPERIMENTAL

For the preparation of *di(p-fluorophenyl)trifluoromethylcarbinol* the variant of the normal procedure already described[3] for similar cases, gives a yield of 70% instead of the reported 24%: from a Grignard solution prepared from 24.3 g. of magnesium turnings and 175 g. of *p*-bromofluorobenzene, the ether was distilled off on a water-bath, and a solution of 49.7 g. of ethyl trifluoroacetate in 100 ml. of anhydrous toluene was added. When the lively reaction had subsided, the mass was heated at 100° for 90 min. and worked up as usual. The *acetate* of the carbinol, prepared in the usual way,[3] was recrystallized from methanol it melted at 58–59°.

Anal. Calc'd for $C_{16}H_{11}F_5O_2$: F, 28.8. Found: F, 28.6.

1,1,1-Trifluoro-2,2-di(p-fluorophenyl)ethane. A mixture of 7.3 g. of the foregoing carbinol, 2.5 g. of red phosphorus, 1 g. of iodine, 15 ml. of glacial acetic acid, and 0.5 ml. of water was refluxed for about 250 hours. The hot solution was filtered and diluted with water, and the oily product was extracted and distilled. B.p. 107° (2 mm.) yield, 6 g. (87%). n^{23}_{D} 1.4971, d^{23}_{23} 1.330. MR, calc'd: 60.20; MR, found: 59.90.

Anal. Calc'd for $C_{14}H_9F_5$: C, 61.8; H, 3.3; F, 34.9. Found: C, 61.9; H, 3.5; F, 33.9.

A *tetranitro derivative* was prepared by heating the compound for one hour on the steam-bath with ten volumes of a mixture of equal parts of fuming nitric and concentrated sulphuric acids. Recrystallized from methanol, it had m.p. 186°. Its solution in benzene gave an intense blue color (λ_{max} 600 mμ), upon addition of 10% methanolic sodium methoxide solution.

Anal. Calc'd for $C_{14}H_5F_5N_4O_8$: N, 12.3. Found: N, 12.2.

Alkaline hydrolysis of 1,1,1-trifluoro-2,2-diphenylethane. A 2-g. quantity of this compound[3] was refluxed for 3 hours with 30 ml. of a 2 *N* alcoholic potassium hydroxide solution. Water was added and the mixture was extracted with ether. Evaporation of the ether left ethyl diphenylacetate, from ethyl acetate, m.p. 58° (yield, 1 g.; 50%), which was identified by comparison with an authentic sample. The alkaline solution was acidified with hydrochloric acid and extracted with ether. Thus 0.4 g. (20%) of diphenylacetic acid was obtained, m.p. 148° (from benzene), equally identified by comparison with an authentic sample.

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(4) McElvain, Mirviss, and Stevens, *J. Am. Chem. Soc.*, **73**, 3807 (1951).

(5) McElvain and Venerable, *J. Am. Chem. Soc.*, **72**, 1661 (1950).

(6) McElvain and Stevens, *J. Am. Chem. Soc.*, **68**, 1917 (1946).

(7) Kirkwood and Dacey, *Can. J. Research*, **24B**, 69 (1946).

(8) Riemschneider, *Z. Naturforschung*, **2b**, 245 (1947).

The results of the hydrolysis of other 1,1,1-trifluoro-2,2-diarylethanes with alcoholic potassium hydroxide solution are summarized in Table I.

The hydrolysis of 1,1,1-trifluoro-2,2-diphenylethane and of 1,1,1-trifluorodi(*p*-chlorophenyl)ethane with sodium ethoxide in anhydrous ethanol, carried out as described above, gave only ethyl diphenylacetate, m.p. 58°, and ethyl di(*p*-chlorophenyl)acetate, m.p. 89°, respectively. With sodium methoxide in anhydrous methanol, methyl diphenylacetate, m.p. 60°, and methyl di(*p*-chlorophenyl)-acetate, b.p. 173°/2 mm., m.p. 35°, were obtained.

Di(p-chlorophenyl)ketene diethyl acetal. 1,1,1-Trifluoro-2,2-di(*p*-chlorophenyl)ethane (1.6 g.) was refluxed with 25 ml. of 1.5 *N* sodium ethoxide solution in anhydrous ethanol for 2 hours. The solvent then was evaporated under reduced pressure and the dry residue was extracted with anhydrous ether and isolated by evaporation of the solvent *in vacuo.* Thus, 1 g. of di(*p*-chlorophenyl)ketene diethyl acetal was obtained, which melted after recrystallization from ligroin at 102.5–103°. The substance was fluorine-free and decolorized a bromine solution.

Anal. Calc'd for $C_{18}H_{18}Cl_2O_2$: C, 64.1; H, 5.3. Found: C, 64.4; H, 5.3.

Acid hydrolysis of the ketene acetal. A solution of 0.4 g. of the ketene acetal in 3 ml. of 50% ethanol, to which 0.5 ml. of conc'd sulphuric acid had been added, was refluxed for 2 hours, and kept for 24 hours at 0°. The crystals that collected were filtered and extracted with petroleum ether. From the extract, 0.25 g. of ethyl di(*p*-chlorophenyl)acetate was isolated, while the petroleum ether-insoluble residue (0.025 g.) consisted of di(*p*-chlorophenyl)acetic acid.

Acknowledgment. Thanks are due to Dr. Tahori of these laboratories for the biological tests.

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The Reduction of Nitrobenzene to Azoxybenzene by Sodium Borohydride[1]

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Received March 8, 1956

The versatility of sodium borohydride as a reducing agent has been demonstrated in recent publications.[2,3,4] The work of Brown and Subba Rao[3] and, Brown, Mead, and Subba Rao[4] has been valuable in extending the application of this reagent.

Brown, Mead, and Subba Rao[4] report a vigorous reaction with nitrobenzene if an equimolar amount of LiBr is added. They did not isolate any product. It has been found in this laboratory that nitrobenzene can be reduced to azoxybenzene by sodium borohydride if the reaction is conducted at 90–100° in the diglyme solvent (dimethyl ether of diethylene glycol) used in the work mentioned above.[3,4] Experiments conducted with 1-nitropropane under similar conditions have been unsuccessful.

EXPERIMENTAL

The diglyme solvent was purified by storage over NaOH pellets. Then it was refluxed over $NaBH_4$ and distilled. These operations were carried out in a nitrogen atmosphere.

Nitrobenzene (12 g.) was mixed with 20 ml. of the purified diglyme, and 2.0 g. of $NaBH_4$ were added. The reaction was heated under reflux at 90–100° for six hours. The reaction mixture then was diluted with water, acidified, and steam-distilled. The steam-distillate was discarded. The residue was extracted with *n*-hexane. Removal of the hexane yielded 5.5 g. (58%) of an orange product. Recrystallization yielded 5.2 g. (55%) of a yellow solid melting at 35°. Mixture melting point experiments conducted with Eastman Kodak azoxybenzene did not cause any depression of the melting point.

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[1] This work was conducted under a research grant provided by Metal Hydrides Inc. of Beverly, Mass.

[2] Kollonitsch, Fuchs, and Gabor, *Nature,* **173,** 125 (1954).

[3] Brown and Subba Rao, *J. Am. Chem. Soc.,* **77,** 3164 (1955).

[4] Brown, Mead, and Subba Rao, *J. Am. Chem. Soc.,* **77,** 6209 (1955).

1,4-Dibenzoyl-2,3-diphenyl-1,3-butadiene[1]

Howard W. Bost and Philip S. Bailey[2]

Received March 9, 1956

During the course of another study it was thought advisable to prepare 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene (III). Although the substance is unequivocally listed by Bielstein's *Handbuch,* a study of the original literature showed that an element of doubt still exists concerning its structure. In 1898 Wislicenus and and Lehmann[3] reported the condensation of benzil (I) with acetophenone to give *cis*-1,2-dibenzoyl-1-phenylethylene[4] (II) and/or a dibenzoyldiphenylbutadiene which, in view of its preparative method, could be either 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene (III) or 1,4-dibenzoyl-1,3-diphenyl-1,3-butadiene (IV). This is especially true since the authors also obtained it by the condensation of the dibenzoylphenylethylene (II) with acetophenone. The authors made no attempt to distinguish between the two possibilities, although they favored structure III because one of the several products of chemical reduction was a substance

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[1] Taken from a portion of the Ph.D. dissertation of H. W. B., January, 1955. This work was supported in part by a grant from The University of Texas Research Institute.

[2] To whom requests for reprints should be directed.

[3] Wislicenus and Lehmann, *Ann.,* **302,** 195 (1898).

[4] Prepared earlier in a similar manner by Japp and Miller, *J. Chem. Soc.,* **47,** 35 (1885). Configuration assigned by Japp and Wood, *J. Chem. Soc.,* **87,** 707 (1905).