about 0.5° or less. Solvents were measured by volume at room temperature. A small portion of the ether was withheld for addition of the substrate.

A kinetic run was started by injection of the substrate solution. Temperature equilibrium was attained again within about 1 min. Acid was titrated as formed with a solution of tri-*n*-butylamine (b.p. 208–209°) in 60% ether–40% ethanol. The acid end point of thymol blue (pH 1.2–2.8 in water) was shown to be satisfactory by potentiometric titration. Between 12 and 45 points were taken during an individual run. Runs at −45° were followed through the range from about 45 to 90% completion; the beginning of the reaction was inaccessible due to the time needed for temperature equilibration. Reactions at −65° were followed to about 80% completion; those at −82° were followed only to 20% completion because of their slowness.

The rate constant k_1 and the ratio k_2/k_3 were evaluated in three ways.

Method A.—The customarily obtained steady state rate expression[5], eq. 2, may be rearranged to yield eq. 3 as follows.

$$\frac{d[\mathrm{RCl}]}{dt} = \frac{k_1[\mathrm{RCl}]}{\frac{k_2[\mathrm{Cl}^-]}{k_3[\mathrm{C_2H_5OH}]} + 1} = \frac{k_1[\mathrm{RCl}]}{\frac{k_2[\mathrm{Cl}^-]}{k'_3} + 1} = k_{\mathrm{inst}}[\mathrm{RCl}] \quad (2)$$

$$k_{\mathrm{inst}} = k_1 - \frac{k_2}{k'_3} k_{\mathrm{inst}}\,[\mathrm{Cl}^-] \quad (3)$$

Then a plot of k_{inst} *vs.* k_{inst} $[\mathrm{Cl}^-]$ should yield a straight line of slope k_2/k_3 and y-intercept k_1. Instantaneous rate constants obtained from the slope of the curved "first-order" plots at several points were treated in this manner.

Method B.—The substitution $[\mathrm{Cl}^-] = c + r - [\mathrm{RCl}]$ is made in eq. 2, where c is chloride concentration at a time taken as $t = 0$ and r is the concentration of substrate at $t = 0$. This equation may now be integrated to yield, after rearrangement

$$2.303 \log \frac{[\mathrm{RCl}]}{r} \Big/ t = \frac{k_1}{\frac{k_2}{k'_3}(c + r) + 1} + \frac{k_2/k'_3}{\frac{k_2}{k'_3}(c + r) + 1} \frac{([\mathrm{RCl}] - r)}{t} \quad (4)$$

A linear plot is again obtained, from which k_1 and k_2/k_3 may be evaluated as functions of the slope and intercept.

Method C was used in runs with too much scatter for application of methods A or B. The average value of k_2/k_3 for runs in that temperature range was assumed, and k_1 was calculated from eq. 2. (It should be noted that these were in general still quite acceptable kinetic plots for most purposes, with no point deviating from a reasonable curve by more than 1% of the total final titer. However, both of the simultaneous rate constant evaluations are in principle a measurement of the deviation from linearity, and as such are very sensitive to experimental errors.) Error limits were assigned to values of k_1 by inspection of plots obtained from methods A and B. In general, k_2/k_3 was more sensitive to scatter in the data, and so values quoted are less reliable.

Product Study.—A sample of the chloride (0.054 g., 0.22 mmole) was solvolyzed as in a kinetic run. The solvent was evaporated under reduced pressure. The residue was extracted with pentane and diluted with heptane to obtain the visible spectrum. The spectrum was qualitatively the same as that of α-ferrocenylethanol [$\lambda_{\max}$ 437 mμ (ε 105) in 12.5:1 heptane–ether], and, if the extinction coefficient is assumed to be the same for the two spectra, the product solution is calculated to contain 0.198 mmole of ferrocene chromophore, or 90% of the starting chloride. The pentane-insoluble residue of ammonium salts contained the indicator, but nothing with the ferrocene chromophore.

The reaction product was chromatographed on alumina with benzene as eluent. Two yellow bands which passed through the column close together were isolated. The first was present in a trace amount too small to characterize. The second was an orange oil whose n.m.r. spectrum[8] was consistent for the ethyl ether of α-ferrocenylethanol.[1c] It had a triplet centered at 8.89 and a quartet at 6.63 τ with splittings of 6.5 c.p.s., corresponding to the ethyl group. The ring proton resonance came at 5.95 τ. The $-CH-CH_3$ group should appear as a doublet and a quartet. The doublet appeared at 8.56 τ, but the quartet was partially obscured by the ring protons. Two peaks of the quartet, with splitting of 5.5 c.p.s. (the same as the doublet) were readily visible, and shoulders on the ring proton resonance fell at the proper places to complete a quartet centered at 5.83 τ.

The Ritter Reaction of Tertiary Trihalomethylcarbinols and Related Substances

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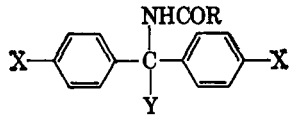
It has been shown[1-3] that the transformation of diaryltrifluoromethylcarbinols (I) into substituted fluorenes by successive treatment with concentrated sulfuric acid and a compound containing reactive hydrogen proceeds through a carbonium ion. Likewise, the rearrangement of diaryltrichloromethylcarbinols (II) into benzils under similar conditions[4] can be rationalized as involving carbonium ion intermediates. As it has been proved, on the other hand, especially by the experiments of Mousseron and co-workers,[5] that the so-called Ritter reactions of carbinols with nitriles in concencentrated sulfuric acid proceed *via* carbonium ion intermediates, it seemed of interest to study this reaction on compounds of type I and II.

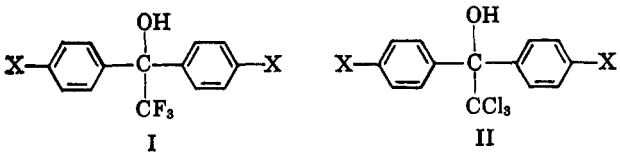
When a solution of di(*p*-chlorophenyl)trifluoromethylcarbinol (I, X = Cl) in concentrated sulfuric acid was added to acetonitrile, the intense color of the carbonium ion faded immediately, and a white crystalline compound was formed, which according to the analysis was the expected N-[1,1-di(*p*-chlorophenyl)-2,2,2-trifluoroethyl]acetamide (III). Analogously, with benzonitrile the benzamide derivative was obtained. These compounds are extremely resistant to hydrolysis with either acidic or alkaline reagents, which was not altogether unexpected[6]; N-triphenylmethylacetamide could not be deacetylated.[7] Di(*p*-chlorophenyl)- and di(*p*-fluorophenyl)trichloromethylcarbinol (II, X = Cl, F) behave similarly towards acetonitrile, giving IV (X = Cl, F). The products of positive Ritter reactions of other diarylperfluoroalkylcarbinols are summarized in Table I. This table also includes the reaction of benzilic acid with acetonitrile and concentrated sulfuric acid, which expectedly gave acetamidodiphenylacetic acid (V); treatment of V with alkali did not cause deacetylation, but decarboxylation, giving N-benzhydrylacetamide (VI).[8]

(1) S. Cohen, *J. Am. Chem. Soc.*, **79**, 1499 (1957).
(2) S. Cohen and A. Kaluszyner, *Experientia*, **13**, 236 (1957).
(3) A. Kaluszyner and S. Cohen, *Tetrahedron*, **11**, 252 (1960).
(4) A. Kaluszyner, *J. Org. Chem.*, **24**, 995 (1959).
(5) H. Christol, A. Laurent, and M. Mousseron, *Bull. soc. chim. France*, 2313, 2319 (1961); *Compt. rend.*, **248**, 1904 (1959).
(6) Houben-Weyl, "Methoden der Organischen Chemie," Vol. XI/1, G. Thieme, Stuttgart, 1957, p. 926.
(7) O. Nauen, *Ber.*, **17**, 442 (1884).
(8) This Ritter reaction has been described very recently by K. Hohenlohe-Oehringen and H. Bretschneider, *Monatsh.*, **93**, 645 (1962); *cf.* C. W. Bird, *J. Org. Chem.*, **27**, 4091 (1962); K. Hohenlohe-Oehringen, *Monatsh.*, **93**, 639 (1962).

TABLE I

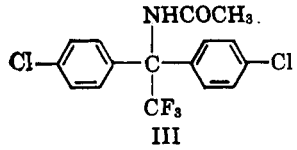


No.	X	Y	R	Yield, %	M.p., °C. (solvent)	Formula	Analysis, % C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	Remarks
1	H	CF_3	CH_3	88	197–198 (MeOH)	$C_{16}H_{14}F_3NO$	65.5	66.0	4.8	4.8			F: calcd., 19.5; found, 19.4
2	F	CF_3	CH_3	90	178–178.5 (MeOH)	$C_{16}H_{12}F_5NO$	58.3	58.0	3.7	4.3			
3	Cl	CF_3	CH_3	90	214–214.5 (MeOH)	$C_{16}H_{12}Cl_2F_3NO$	53.1	53.5	3.3	3.5	3.9	4.2	Cl: calcd., 19.6; found, 19.8 F: calcd., 15.7; found, 15.1
4	Cl	CF_3	C_6H_5	96	165–167 (EtOH)	$C_{21}H_{14}Cl_2F_3NO$	59.5	59.1	3.3	3.4	3.3	3.3	Cl: calcd., 16.7; found, 16.5 F: calcd., 13.5; found, 13.5
5	Cl	C_2F_5	CH_3	72	156–157 (MeOH)	$C_{17}H_{12}Cl_2F_5NO$	49.5	48.7	2.9	3.1	3.4	3.4	
6	Cl	C_3F_7	CH_3	94	169–170 (MeOH)	$C_{18}H_{12}Cl_2F_7NO$	46.8	46.7	2.6	2.9	3.0	3.2	F: calcd., 28.8; found, 29.1
7	F	CCl_3	CH_3	93	206–207 (MeOH)	$C_{16}H_{12}Cl_3F_2NO$	50.8	50.7	3.2	3.5	3.7	3.8	F: calcd., 10.1; found, 10.1 (Acetate was used as starting material)
8	Cl	CCl_3	CH_3	95	214–215 (EtOH)	$C_{16}H_{12}Cl_5NO$	46.9	46.4	2.9	3.1	3.4	3.6	Cl: calcd., 43.1; found, 43.6
9	H	COOH	CH_3	99	201 dec. (EtOH)	$C_{16}H_{15}NO_3$	71.4	71.3	5.6	5.3	5.2	5.4	



I

II



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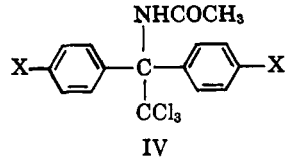
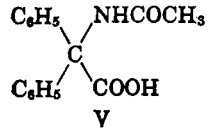
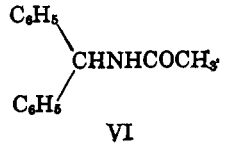


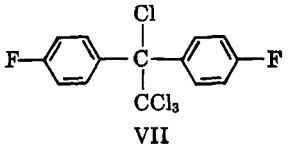
IV



V



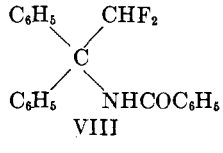
VI



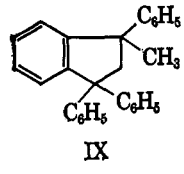
VII

From the point of view of the mechanism of this reaction, it is interesting—though unexpected—to report that 1,1-di(*p*-fluorophenyl)-1,2,2,2-tetrachloroethane (VII) did not react as the corresponding II. Compound VII, obviously, is inert under conditions under which II (X = F) forms the carbonium ion involved in the Ritter reaction.

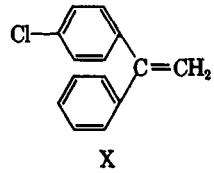
In all the experiments so far reported, the carbonium ion formed has no possibility of forming an olefin by loss of a proton. It thus seemed of interest to study some diarylmethylcarbinols, in which the methyl group was not substituted, or substituted with not more than two halogen atoms. As Table II shows, in all cases but one (that of diphenyl*di*fluoromethylcarbinol which gave VIII), the compounds were refractory to the nitrile (or hydrocyanic acid) under the conditions of the Ritter reaction and only lost water to give the corresponding ethylenes when the solution in concentrated sulfuric acid was diluted.[9] In the case of diphenylmethylcarbinol, the olefin dimerized to the known[10] hydrindene derivative (IX). In accordance with these observations, neither 1-(*p*-chlorophenyl)-1-phenylethylene (X) nor 1,1-di(*p*-chlorophenyl)-2,2-dichloroethylene (XI) could be induced to react with nitriles. On the other hand it is well known[11] that benzhydrol undergoes this reaction, giving N-benzhydrylbenzamide (XII).



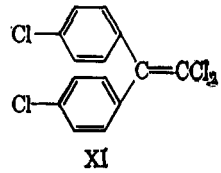
VIII



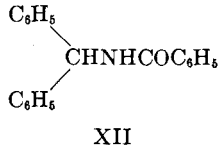
IX



X



XI



XII

Experimental

The starting materials for the compounds listed in Table I were prepared according to previous publications from this laboratory[12,13]; this applied also to VII. X was obtained according to Bergmann and Bondi.[14]

General Procedure.—When 8–10 ml. of concentrated sulfuric

(9) This has been observed for diphenylmethyl-, -ethyl-, and -isopropylcarbinol recently by H. Christol, A. Laurent and G. Solladie, *Bull. soc. chim. France*, 877 (1963).

(10) E. D. Bergmann and H. Weiss, *Ann.*, **480**, 49 (1930).

(11) *Cf.* H. Christol, A. Laurent, and G. Solladie, ref. 9.

(12) A. Kaluszyner, S. Reuter, and E. D. Bergmann, *J. Am. Chem. Soc.*, **77**, 4164 (1955).

(13) E. D. Bergmann and A. Kaluszyner, *J. Org. Chem.*, **23**, 1306 (1958).

(14) E. D. Bergman and A. Bondi, *Ber.*, **64**, 1455 (1931).

TABLE II

ATTEMPTED RITTER REACTION

	Starting material	Nitrile	Product isolated	Remarks
1.	Methyldiphenylcarbinol[a]	Acetonitrile	IX	M.p. 143°. *Anal.* Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7. Found: C, 93.1 H, 6.8
2.	Methyldiphenylcarbinol	Benzonitrile	IX	
3.	Methyldiphenylcarbinol	Chloroacetonitrile	IX	
4.	Methyldiphenylcarbinol	Hydrocyanic acid[b]	IX	
5.	Chloromethyldiphenylcarbinol[c]	Benzonitrile	1-Chloro-2,2-diphenylethylene	M.p. 41°.[d] *Anal.* Calcd. for $C_{14}H_{11}Cl$: C, 78.4; H, 5.1; Cl, 16.5. Found: C, 78.2; H, 5.0; Cl, 16.1
6.	Chloromethyldiphenylcarbinol	Acetonitrile	1-Chloro-2,2-diphenylethylene	
7.	Dichloromethyldiphenylcarbinol[e]	Benzonitrile	1,1-Dichloro-2,2-diphenylethylene	M.p. 77°. *Anal.* Calcd. for $C_{14}H_{10}Cl_2$: C, 67.5; H, 4.0; Cl, 28.5. Found: C, 67.4; H, 4.1; Cl, 28.4
8.	Methyldi(*p*-chlorophenyl)carbinol[f]	Benzonitrile	1,1-Di(*p*-chlorophenyl)ethylene	M.p. 86°.[f] *Anal.* Calcd. for $C_{14}H_{10}Cl_2$: C, 67.5; H, 4.0; Cl, 28.5. Found: C, 67.3; H, 4.1; Cl, 28.1
9.	Difluoromethyldiphenylcarbinol[g]	Benzonitrile	VIII (quant. yield)	M.p. 172° (from ethanol). *Anal.* Calcd. for $C_{21}H_{17}F_2NO$: C, 74.7; H, 5.0; N, 4.1; F, 11.3. Found: C, 74.6; H, 5.0; N, 3.8; F, 11.3

[a] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 226. [b] See ref. 5. [c] F. Bergmann and A. Kalmus, *J. Am. Chem. Soc.*, **76**, 4137 (1954). [d] W. P. Buttenberg, *Ann.*, **279**, 324 (1894). [e] M. A. Avy, *Bull. soc. chim. France*, [4] **49**, 12 (1931). [f] See ref. 11. [g] J. Bornstein, M. S. Blum, and J. T. Pratt, *J. Org. Chem.*, **22**, 1210 (1957).

acid was added to a mixture of 0.05 mole of the carbinol and 0.1 mole of the nitrile, each drop produced a red to violet color which faded quickly. The mixture was stirred and heated at 60–70° until an additional drop of acid no longer produced a color reaction (usually 15 min.). The mass was diluted with ice–water and the product filtered and crystallized from methanol or ethanol. The reaction of methyldiphenylcarbinol with hydrocyanic acid was carried out according to Mousseron, *et al.*[5]

Attempts to Deacetylate N-[1,1-Di(*p*-fluorophenyl)-2,2,2-trifluoroethyl]acetamide (as III).—The following reagents were tried, but without result: boiling trifluoroacetic acid at 100°, concentrated sulfuric acid at 25° during 3 days (although the solution turned yellow and fluorescent), sulfuric acid in boiling 75% acetic acid, and boiling ethanolic sodium hydroxide. Potassium hydroxide in boiling diethylene glycol appeared to lead to complete destruction of the molecule.

N-Benzhydrylacetamide (VI).—When 5.4 g. of V was refluxed for 3 hr. with a solution of 4 g. of sodium hydroxide in 100 ml. of anhydrous ethanol, one obtained, upon cooling, white crystals (3.8 g.) which were neutral and melted at 152°, as reported for VI.[15]

(15) A. Rahman and M. O. Farooq, *Rec. trav. chim.*, **73**, 423 (1954).

Dihydroazepinone Chemistry. III. The Base-Catalyzed Deuterium Exchange of 1,3-Dihydro-1,3,5,7-tetramethyl-2*H*-azepin-2-one[1]

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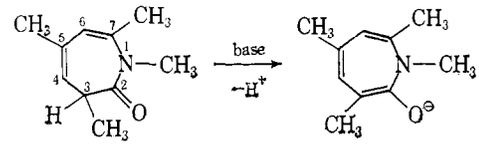
Department of Chemistry, Upjohn Company, Kalamazoo, Michigan

Received July 1, 1963

During the course of an extensive study of the chemistry of the dihydroazepinone ring system,[1,3] we were led to investigate the behavior of 1,3-dihydro-1,3,5,7-tetramethyl-2*H*-azepin-2-one (I)[1] with various basic reagents. Of particular interest was the possibility that, if enolization of the proton at position 3 (alpha to the carbonyl) could be made to occur, the unusual azepinoid anion II would result.[4]



I II

Prolonged treatment of I with potassium amide in liquid ammonia or with sodium hydride in dimethylformamide at 70° failed to consume these basic reagents, and I was readily recovered on appropriate work-up. However, addition of a solution of I in dry dimethyl sulfoxide (DMSO) to a hot (70°) solution of the methylsulfinyl carbanion ($Na^+{}^-CH_2SOCH_3$) in DMSO[5] produced a highly colored red-brown solution. The reaction mixture was stirred at this temperature for one hour, cooled, and treated with excess methyl iodide.[6] The deep color was discharged and a pale yellow mixture was obtained. Water was added and the product which was obtained by methylene chloride extraction proved, however, to be unchanged I (70+% recovery).

Despite the fact that I was not alkylated under these conditions, the deep color of the solution encouraged us to examine this reaction in greater detail. Treatment of the dihydroazepinone I with the methylsulfinyl carbanion prepared from sodium hydride and completely

(1) For paper II of this series, see L. A. Paquette, *J. Am. Chem. Soc.*, **85**, 3288 (1963).

(2) Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

(3) Paper I, L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962), and future papers to be published.

(4) The negative charge of carbanions situated alpha to carbonyl functions almost exclusively resides on the more electronegative atom, oxygen. For a discussion of this subject, see J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chap. XI.

(5) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963).

(6) Several other alkylating agents were likewise employed with similar negative results.