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Reactions of α-Alkyl- and α-Aryl-substituted N-Benzylideneamines with Trihaloacetylating Agents

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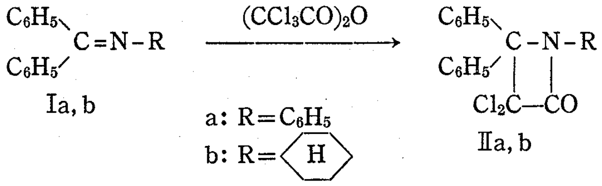
Reactions of imines with trichloroacetylating agents rely upon their structural differences. 3,3-Dichloro-2-azetidinone formation was effected by the reaction of α-aryl-substituted N-benzylideneamines similarly to that of N-benzylideneamines. The imines, of which imino carbons are bound to alkyls possessing at least one hydrogen at C_1 of the alkyls, however, reacted with trichloroacetic anhydride and trichloroacetyl chloride to give β-trichloroacetylated enamines. In the reaction with trifluoroacetic anhydride in place of trichloroacetic anhydride N-trifluoroacetylenamines were obtained instead, but the products easily undergo N→C migration on heating in xylene to give β-trifluoroacetylated enamines. Acid-catalyzed quinoline ring-closures of the β-trihaloacetylated enamines obtained above are also described.

Keywords——imines; acylation; trihaloacetylation; acylenamines (enamides); aminoenones (trihaloacetylated enamines); azetidinones; acyl migration; quinoline ring-closure

Our previous papers[2] reported that the formation of 3,3-dichloro-2-azetidinones was effected by the reaction of N-benzylideneamines (ArCH=NR) with trichloroacetic anhydride and with trichloroacetyl chloride-triphenylphosphine. When imino carbon-hydrogen of N-benzylideneamines is replaced by phenyl, a similar reaction proceeded with trichloroacetic anhydride to give 3,3-dichloro-4,4-diphenyl-2-azetidinones (IIa,b), as realized by the reactions with N-(diphenylmethylene)amines (Ia,b).



On the other hand, it has been known with several examples[3,4a,b] that the imines, of which imino carbons are bound to alkyls possessing at least one hydrogen at C_1, react with acid anhydrides or acyl halides to give N-acylenamines. The reaction of N-(α-alkylbenzylidene)anilines (IIIa—c) with acetylating agents, which has not been described, was examined by heating with acetic anhydride and by refluxing with acetyl chloride-pyridine in benzene to give the corresponding N-(1-phenylalkenyl)acetanilides (IVa—c).

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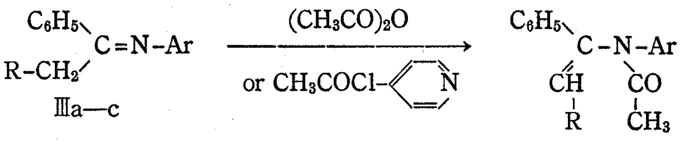
[1] Location: 2-2-1, *Oshika, Shizuoka.*

[2] M. Sekiya and T. Morimoto, *Chem. Pharm. Bull.* (Tokyo), **23**, 2353 (1975); T. Morimoto and M. Sekiya, *ibid.*, **24**, 1935 (1976).

[3] H. Breederveld, *Rec. Trav. Chim.*, **79**, 401 (1960); *idem, ibid.*, **79**, 1197 (1960).

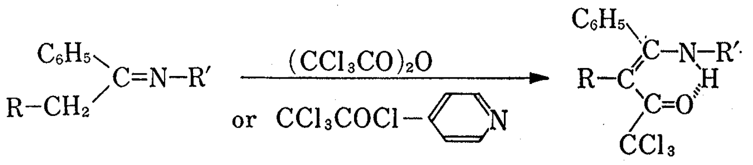
[4] *a*) I. Ninomiya, T. Naito, and T. Mori, *J. Chem. Soc.*, Perkin I, **1973**, 505; N.C. Yang and G.R. Lenz, *Tetrahedron Letters*, **1967**, 4897; *b*) I. Ninomiya, T. Naito, T. Kiguchi, and T. Mori, *J. Chem. Soc.*, Perkin I, **1973**, 1696; I. Ninomiya, T. Naito, and T. Kiguchi, *ibid.*, **1973**, 2257; *idem, ibid.*, **1973**, 2261.



IIIa—c IVa—c

a: $R=H$, $Ar=C_6H_5$
b: $R=H$, $Ar=C_6H_4OCH_3$-*p*
c: $R=CH_3$, $Ar=C_6H_5$

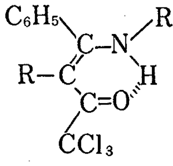
Contrary to this fact, N-(α-alkylbenzylidene)anilines (IIIa—c) underwent a reaction with trichloroacetylating agents giving β-trichloroacetylated enamines (Va—c). The reactions with trichloroacetic anhydride and with trichloroacetyl chloride-pyridine proceeded at room temperature in benzene to give 4-anilino-4-phenyl-1,1,1-trichloro-3-buten-2-ones (Va—c).



IIIa—e Va—e

a: $R=H$, $R'=C_6H_5$
b: $R=H$, $R'=C_6H_4OCH_3$-*p*
c: $R=CH_3$, $R'=C_6H_5$
d: $R=H$, $R'=$ ⟨H⟩
e: $R=H$, $R'=CH_2C_6H_5$

TABLE I. 4-Amino-4-phenyl-1,1,1-trichloro-3-buten-2-ones



Compd. No.	R	R′	Yield (%)	Appearance (recryst. solv.)	mp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N
Va	H	C_6H_5	87[a] 80[b]	yellow needles (EtOH)	123—124	$C_{16}H_{12}ONCl_3$	56.41 (56.54)	3.55 (3.62)	4.11 (4.27)
Vb	H	$C_6H_4OCH_3$-*p*	94[a] 80[b]	yellow needles (isopropyl alcohol)	143—144	$C_{17}H_{14}O_2NCl_3$	55.08 (55.15)	3.81 (3.93)	3.78 (3.88)
Vc	CH_3	C_6H_5	92[a]	yellow prisms (isopropyl ether)	138—139	$C_{17}H_{14}ONCl_3$	57.57 (57.21)	3.98 (4.11)	3.95 (3.88)
Vd	H	⟨H⟩	96[a]	needles (*n*-hexane)	97— 98	$C_{16}H_{18}ONCl_3$	55.43 (55.69)	5.23 (5.23)	4.04 (4.27)
Ve	H	$CH_2C_6H_5$	75[a]	needles (EtOH)	74— 75	$C_{17}H_{14}ONCl_3$	57.57 (57.47)	3.98 (4.08)	3.95 (3.94)

a) A run with trichloroacetyl chloride–pyridine in benzene
b) A run with trichloroacetic anhydride in benzene

The products were assigned as the hydrogen-bonded chelating structures by noting correspondences of their infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectra with those of the analogs reported previously.[5] Several extensive experiments with

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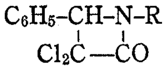
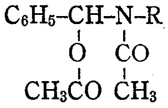
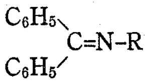
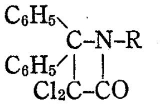
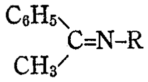
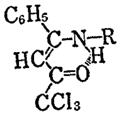
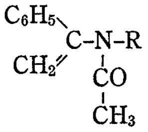
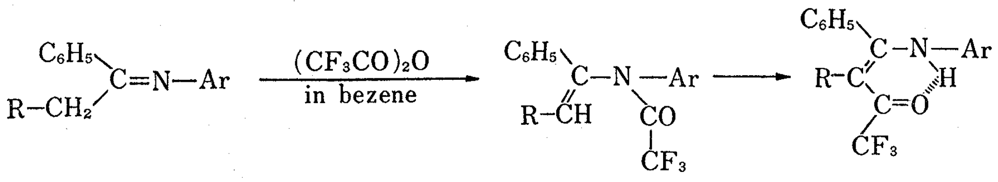
[5] J. Dabrowski and V. Dabrowski, *Chem. Ber.*, **101**, 2365 (1968); D.L. Ostercamp, *J. Org. Chem.*, **35**, 1632 (1970); G.O. Dudek and R.H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961); *idem*, *ibid.*, **84**, 2691 (1962); G.O. Dudek and G.O. Volpp, *ibid.*, **85**, 2697 (1963).

a series of N-(α-alkylbenzylidene)amines are summarized in Table I. The reaction indicates a direct C-acylation which is unique with trichloroacetylating agents. It is then emphasized that chemical behavior of trichloroacetic anhydride toward every type of imines is distinguished from that of acetic anhydride, as summarized in Table II.

TABLE II

Starting material	Product	
	$(CCl_3CO)_2O$	$(CH_3CO)_2O$
$C_6H_5{-}CH{=}N{-}R$		
 $(C_6H_5)_2C{=}N{-}R$		—
 $C_6H_5(CH_3)C{=}N{-}R$		

N-(α-Methylbenzylidene)aniline (IIIa) was then allowed to react with trifluoloacetic anhydride instead of trichloroacetic anhydride. Being distinguished from that of trichloroacetic anhydride this reaction resulted in the N-trifluoroacetylation giving N-(1-phenylvinyl) trifluoroacetanilide (VIa). In addition, it was found that this N-trifluoroacetylenamine underwent a N→C migration of trifluoroacetyl to give 4-anilino-4-phenyl-1,1,1-trifluoro-3-buten-2-one (VIIa) on refluxing in xylene. Similarly, N-(α-methylbenzylidene)-*p*-anisidine (IIIb) and N-(α-ethylbenzylidene)aniline (IIIc) reacted with trifluoroacetic anhydride and the resulting crude N-trifluoroacetylenamines (VIb,c) were heated in xylene to give the corresponding C-trifluoroacetylated products (VIIb,c). Such thermal N→C migration of trifluoroacetyl has not been encountered in literature, although similar acyl migration has been known to occur by irradiation.[4a,6]



IIIa — c VIa — c VIIa — c

a: $R{=}H$, $Ar{=}C_6H_5$
b: $R{=}H$, $Ar{=}C_6H_4OCH_3$-*p*
c: $R{=}CH_3$, $Ar{=}C_6H_5$

When N-(α-methylbenzylidene)cyclohexylamine (IIId) reacted with trifluoroacetic anhydride in benzene at room temperature, were isolated not only C-mono- but also C-ditrifluoroacetylated products, 4-cyclohexylamino-4-phenyl-1,1,1-trifluoro-3-buten-2-one (VIId) and 4-cyclohexylamino-4-phenyl-1,1,1-trifluoro-3-trifluoroacetyl-3-buten-2-one (VIII) in 33% and 20% yield, respectively. Addition of pyridine in this reaction decreased the yield of VIII giving VIId in 79% yield.

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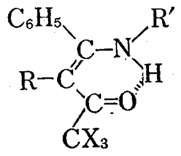
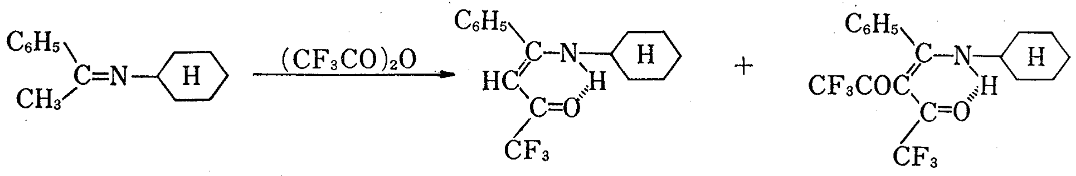
[6] R.W. Hoffman and K.R. Eicken, *Tetrahedron Letters*, **1968**, 1759; *idem*, *Chem. Ber.*, **102**, 2987 (1969).

Table III. Spectral Data of 4-Amino-4-phenyl-1,1,1-trihalo-3-buten-2-ones



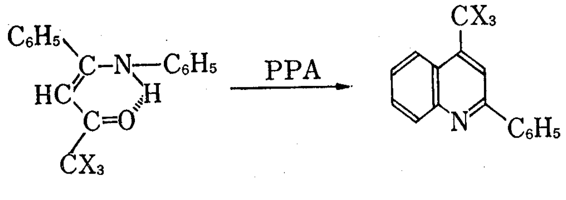
Compd. No.	R	R′	X	IR ν_{max}^{KBr} cm^{-1}	UV λ_{max}^{EtOH} mμ (ε)	NMR δ (in $CDCl_3$) J=Hz $=\dot{C}H$ 1H, s	 $-\dot{N}-H\cdots O=$ 1H, br	 Aromatic H	 Other H
Va	H	C_6H_5	Cl	1608 1568	237(13600) 363(15200)	5.96	11.88	6.6—7.35, 10H, m	
Vb	H	$C_6H_4OCH_3$-*p*	Cl	1608 1557	234(12000) 301(inf 7800) 368(15500)	5.90	11.95	6.58, 4H, s, C_6H_4 7.15, 5H, s, C_6H_5	3.63, 3H, s, CH_3O
Vc	CH_3	C_6H_5	Cl	1608 1564	235(inf 10000) 373(10200)	—	13.00	6.45—6.70, 2H, m 6.70—7.35, 8H, m	1.93, 3H, s, CH_3
Vd	H		Cl	1597 1572	245(5700) 339(15900)	5.58	10.7	7.1—7.45, 5H, m	0.90—2.0, 10H, m, 5×CH_2 3.30, 1H, m, >CH
Ve	H	$CH_2C_6H_5$	Cl	1607 1596 1569	245(11300) 340(14200)	5.71	10.9	7.1—7.4, 10H, m	4.37, 2H, d, J=6.1, CH_2
VIIa	H	C_6H_5	F	1610 1566	227(8910) 280(6430) 354(17800)	5.65	12.4	6.6—7.4, 10H, m	
VIIb	H	$C_6H_4OCH_3$-*p*	F	1610 1567	232(13700) 302(10300) 364(16600)	5.56	12.40	6.57, 4H, s, C_6H_4 7.15, 5H, s, C_6H_5	3.62, 3H, s, CH_3O
VIIc	CH_3	C_6H_5	F	1600 1554	234.5(9600) 367(16700)	—	13.43	6.4—6.9, 2H, m 6.9—7.5, 8H, m	1.75, 3H, q, J=2.0, CH_3
VIId	H		F	1606 1575	249(5000) 333(18700)	5.30	11.2	7.2—7.5, 5H, m	0.9—2.1, 10H, m, 5×CH_2 3.34, 1H, m, >CH
VIII	F_3CCO		F	1707 1610 1590 1570	252(inf 6920) 258(7380) 264(6920) 316(12600)	—	12.05	7.1—7.6, 5H, m	0.9—2.0, 10H, m, 5×CH_2 3.3, 1H, m, >CH

The following abbreviations are used: inf=inflection, s=singlet, d=doublet, q=quartet, m=multiplet, br=broard.



IIId VIId VIII

It has been known that anils of β-diketones are capable of formation of quinolines by the influence of acid catalyst. The foregoing C-trihaloacetylation products obtained from IIIa are referred to as analogs of anils of β-diketones. In the hope of performance of quinoline ring-closure, Va and VIIa, selected as model substrates, were allowed to react with excess of polyphosphoric acid on heating at 115—120°. Thus, the corresponding 2-phenyl-4-trihalomethylquinolines (IXa,b) were obtained from Va and VIIa in good yields.



Va, VIIa IXa, b

Va, IXa: X=Cl
VIIa, IXb: X=F

Experimental

All melting points are uncorrected. IR spectra were obtained with a Hitachi EPI-G2 spectrophotometer. UV spectra were recorded on a Hitachi EPS-3T spectrophotometer. NMR spectra were taken with a Hitachi R-24 spectrometer using tetramethylsilane as an internal standard.

3,3-Dichloro-1,4,4-triphenyl-2-azetidinone (IIa)——A solution of 7.7 g (0.03 mole) of N-(diphenylmethylene)aniline (Ia) and 12.0 g (0.039 mole) of trichloroacetic anhydride in chlorobenzene (30 ml) was heated with stirring in a stream of dry air in order to check emitting CO_2 by aq. $Ba(OH)_2$ till subsidence of CO_2 emission. After heated at 125—135° for 12 hr, the reaction mixture was concentrated under reduced pressure and the residue was triturated with ether–petr. ether. The resulting crystals were collected by filtration and washed with the same solvent. Recrystallization from EtOH gave 8.0 g (72%) of IIa as colorless prisms, mp 147—148°. *Anal.* Calcd. for $C_{21}H_{15}ONCl_2$: C, 68.49; H, 4.11; N, 3.80. Found: C, 68.42; H, 4.00; N, 3.70. IR ν_{max}^{KBr} cm^{-1}: 1787 (C=O). NMR δ (in $CDCl_3$): 7.29 (10H, s, $2\times C_6H_5$), 6.9—7.2 (5H, m, N–C_6H_5).

1-Cyclohexyl-3,3-dichloro-4,4-diphenyl-2-azetidinone (IIb)——Using anisole as a solvent instead of chlorobenzene, the reaction of N-(diphenylmethylene)cyclohexylamine (Ib) with trichloroacetic anhydride was carried out by the same procedure as described above. Reaction temperature: 153—155°, reaction period: 3 hr. IIb was obtained in 66% yield as colorless prisms (AcOEt), mp 189—190°. *Anal.* Calcd. for $C_{21}H_{21}ONCl_2$: C, 67.39; H, 5.66; N, 3.74. Found: C, 67.34; H, 5.63; N, 3.61. IR ν_{max}^{KBr} cm^{-1}: 1782 (C=O). NMR δ (in $CDCl_3$): 0.9—2.2 (10H, m, $5\times CH_2$), 3.17 (1H, m, $>$CH), 7.38 (10H, s, $2\times C_6H_5$).

N-(1-Phenylalkenyl)acetanilides (IVa—c)——a) Reaction of N-(α-Methylbenzylidene)aniline (IIIa) with Acetic Anhydride: A solution of 11.5 g of IIIa in 100 ml of acetic anhydride was heated under refluxing for 10 hr. After excess of acetic anhydride was evaporated under reduced pressure, the resulting residue was distilled *in vacuo* to give a solid distillate of N-(1-phenylvinyl)acetanilide (IVa) weighing 11.0 g (67%), bp 140—145° (0.07 mmHg), mp 72—73°. Recrystallization from isopropyl ether gave prisms, mp 73—74°. *Anal.* Calcd. for $C_{16}H_{15}ON$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.19; H, 6.43; N, 6.01. IR ν_{max}^{KBr} cm^{-1}: 1668 (C=O), 1626 (C=C). UV λ_{max}^{EtOH} mμ (ε): 246 (16800). NMR δ (in $CDCl_3$): 2.00 (3H, s, CH_3), 5.09 (1H, s) and 5.55 (1H, s, $=CH_2$), 6.6—7.5 (10H, m, $2\times C_6H_5$).

b) Reactions of N-(α-Alkylbenzylidene)anilines (IIIa—c) with Acetyl Chloride: These reactions were processed by the following general procedures. To a stirred solution of 0.03 mole each of IIIa, b, c and 3.1 g (0.039 mole) of pyridine in benzene (30 ml) was added dropwise 2.8 g (0.036 mole) of acetyl chloride in benzene (10 ml) with cooling. After the mixture was refluxed for 3 hr, the precipitated pyridine hydrochloride was filtered off and washed with benzene. The filtrate combined with the washings was concentrated under reduced pressure and the residue was crystallized by trituration with isopropyl ether. Recrystallization from isopropyl ether gave an analytical sample. Thus were obtained the following products.

N-(1-Phenylvinyl)acetanilide (IVa): Yield, 90%. Prisms, mp 72.5—74°. This product was identical with that obtained in a).

N-(1-Phenylvinyl)-*p*-acetanisidine (IVb): Yield, 77%. Needles, mp 55.5—56.5°. *Anal.* Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.43; H, 6.38; N, 5.25. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1669 (C=O), 1625 (C=C). UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε): 245 (20700). NMR δ (in $CDCl_3$): 2.10 (3H, s, CH_3CO), 3.66 (3H, s, OCH_3), 5.20 (1H, s) and 5.63 (1H, s, $=CH_2$), 6.65 (2H, d, $J=8.5$ Hz) and 7.0—7.5 (7H, m, aromatic H).

N-(1-Phenyl-1-propenyl)acetanilide (IVc): Yield, 82%. Prisms, mp 97—98°. *Anal.* Calcd. for $C_{17}H_{17}ON$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.40; H, 6.81; N, 5.45. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1668 (C=O). UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε): 239 (20600). NMR δ (in $CDCl_3$): 1.89 (3H, d, $J=6.5$ Hz, CH_3), 2.19 (3H, s, CH_3CO), 5.39 (1H, q, $J=6.5$ Hz, $=\overset{|}{C}H$), 7.05—7.45 (10H, m, $2\times C_6H_5$).

4-Amino-4-phenyl-1,1,1-trichloro-3-buten-2-ones (Va—e)——a) Reactions of N-(α-alkylbenzylidene)-amines (IIIa—e) with Trichloroacetyl Chloride: These reactions were processed by the following general procedures. To a stirred solution of 0.02 mole each of IIIa—e and 1.7 g (0.022 mole) of pyridine in benzene (20 ml) was added dropwise a solution of 3.7 g (0.02 mole) of trichloroacetyl chloride in benzene (10 ml) during 1 hr. The reaction was exothermic and the mixture was stirred overnight at room temperature. The resulting precipitate of pyridine hydrochloride was filtered off and washed with benzene. The filtrate combined with the washings was treated with aq. $NaHCO_3$ and dried over anhydrous $MgSO_4$. After filtration, concentration of the benzene solution under reduced pressure left crystals, which were recrystallized from an appropriate solvent. Thus were obtained Va—e, of which yields, physical and analytical data are recorded in Table I, and spectral data in Table III.

b) Reactions of N-(α-methylbenzylidene)anilines (IIIa, b) with Trichloroacetic Anhydride: To a stirred solution of 0.03 mole each of IIIa, b in benzene (30 ml) was added dropwise a solution of 0.03 mole of trichloroacetic anhydride in benzene (10 ml). The reaction mixture was stirred overnight at room temperature. After the reaction mixture was washed with aq. $NaHCO_3$ and dried over anhydrous $MgSO_4$, evaporation gave the corresponding product. The products obtained, 4-anilino-4-phenyl-1,1,1-trichloro-3-buten-2-one (Va) and 4-*p*-anisidino-4-phenyl-1,1,1-trichloro-3-buten-2-one (Vb), were identical with those obtained in a). Their yields are recorded in Table I.

N-(1-Phenylalkenyl)trifluoroacetanilides (VIa—c)——To a stirred solution of 0.03 mole each of IIIa, b, c in benzene (40 ml) was added dropwise 6.3 g (0.03 mole) of trifluoroacetic anhydride during 1 hr. The reaction mixture was stirred overnight at room temperature. After the reaction mixture was washed with aq. $NaHCO_3$ and dried over anhydrous $MgSO_4$, concentration under reduced pressure gave the product (VIa—c) as a viscous oil. In the case of VIa, the residue was crystallized on standing in a refrigerator. Recrystallization of the crystals (7.8 g, 89%) from EtOH gave N-(1-phenylvinyl)trifluoroacetanilide (VIa) as colorless prisms, mp 69—70°. *Anal.* Calcd. for $C_{16}H_{12}ONF_3$: C, 65.98; H, 4.15; N, 4.81. Found: C, 65.98; H, 4.10; N, 4.78. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1704 (C=O), 1634 (C=C). UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε): 247 (12900). NMR δ (in $CDCl_3$): 5.35 (1H, s) and 5.76 (1H, s, $=CH_2$), 7.0—7.5 (10H, m, $2\times C_6H_5$). Although difficulties were encountered in crystallization, the viscous oily materials obtained from IIIa and IIIb were identified as almost pure VIb and VIc by the following spectral assignment. VIb: IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1704 (C=O). NMR δ (in $CDCl_3$): 3.61 (3H, s, OCH_3), 5.21 (1H, s) and 5.60 (1H, s, $=CH_2$), 6.59 (2H, d, $J=8$ Hz) and 6.9—7.3 (7H, m, aromatic H). VIc: IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1700 (C=O). NMR δ (in $CDCl_3$): 1.63 (3H, d, $J=6.5$ Hz, CH_3), 5.7 (1H, q, $J=6.5$ Hz, $=\overset{|}{C}H$), 7.0—7.3 (10H, m, $2\times C_6H_5$).

4-Arylamino-4-phenyl-1,1,1-trifluoro-3-buten-2-ones (VIIa—c)——Thermal conversion of N-(1-phenylalkenyl)trifluoroacetanilides (VIa—c) were processed by the following general procedure. A solution of 1.5 g of the substrate in xylene (15 ml) was heated under refluxing (15 hr for VIa, b and 4 hr for VIc). The reaction mixture was concentrated under reduced pressure to give yellow crystalline residue, which was recrystallized from an appropriate solvent. Thus were obtained the following products, of which spectral data are recorded in Table III.

4-Anilino-4-phenyl-1,1,1-trifluoro-3-buten-2-one (VIIa): Yield, 99%. Yellow prisms (EtOH), mp 65.5—66.5°. *Anal.* Calcd. for $C_{16}H_{12}ONF_3$: C, 65.98; H, 4.15; N, 4.81. Found: C, 65.81; H, 4.06; N, 4.80.

4-*p*-Anisidino-4-phenyl-1,1,1-trifluoro-3-buten-2-one (VIIb): Yield, 83% (calculated from IIIb). Yellow prisms (EtOH), mp 97—98°. *Anal.* Calcd. for $C_{17}H_{14}O_2NF_3$: C, 63.39; H, 4.32; N, 4.29. Found: C, 63.55; H, 4.39; N, 4.36.

4-Anilino-3-methyl-4-phenyl-1,1,1-trifluoro-3-buten-2-one (VIIc): Yield, 67% (calculated from IIIc). Yellow plates (*n*-hexane), mp 92—93°. *Anal.* Calcd. for $C_{17}H_{14}ONF_3$: C, 66.88; H, 4.62; N, 4.57. Found: C, 66.68; H, 4.62; N, 4.51.

4-Cyclohexylamino-4-phenyl-1,1,1-trifluoro-3-buten-2-one (VIId) and 4-Cyclohexylamino-4-phenyl-1,1,1-trifluoro-3-trifluoroacetyl-3-buten-2-one (VIII)——a) Reaction of N-(α-methylbenzylidene)cyclohexylamine (IIId) with trifluoroacetic anhydride: The reaction was carried out using 6.0 g (0.03 mole) of IIId and 6.3 g (0.03 mole) of trifluoroacetic anhydride by the same procedure as described above. After usual treatment, a concentrated oily residue was distilled under reduced pressure to give 6.7 g of a pale yellow oil, bp 112—128° (0.09 mmHg). This was dissolved in benzene and chromatographed on silica gel (Merck, Kieselgel 60) using petr. ether–benzene as an eluent. From the first effluent fraction, 2.4 g (20%) of VIII (mp 62—63°) was obtained and recrystallized from petr. ether to give colorless prisms, mp 62.5—63.5°. *Anal.* Calcd. for $C_{18}H_{17}O_2NF_3$: C, 54.97; H, 4.36; N, 3.56. Found: C, 55.23; H, 4.35; N, 3.61. From the second effluent fraction, 2.9 g (33%) of VIId (mp 89.5—91°) was obtained and recrystallized from petr. ether to give colorless prisms, mp 91—92°. *Anal.* Calcd. for $C_{16}H_{18}ONF_3$: C, 64.64; H, 6.10; N, 4.71. Found: C, 64.68; H, 6.12; N, 4.72. Spectral data of VIId and VIII are recorded in Table III.

b) Reaction in the Presence of Pyridine: The reaction of IIId (0.03 mole) with trifluoroacetic anhydride (0.03 mole) was carried out in the presence of pyridine (0.033 mole). After usual treatment, a concentrated residue was triturated with petr. ether and cooled. Deposited crystals were collected by filtration to give 4.1 g of VIId (mp 87—89°). From the filtrate additional crystals (1.9 g) of VIId were obtained. Concentration of the above filtrate gave an oily residue, which was distilled under reduced presssure to give 1.8 g of an oil, bp 125—133° (0.2 mmHg). This was dissolved in benzene and chromatographed on silica gel in the same manner as described for a), giving 0.3 g (2%) of VIII (mp 58—60°) and 1.0 g of VIId were obtained. Total yield of VIId, 7.0 g (79%).

2-Phenyl-4-trihalomethylquinolines (IXa, b)——A mixture of 1.50 g of finely powdered Va (or VIIa) and 15 g of polyphosphoric acid was heated with stirring at 115—120° for 2.5 hr. After cooling, the reaction paste was poured into 20 ml of cold water with stirring and the resulting solution was basified with 50% aq. KOH under cooling. A liberated material was extracted with ether and dried over anhydrous $MgSO_4$. The ether solution was concentrated to give a pasty residue, which was crystallized by trituration with petr. ether. Deposited crystals were collected by filtration and recrystallized from EtOH.

2-Phenyl-4-trichloromethylquinoline (IXa): Yield, 66%. Colorless needles (EtOH), mp 78—80°. *Anal.* Calcd. for $C_{16}H_{10}Cl_3$: C, 59.57; H, 3.12; N, 4.34. Found: C, 59.75; H, 3.39; N, 4.47. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε): 276 (23000), 355 (6130).

2-Phenyl-4-trifluoromethylquinoline (IXb): Yield, 88%. Colorless needles (EtOH), mp 59—60°. *Anal.* Calcd. for $C_{16}H_{10}F_3$: C, 70.33; H, 3.69; N, 5.13. Found: C, 70.29; H, 3.94; N, 5.15. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε): 265 (34200), 331 (8930), 340 (inf. 8200).

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