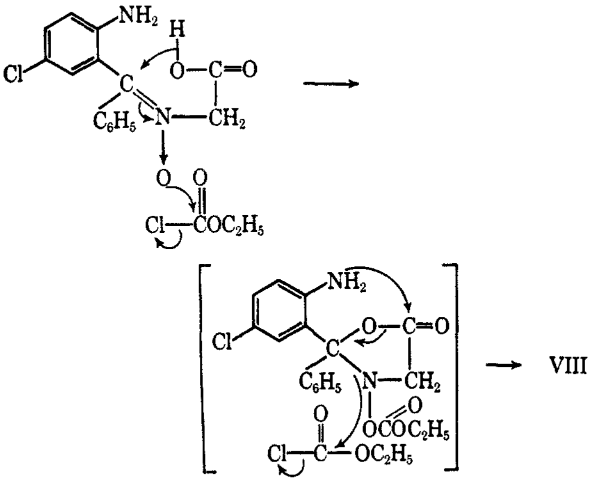
mation of a reactive cyclic intermediate is facilitated by the ethoxycarbonyloxy group on the nitrogen. Intramolecular nucleophilic attack on the lactone carbonyl group results in ring opening to form product VIII.



(1)

Experimental Section[10]

2′-Benzoyl-4′-chloro-2-ethoxy-2-ethoxycarbonylaminoacetanilide (VII). Method A.—A mixture of 4.0 g of 2-amino-5-chloro-α-phenylbenzylidenaminoacetic acid N-oxide (II) in 30 ml of ethyl chloroformate and 30 ml of chloroform was refluxed for 1.5 hr. The solvent was removed *in vacuo* and the residue was dissolved in ethanol and made basic with 10 ml of sodium hydroxide. Dilution with water and acidification with acetic acid gave 1.4 g of VII. After recrystallization from ethanol the compound had a mp of 171–172°.

The infrared spectrum (KBr) of VII showed carbonyl peaks at 5.85 (NHC(=O)OC$_2$H$_5$), 5.90 (—NHC(=O)—), and 6.10 μ (diaryl ketone) and NH peaks at 3.09 and 6.55 μ (shoulder) (amide II). The nmr spectrum (CDCl$_3$) had peaks at δ 1.27 (CH$_3$, t, J = 7 cps), 1.38 (CH$_3$, t, J = 7 cps), 3.83 (CH$_2$, q, ether), 4.20 (CH$_2$, q), and 5.5 (-CH-, d, J = 9 cps), which on warming in D$_2$O was converted to a singlet.

Anal. Calcd for $C_{20}H_{21}ClN_2O_5$: C, 59.34; H, 5.23; N, 6.92; Cl, 8.76. Found: C, 59.58; H, 5.33; N, 6.96; Cl, 8.80.

Method B.—To a suspension of 200 mg of VIII in ethanol was added an excess of alkali. The resultant alkaline solution was diluted with water and the product was recrystallized from ethanol. The compound (mp 171–172°) was the same as that prepared by method A.

Ethyl 7-Chloro-1,3-dihydro-2-oxo-5-phenyl-2H-1,4-benzodiazepine-3-carbamate (V). Method A.—To a solution of 10 ml of concentrated ammonium hydroxide and 20 ml of ethanol was added 300 mg of VIII. The mixture was heated to boiling, concentrated to one-half of the original volume and diluted with water. The hot solution was acidified with acetic acid and filtered from impurities. Upon cooling, 150 mg of product (mp 253–255°) was collected.

Anal. Calcd for $C_{18}H_{16}ClN_3O_3$: C, 60.42; H, 4.51; N, 11.74; Cl, 9.91. Found: C, 60.58; H, 4.21; N, 12.00; Cl, 9.90.

Method B.—To a chilled solution of 2.0 g of 3-amino-7-chloro-1,3-dihydro-5-phenyl-2H-1,4-benzodiazepin-2-one hydrochloride (VI) in pyridine was added, dropwise, 0.75 g of ethyl chloroformate. The solution was diluted with water to give 1.8 g of product. After recrystallization from acetonitrile the compound had a melting point of 251–253° and was the same as that prepared by method A.

Method C.—A mixture of 4.0 g of II in 30 ml of ethyl chloroformate and 30 ml of chloroform was refluxed for 1.5 hr. The solvent was removed *in vacuo* and the residue was treated with ethanol and ammonium hydroxide as in method A. The product had a melting point of 251–253° after recrystallization from acetonitrile and was the same as that prepared by methods A or B.

2′-Benzoyl-2-(N-ethoxycarbonyl-N-ethoxycarbonyloxyamino)-4′-chloroacetanilide (VIII).[11] **Method A.**—A mixture of 4.0 g of 2-amino-5-chloro-α-phenylbenzylideneaminoacetic acid N-oxide (II), 25 ml of chloroform, and 25 ml of ethyl chloroformate was refluxed for 2 hr. The solvent was removed *in vacuo* and the residue was dissolved in 30 ml of ethyl acetate and 20 ml of hexane. The solution was filtered from impurities and diluted with 130 ml of hexane and cooled. After 24 hr, 1.9 g of product, mp 100–102°, was collected. The infrared absorption spectrum (KBr) of VIII showed carbonyl peaks at 5.61 (N—OC(=O)OC$_2$H$_5$), 5.79 (N—C(=O)OC$_2$H$_5$), 5.87 (NH—C(=O)—), and 6.09 μ (diaryl ketone) and NH peaks at 3.11 and 6.62 μ (amide II). The nmr spectrum (CDCl$_3$) had peaks for the two ethoxy groups at δ 1.25 (CH$_3$, t, J = 7 cps), 1.30 (CH$_3$, t, J = 7 cps), 4.29 (CH$_2$, q), and 4.32 (CH$_2$, q) and a -CH$_2$- singlet at 4.46.

Anal. Calcd for $C_{21}H_{21}ClN_2O_7$: C, 56.20; H, 4.72; N, 6.23; Cl, 7.90. Found: C, 55.98; H, 4.75; N, 5.81; Cl, 7.90.

Method B.—A mixture of 0.5 g of 2′-benzoyl-4′-chloro-2-hydroxyaminoacetanilide (IX) and 15 ml of ethyl chloroformate was refluxed for 3 hr. The solvent was removed *in vacuo* and the residue was treated with a small amount of cold ethanol. From the ethanol was filtered off 0.15 g of solid, (mp 101–102°) which was the same as the material produced by method A.

Registry No.—Ethyl chloroformate, 541-41-3; II, 793-99-7; V, 14789-64-1; VII, 14789-65-2; VIII, 14789-66-3.

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[10] The nmr spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as the internal reference.

[11] The author is indebted to Mr. Bruce Hofmann for the infrared spectra and his proposal for the structure of compound VIII.

Further Studies on Reactions of Perfluorophenolates with Substituted Pentafluorobenzenes and Perfluorocyclohexene

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Received July 25, 1967

Previous reports have indicated that pentafluorophenoxide is a poor nucleophile.[1,2] We have recently shown that sodium pentafluorophenolate reacts with a series of substituted pentafluorobenzenes in dipolar aprotic solvents giving rise to substituted perfluorinated diphenyl ethers.[3] Our studies have now been extended to the preparation of the disodium salt of tetrafluorohydroquinone (I) and the dilithium salt of tetrafluororesorcinol (VI) and their subsequent reactions with activated fluorinated substrates.[4]

Compound I was prepared by proton exchange with sodium methoxide in methanol. This salt turned black on exposure to air which necessitated its storage under nitrogen. It reacted with pentafluorobenzonitrile in acetone and octafluorotoluene in N,N-

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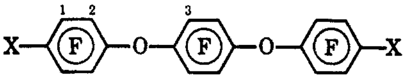
(1) W. J. Pummer and L. A. Wall, *J. Res. Nat. Bur. Std.*, **68A**, 277 (1964).

(2) E. S. Blake, G. A. Richardson, and J. A. Webster, Air Force Materials Laboratory Technical Report, RTD-TDR-63-4186.

(3) R. J. De Pasquale and C. Tamborski, *J. Org. Chem.*, **32**, 3163 (1967).

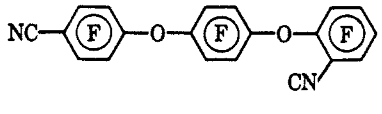
(4) The fluorine atom of hexafluorobenzene is readily replaced by numerous nucleophiles, *e.g.*, OH$^-$, SH$^-$, NH$_2^-$, R$^-$, etc. In certain monosubstituted compounds as, for example, C$_6$F$_5$X where X = CF$_3$,CO$_2$C$_2$H$_5$, substitution of a fluorine atom *para* to X is enhanced by the group X (see ref 3). Such C$_6$F$_5$X compounds are referred to in this paper as activated fluorinated substrates.

dimethylacetamide (DMAC) yielding the expected triphenyl ethers II and III.[5,6]



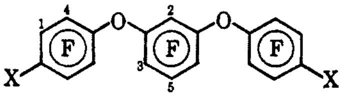
II, X = CN (isomeric mixture)
III, X = CF_3
IV, X = $CONH_2$
V, X = CO_2H

In the preparation of II, the crude reaction mixture contained a minor volatile product (indicated by vpc) whose retention time was similar to that of II. Since pentafluorobenzonitrile undergoes nucleophilic substitution at both the *ortho* and *para* positions,[7] this by-product was assumed to be an isomer, *e.g.*,



Treatment of II with sulfuric acid afforded the diamide IV which under more stringent hydrolysis conditions was converted to the diacid V.

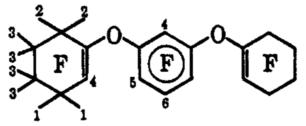
The disodium salt of tetrafluororesorcinol prepared similarly to I was extremely unstable to the air and detonated on drying. However, preparation of the dilithium salt VI from tetrafluororesorcinol and butyl lithium, proved more convenient. Unlike the disodium salt, VI was surprisingly stable to air and totally soluble in DMAC. It readily reacted with pentafluorobenzonitrile and octafluorotoluene in DMAC to give VII (isomeric mixture) and VIII, respectively.



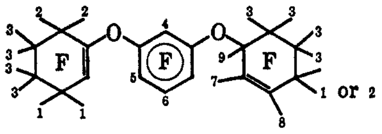
VII, X = CN (isomeric mixture)
VIII, X = CF_3
IX, X = CO_2H

VIII was unreactive toward 98% sulfuric acid at 150° but was converted to the diacid IX in 60% fuming sulfuric acid.

The reaction of VI with decafluorocyclohexene afforded a 2:1 mixture (indicated by vpc) of volatile products of similar retention time. Elemental analysis and mass spectrum of this mixture indicated their isomeric relationship. From this data, substantiated by F^{19} nuclear magnetic resonance (nmr) and infrared spectra, the structures X (major) and XI (minor) were assigned to the products.



X



XI

This mixture of isomers is analogous to the reported reaction of decafluorocyclohexene with methoxide ion which resulted in the formation of vinyl and allyl substituted methoxy ethers.[8] The yield of the product mixture X and XI was low (12%) and is by no means representative of the reactivity of perfluorinated phenoxides with decafluorocyclohexene.[7]

The analytical and spectroscopic data of compounds discussed in this work are presented in Table I.

Experimental Section

The fluoroaromatics in this work were purchased from Imperial Smelting (N. S. C.) Limited, Avonmouth, England, and were used without further purification. The DMAC was analytical grade and dried over molecular sieve (5 A) prior to use; all other solvents utilized were analytical grade.

Melting points were determined in an oil-bath apparatus. Boiling points and melting points were uncorrected. The F^{19} nmr spectra were recorded on a Varian V-4300-2-DP spectrometer at 40 Mc. Chemical shifts are reported in parts per million from external trifluoroacetic acid (TFAA). Acetone was used as the solvent unless otherwise stated. Infrared spectra were run on a Perkin-Elmer Infracord spectrophotometer as KBr pellets or as liquid films. Vapor phase chromatography analysis was done on a F & M Model 500 instrument using a helium flow of 60 cc/min, a 6 ft × 0.25 in. column, 20% Apiezon L on 60–80 mesh Chromosorb W and programmed from 100–275° (21°/min) after which it was held at this temperature. The mass spectra were recorded on an AEI MS-9 mass spectrometer.

1. **Disodium Salt of Tetrafluorohydroquinone (I).**—In an atmosphere of nitrogen, tetrafluorohydroquinone (37.0 g, 0.203 mole) dissolved in 100 ml of methanol was added dropwise to a stirred solution of methanolic sodium methoxide (9.34 g of sodium in 700 ml of methanol). The temperature of the reaction was kept at −10°. At the completion of the addition, the methanol was removed at reduced pressure (water aspirator) depositing a yellowish white salt which rapidly turned black on exposure to the atmosphere. The salt was triturated under dry nitrogen with cold tetrahydrofuran (THF) and dried in a vacuum dessicator to yield 38.1 g (83%) of an off-white solid which did not melt up to 400°.

2. **1,4-Bis(4-Cyano-2,3,5,6-tetrafluorophenoxy)tetrafluorobenzene (II).**—I (10.0 g, 0.0422 mole), pentafluorobenzonitrile (33.0 g, 0.177 mole), and 250 ml of anhydrous acetone were stirred at room temperature in a dry nitrogen atmosphere. As the heterogeneous reaction proceeded, two volatile product peaks appeared (vpc analysis) and were maximized after 12 days. The solvent was removed and 100 ml of distilled water was added to the dark residue. This resulting mixture was extracted with three 100-ml portions of methylene chloride. The combined organic extracts were dried ($MgSO_4$) and concentrated leaving 21.8 g (94%) of a tan solid, mp 128–132°. Analysis (vpc) of this crude material showed only the presence of two high boiling products (probably isomers) of similar retention times with a 7:93 (order of elution) ratio. This material was triturated with 150 ml of hot ethanol leaving 14.2 g of an off-white solid, mp 151–154°. This latter material was recrystallized twice from isopropyl alcohol affording isomer-free compound II, mp 157–158°.

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(5) For purpose of clarity and economy of space, the following symbols are employed. Only substituents other than fluorine are indicated.

= C_6H_6

= decafluorocyclohexene

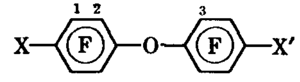
(6) The structural numbering system employed refers to the fluorine positions as they appeared (increasing field) in the F^{19} nmr.

(7) (a) Results to be published by the authors. (b) E. Felstead, H. C. Fielding, and B. J. Wakefield, *J. Chem. Soc.*, 708 (1966).

(8) A. B. Clayton, J. Raylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, *ibid.*, 7358, 1965.

TABLE I
ANALYSIS OF PRODUCTS

Compd	Calcd, %				Found, %				F¹⁹ Nmr[a]									Mol wt[b]	
	C	H	F	N	C	H	F	N	CF_3	F_1	F_2	F_3	F_4	F_5	F_6	Rel area	Ir, μ[d]	Calcd	m/e
II	45.42		43.18	5.31	45.70		43.17	5.49		59.5 (m)[c]	82.6 (m)[c]	83.6 (q, J = 1.5 cps)				1:1:1	CN = 4.45		
III	39.09		55.70		39.34		55.49		−21 (t, J = 22 cps)	62.9 (m)	76.9 (m)	77.6 (q, J = 1.5 cps)				3:4:4:4	ArO = 8.60		
IV	42.57	0.72	40.40	4.97	42.48	0.58	40.56	5.08									NH = 2.85, 3.00, 3.10 C═O = 5.90	563.9	563.9
V	42.43	0.36	40.26		42.80	0.65	39.81										OH = 3.30 (b) C═O = 5.85	477.9	m/e − $2CO_2$ = 477.9
VII	45.45			5.30	45.65			5.72		57.1 (m)[c]	73.6 (m)	76.4 (d fs, J = 22 cps)	79.6 (m)[c]	87.0 (d of t, J_{25} = 6 cps)		4:1:2:4:1	CN = 4.45		
VIII	39.09		55.70		39.09		55.49		−21.2 (t, J = 24 cps)	65.4 (m)	73.4 (m)	77.0 (d fs, J_{35} = 21 cps)	80.0 (m)	87.0 (d of t, J_{25} = 6 cps)		3:4:1:2:4:1	ArO = 8.60		
IX	42.40	0.35	40.28		42.71	0.37	40.18										CH = 3.30 (b) C═O = 5.90		
X and XI	32.45		62.75		32.82		62.69			40.1 or 42.0 (b s)[d]		57.7 (s)	72.9 (b s)	74.7 (d, J = 21 cps)	83.8 (t fs)	4:4:8:3:2:1	ROC═C = 5.80 FC═CF = 5.75 (film)	665.9	665.9

[a] Abbreviations used are s (singlet), d (doublet), t (triplet), m (multiplet), q (quintet), fs (fine structure), and b (broad). [b] Molecular weight was determined by mass spectroscopy. [c] One of the referees questioned the assignment of the F_1 and F_2 atoms in II and F_1 and F_4 atoms in VII. To clarify this point, the following is offered: in the nmr spectrum of a 4 or 4,4′-substituted fluorinated diphenyl ether where the substituent X is incapable of magnetic coupling, *e.g.*,  where X = CN, CO_2Et, Br, Cl, and X′ = F, OC_6F_5, F_1 appears as one-half of a classic AA′XX′ pattern while F_2, the remaining half, is considerably broadened by further coupling with F_3. [d] In CCl_4 solvent. Atoms 7, 8, and 9 could not be definitely assigned.

3. **1,4-Bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenoxy)tetrafluorobenzene (III).**—Compound I (10.0 g, 0.0442 mole), octafluorotoluene (31.4 g, 0.133 mole), and 200 ml of DMAC were stirred and heated to 100° for *ca.* 5 hr in an atmosphere of dry nitrogen. The reaction mixture was allowed to cool and then added to 750 ml of distilled water. The precipitate that settled was filtered, washed with water, and dried, yielding 21.0 g (78%) of crude product, mp 100–104° (96% of one component by vpc). This material was dissolved in 80:20 petroleum ether (30–60°)-benzene and eluted with the same solvent mixture from an alumina column to afford an analytical sample, mp 111–112°.

4. **1,4-Bis(4-amido-2,3,5,6-tetrafluorophenoxy)tetrafluorobenzene (IV).**—Compound II (4.0 g, 7.6 mmoles) was added to 30 ml of 90% H_2SO_4. This mixture was heated to 60° and stirred for 3 hr. The resultant dark solution was added to 100 ml of distilled water and filtered. The filter cake was washed with water and dried yielding 4.1 g (94%) of an off-white solid, mp 281–286° dec. This material was precipitated twice from hot DMAC with water affording an analytical sample, mp 343–344° dec.

5. **1,4-Bis(4-Carboxy-2,3,5,6-tetrafluorophenoxy)tetrafluorobenzene (V).**—Compound IV (1.3 g, 2.3 mmoles) was added to 30 ml of 75% H_2SO_4. This mixture was stirred and heated to 145° for 3 hr, cooled, added to 100 ml of distilled water, and filtered. The precipitate was washed with water and dried yielding 1.2 g (92%) of a tan solid, mp 271–273° dec. This material was dissolved in and eluted from an alumina column with acetone affording an analytical sample, mp 272–273° dec.

6. **Dilithium Salt of Tetrafluororesorcinol (VI).**—An attempt to prepare and isolate the disodium salt of tetrafluororesorcinol resulted in the formation of a golden brown solid which was extremely unstable to air and exploded on drying (vacuum oven) leaving a black carbonous residue. Further work with this material was abandoned.

In an atmosphere of dry nitrogen, tetrafluororesorcinol (8.75 g, 0.0480 mole) was dissolved in 125 ml of anhydrous ether. To this stirred solution, cooled to −10°, was added 59 ml of *n*-butyllithium (0.0760 mole) dropwise so that the temperature did not exceed 0°. During the addition a white insoluble material was formed. After adding the *n*-butyllithium, vacuum was applied directly to the flask (water aspirator), removing the ether and leaving the dilithium salt as a white powdery solid. Dry nitrogen was then bled into the evacuated flask. A small amount of this material was withdrawn on a spatula and was surprisingly stable to air, only darkening after several hours of exposure (mp over 400°). The salt was stored in a vacuum dessicator and opened to the atmosphere only prior to use.

7. **1,3-Bis(4-Cyano-2,3,5,6-tetrafluorophenoxy)tetrafluorobenzene (VII).**—DMAC (125 ml) was added to a flask containing VI prepared from 8.75 g of tetrafluororesorcinol as described above. The salt completely dissolved after several minutes of stirring at room temperature. To this solution, pentafluorobenzonitrile (23.1 g 0.120 mole) was rapidly introduced (slightly exothermic). After 3 days of stirring at room temperature periodic samples withdrawn for vpc analysis indicated maximization of the two isomeric products. The reaction mixture was added to 500 ml of distilled water and allowed to digest for 24 hr. The aqueous DMAC solution was decanted from the semisolid that had settled. This material was taken up in 300 ml of methylene chloride, filtered (removing insoluble residue, probably LiF), and concentrated yielding 23.8 g of an oily mixture. This mixture was heated at reduced pressure to remove the last traces of solvent and pentafluorobenzonitrile, bp *ca.* 45° (10 mm). The residue was dissolved in a 1:1 solution of methylene chloride–petroleum ether (30–60°) and eluted from an alumina column with the same solvent mixture affording 18.8 g (75%) of a colorless oil that solidified after standing for 2 weeks at room temperature, mp 71–75°. This solid consisted of a 1:9 ratio of two isomeric products (vpc) and gave a pure sample of the major component (98% vpc) after three recrystallizations from isopropyl alcohol, mp 81–82°.

8. **1,3-Bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenoxy)tetrafluorobenzene (VIII).**—From 14.8 g (0.0815 mole) of tetrafluororesorcinol and 100 ml of *n*-butyllithium (0.163 mole), the dilithium salt VI was prepared as previously described. Octafluorotoluene (48.0 g, 0.202 mole) was rapidly added to this salt dissolved in 250 ml of DMAC. The solution was stirred and heated to 90° for 3 hr. A vpc analysis indicated one major product peak. The tan solution was allowed to cool, added to

750 ml of distilled water, and digested overnight. The tan precipitate was filtered, washed with water, dried (vacuum oven), and weighed 48.1 g (96% pure by vpc), mp 64–66°. A 15-g portion of this material was dissolved and eluted from an alumina column with petroleum ether (30–60°). Two recrystallizations from methanol yielded 13.1 g of white needles, mp 67–68°.

9. **1,3-Bis(4-Carboxy-2,3,5,6-tetrafluorophenoxy)tetrafluorobenzene (IX).**—VIII (4.0 g, 6.6 mmoles) was added to 20 ml of 60% fuming H_2SO_4. The reaction mixture was heated and stirred at SO_3 reflux for 19 hr. The dark mixture was then added to crushed ice and the white solid that settled was filtered, washed with water and dried yielding 3.4 g (92%) of crude diacid, mp 253–256°. Recrystallization from aqueous methanol afforded an analytical sample, mp 257–259°.

10. **Reaction of Dilithium Salt of Tetrafluororesorcinol (VI) with Decafluorocyclohexene.**—In an atmosphere of dry nitrogen, decafluorocyclohexene (10.0 g, 0.0380 mole), VI (from 3.44 g (0.0185 mole) of tetrafluororesorcinol and 23 ml of *n*-butyllithium (0.0370 mole)), and 70 ml of DMAC were stirred and heated at 65° for 2 days. After the reaction cooled, it was added to 300 ml of distilled water. The aqueous DMAC layer (top) was decanted and the bottom layer was taken up in 100 ml of benzene. This benzene solution was filtered (removing the inorganic salt), extracted with water, and concentrated, leaving 3.5 g of a dark liquid. This material was dissolved in petroleum ether (30–60°) and eluted from an alumina column with the same solvent, affording 2.9 g of a colorless liquid. Distillation of this liquid gave 1.4 g (12%) of 2:1 isomeric mixture (vpc) of X and XI, bp 80–82° (0.1 mm).

Registry No.—Perfluorocyclohexene, 355-75-9; II, 15053-71-1; III, 15077-30-2; IV, 14796-02-2; V, 14796-03-3; VII, 14796-04-4; VIII, 15038-90-1; IX, 14901-49-6; X, 14796-05-5; XI, 14901-50-9.

Aza Steroids. IV. Reaction of Arylamines with Ethyl 2-Ketocyclopentanecarboxylate[1,2]

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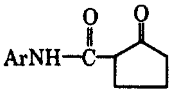
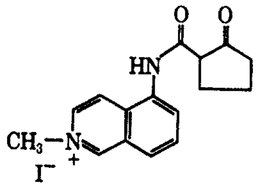
Received August 14, 1967

A possible approach to diaza steroids has been investigated by Bew and Clemo.[4] They prepared amides of the type I by heating ethyl 2-ketocyclopentanecarboxylate with various aminoquinolines and aminoisoquinolines. Attempts to cyclize the amides Ia and Ib failed. In the case of Ic, reduction of the heterocyclic ring before ring closure was attempted, but all attempts led to recovery of starting material or cleavage of the amide linkage. Bew and Clemo[4] also attempted to form the amide III by heating ethyl 2-ketocyclopentanecarboxylate with 5-amino-1,2,3,4-tetrahydro-2-methylisoquinoline but failed.

Since this still appeared to be an attractive route to a number of diaza steroidal systems, the general path of Bew and Clemo was reinvestigated, using the amide obtained from ethyl 2-ketocyclopentanecarboxylate and 5-aminoisoquinoline. The methiodide II was obtained in 90% yield by refluxing the amide Ib in methanol containing methyl iodide. A sample of the methiodide II, which contained carbonyl bands at 1750 and 1665 cm^{-1}, was reduced catalytically in an aqueous ethanol solvent to give a 60% yield of III (which still contained carbonyl bands at 1750 and 1650 cm^{-1}) as a light brown oil. Cyclization of III was attempted without further purification, giving 12-keto-1,2,3,4,11,12,15,16-octahydro-3-methyl-3,11-diazacyclopenta[*a*]phenanthrene (IV) as a light yellow solid. The infrared spectrum contained a single carbonyl band at 1650 cm^{-1} typical of a quinolin-2-one. Elemental analysis of IV indicated that a hydrate with formula $C_{16}H_{18}N_2O \cdot 0.5H_2O$ had been isolated. The same sample was dried *in vacuo* at 100° and analysis of the dried sample confirmed the formula $C_{16}H_{18}N_2O$.

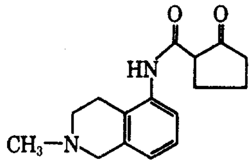


I

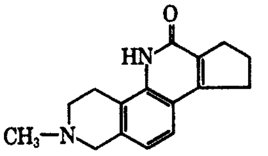


II

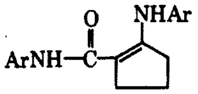
a, Ar = 8-quinolyl
b, Ar = 5-isoquinolyl
c, Ar = 1-isoquinolyl
d, Ar = 5-quinolyl



III



IV



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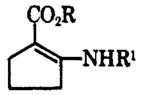

VI

Reaction of 5-aminoquinoline with ethyl 2-ketocyclopentanecarboxylate gave Id. Repetition of Bew and Clemo's preparation[4] of Ia gave a small amount of product from reaction at the keto group in addition to reaction at the ester. Nmr evidence indicates the structure V for this product.

Several model experiments were carried out with ethyl 2-ketocyclopentanecarboxylate and simple aromatic amines. In this manner ten aniline derivatives were converted to the bis adduct. Four of these were new compounds and are included in Table I while the

TABLE I

DERIVATIVES OF ETHYL 2-CYCLOPENTANEONECARBOXYLATE

Ar	Type	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
o-FC_6H_4–	V	122–124[a]	68.78	5.13	8.91	69.18	5.17	8.82
p-FC_6H_4–	V	135–137[a]	68.78	5.13	8.91	68.61	5.15	8.96
p-FC_6H_4–	I	101–102[a]	65.12	5.47	6.33	64.90	5.35	6.17
2,3-$(CH_3)_2C_6H_3$–	V	164–166[b]	79.00	7.84	8.38	78.89	7.76	8.36
2-CH_3-4-FC_6H_3–	V	168–170[a]	70.16	5.89	8.18	70.06	5.91	8.08
3-CH_3-4-FC_6H_3–	I	132–133[a]	66.37	6.00	5.96	66.40	6.35	5.92

[a] Recrystallized from ethanol. [b] Recrystallized from methanol.

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(1) Part III: W. R. Schleigh and F. D. Popp, *J. Chem. Soc., Sect. C*, 760 (1966).

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(3) U. S. Public Health Service Predoctoral Fellow (F1-GM-20,097).

(4) D. G. Bew and G. R. Clemo, *J. Chem. Soc.*, 1775 (1955).