portional to the rate constant k,[8] and the energy of activation ΔH is given by

$$\Delta H = -2.3R\frac{d \log k}{d\left(\frac{1}{T}\right)} = 2.3R\frac{d \log \Delta}{d\left(\frac{1}{T}\right)}$$

The plot of log Δ (corrected by substracting the value of the line width at 27°[9]) *vs.* $1/T$ gives a straight line (Figure 4) from which the activation energy of the conversion was calculated to be 4.1 ± 0.5 kcal/mole.

The temperature independence of the nmr line widths in the keto tautomer of dimedone points to its higher conformational mobility.[10] The nmr signals of its homolog, the 2,2,5,5-tetramethylcyclohexanedione (at 0.98, 1.28, and 2.59 ppm), were also found to remain sharp when the temperature was decreased to −80°. On the other hand, the comparatively higher energy barrier observed in the enolic form of the 1,3-cyclohexanediones may be caused by the rigidity of the three sp^2-hybridized carbon atoms causing a considerable distortion of the bond angles in the conversion of IA to IB.

Experimental Section

Ultraviolet absorption spectra were measured on a Cary 14 spectrophotometer, using cells of 5-, 1-, 0.1-, and 0.01-cm thickness. The proton nmr measurements were done on a Varian A-60 instrument, and the line-width determination was performed on a Varian HR, 100-Mc instrument. The peak positions are given in parts per million (ppm) downfield from tetramethylsilane as an internal reference. The ^{17}O nmr spectrum of dimedone was recorded on a V-4200 Varian wide-line spectrometer operating at 8.13 Mc/sec; the derivative of the absorption line was recorded using a 40-cps sweep modulation. The chemical shift was measured relative to $H_2{}^{17}O$ as an external standard.

The commercially available samples of dimedone and 1,3-cyclohexanedione were purified by repeated crystallization. The solvents used were spectroscopic grade; the chloroform was ethanol free.

Registry No.—I, 126-81-6; II, 504-02-9; III, 13019-14-2.

[8] S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962); *ibid.*, **38**, 1787 (1963); see also J. E. Anderson and J. M. Lehn, *J. Am. Chem. Soc.*, **89**, 81 (1967).

[9] Since at temperatures above 27° the amount of the enol form was negligible, the values of the line width at 27° were used in the calculations as the natural line widths.

[10] The mobility of cyclohexanone and 2,2′-dimethylcyclohexanone is indicated *inter alia* by the temperature independence of their nmr spectra, down to *ca.* −80°: R. Perret, *Bull. Soc. Chim. France*, **5**, 753 (1966).

The Trichloromethylation Reaction. Ring-Chain Tautomerism. II[1]

ANTHONY WINSTON, JOHN C. SHARP, KENNETH E. ATKINS, AND DALE E. BATTIN

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

Received November 21, 1966

Several anhydrides have been subjected to the trichloromethylation reaction using sodium trichloroacetate in dimethoxyethane solution. The trichloromethylation products exist in either of two tautomeric forms, the keto acid or the lactol. If the trichloroacetyl and carboxyl groups are held in fixed coplanarity, the stability of the lactol tautomer is quite high and the compound crystallizes in that form. If the groups are not held coplanar, then the keto acid tautomer is isolated. In solution the compounds are in tautomeric equilibrium and the presence of two tautomeric forms may be detected spectroscopically. The yields of the trichloromethylation products are generally quite good, but, in cases where side reactions are particularly significant, low yields result. Sodium trichloroacetate reacts with aldehydes to give trichloromethylcarbinols, with acetyl chloride to give 1,1,1-trichloro-2-propanone, and with methyl iodide to give 1,1,1-trichloroethane. Sodium tribromoacetate may be used to introduce the tribromomethyl group, reaction occurring with both anhydrides and aldehydes. The use of sodium trifluoroacetate has not been successful. The decomposition of sodium trichloro- and tribromoacetate is strongly accelerated by the presence of the anhydride. The possibility that the trihalomethylation reaction involves a participation by the trihaloacetate ion is suggested.

The decomposition of sodium trichloroacetate in the presence of anhydrides is a useful synthetic method for introducing the trichloromethyl group into organic compounds.[2] A variety of anhydrides readily undergoes the addition reaction to produce trichloromethyl ketones, keto acids, and lactols in high purity, often in excellent yield. The reaction is quite rapid; in certain cases yields of >70% are realized after only 30 min in refluxing dimethoxyethane. Occasionally, lower yields (10–50%) result, and the product may be accompanied by considerable amounts of tarry material. This is due in part to the abstraction of hydrogen or chlorine from the primary product by the trichloromethyl anion, to give an anion which may undergo further reactions. Abstraction reactions of this type are well known[3,4] and often lead to complex condensation products. The isolation of appreciable amounts of dichloroprotoanemonin from the trichloromethylation of succinic anhydride is one instance in which a side reaction product was actually identified.[5]

We have now investigated the trichloromethylation of several additional anhydrides and have extended the general scope of the reaction to include aldehydes, an acid chloride, and an alkyl iodide. The use of sodium tribromo- and trifluoroacetate in the trihalomethylation reaction has also been explored.

Reaction of sodium trichloroacetate with the appropriate anhydride provided reasonably good yields of trichloromethylation products **1**–**4**. Reaction with chlorendic anhydride produced a considerable amount of tar, from which the amorphous trichloromethyl lactol **5** was sublimed. This compound was difficult to purify and a satisfactory analysis was obtained on the methyl ester **6**.

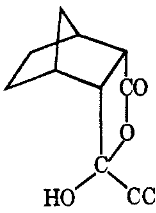
[1] Taken in part from the Ph.D. dissertation of J. C. Sharp, West Virginia University, Oct 1966, and the M.S. theses of K. E. Atkins and D. E. Battin, Kanawha Valley Graduate Center of West Virginia University, 1965.

[2] A. Winston, J. P. M. Bederka, W. G. Isner, P. C. Juliano, and J. C. Sharp, *J. Org. Chem.*, **30**, 2784 (1965).

[3] W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 925 (1962).

[4] W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *ibid.*, **81**, 933 (1962).

[5] A. Winston and J. C. Sharp, *J. Am. Chem. Soc.*, **88**, 4196 (1966).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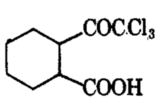
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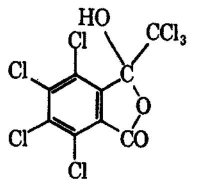
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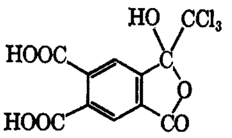
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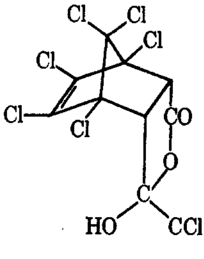
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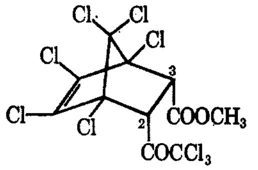

6

The lactol structures **1**, **3**, **4**, and **5** were indicated by the hydroxyl and lactol carbonyl infrared peaks (Table I), while the keto acid structure **2** was evident from the two carbonyl peaks (Nujol). Although only a single carbonyl peak was observed for methyl ester **6**, its location at 1730 cm^{-1} is inconsistent with the pseudo-ester structure, which would be expected to exhibit a peak at about 1800 cm^{-1} for the lactol carbonyl group. Thus, the 1730-cm^{-1} band must represent the unresolved ester and ketone bands of the open-chain form. A slight shoulder does appear at 1745 cm^{-1}. The normal ester structure of **6** is further supported by the nmr singlet at τ 6.30 (Table II) consistent with the usual position of normal methyl esters. For the cyclized pseudo-methyl esters, this line appears at higher fields, about τ 6.6–6.8.[6,7] Under the conditions of esterification (methanol–sulfuric acid, heated under reflux for 28 hr), it is surprising that cyclization of keto ester **6** to the pseudo-ester form did not occur, since the pseudo-ester is often the more stable isomer.[8] In this case, however, the lower stability of the pseudo-ester may possibly be attributed to unfavorable steric requirements for the placement of either the trichloromethyl or the methoxy group close under the bicyclic ring.

TABLE I

INFRARED ABSORPTION OF TRICHLOROMETHYL KETO ACIDS AND LACTOLS

		Absorption, cm^{-1}			
Compd	Phase	OH	Lactol C=O	Ketone C=O	Acid C=O
1	Nujol	3425	1780	. . .	. . .
	$CHCl_3$	3480	1785	. . .	. . .
2	Nujol	. . .	. . .	1730	1700
	$CHCl_3$	3460 w	1800 w	1745	1710
3	KBr	3390	1785	. . .	. . .
4	KBr	3510	1790	. . .	1740
	CH_3CN	3545	1790	. . .	1740
5	Nujol	3290	1790	1725[a]	. . .
	$CHCl_3$	3480	1800	1725[a]	. . .
6	Nujol	. . .	. . .	1745 sh	1730[b]
11	Nujol	3240	1780	. . .	. . .
	$CHCl_3$	3460	1785	. . .	. . .
13	Nujol	3290	1790	. . .	. . .
14	Nujol	. . .	. . .	1745	1715
	$CHCl_3$	. . .	. . .	1735	1705
17	Nujol	. . .	1795	. . .	. . .
	$CHCl_3$	3510 w	1785	. . .	. . .
18	Nujol	. . .	1805	. . .	. . .
	$CHCl_3$	. . .	1785	. . .	. . .
21	Nujol	3200	1750	. . .	. . .
	$CHCl_3$	3560	1820	. . .	. . .

[a] Very weak. [b] Ester carbonyl peak.

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA

Compd	Solvent	Proton assignment	Chemical shift (τ), ppm	Multiplicity	Coupling constants, cps
6	$DCCl_3$	H_2	5.40	d	$J_{2,3} = 10.2$
		H_3	5.82	d	
		OCH_3	6.30	s	
11	$(CD_3)_2CO$	OH	2.37		$J_{1,6} = 1.0$
		H_5, H_6	3.37	m	$J_{4,5} = 1.2$
		H_1	4.53	d	$J_{1,2} = 0$
		H_4	4.77	d	$J_{3,4} = 0$
		H_2	6.77	d	$J_{2,3} = 6.2$
		H_3	6.90	d	
13	$(CD_3)_2CO$	OH	5.23		$J_{2,3} = 8$
		H_1, H_4	5.00	m	$J_{1,2} = 0$
		H_2	6.72	d	$J_{3,4} = 0$
		H_3	6.87	d	
		H_5, H_6	8.28	m	
14	$(CD_3)_2CO$	COOH	−0.1		$J_{2,3} = 4$
		H_1, H_4	5.00	m	$J_{1,2} = 4$
		H_2	5.72	t	$J_{3,4} = 0$
		H_3	6.92	d	
		H_5, H_6	8.28	m	
15	$(CD_3)_2CO$	COOH	−0.31		$J_{1,2} = 4.25$
		H_1, H_4	5.28	m	$J_{2,3} = 4.25$
		H_2	6.61	t	$J_{3,4} = 0$
		H_3	7.04	d	
		H_5, H_6	8.27	m	
17	$(CD_3)_2CO$	H_6	1.05	q	$J_{4,6} = 1.4$
		H_4	1.72	q	$J_{4,5} = 7.5$
		H_5	2.23	q	$J_{5,6} = 4.8$
		OH	1.75		
18	$(CD_3)_2CO$	H_6	1.03	q	$J_{4,6} = 1.4$
		H_4	1.54	q	$J_{4,5} = 8.0$
		H_5	2.21	q	$J_{5,6} = 4.9$
		OH	1.75		

Reaction of sodium trichloroacetate with tetraphenyldihydrophthalic anhydride (**7**) produced only the dehydrogenated product, tetraphenylphthalic anhydride (**8**). This is the first observation of a dehydrogenation occurring in a trichloromethylation reaction with sodium trichloroacetate. Although the initial abstraction of a proton is a characteristic reaction of the trichloromethyl anion,[3-5] the path by which the second hydrogen is lost is not clear. In an independent reaction with tetraphenylphthalic anhydride, the trichloromethylation reaction failed and only starting material was recovered.

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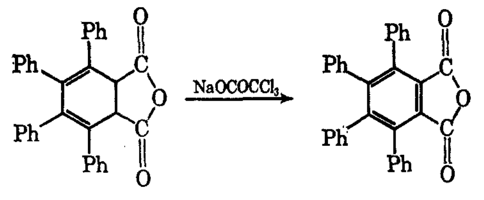
(6) P. T. Lansbury and J. F. Bieron, *J. Org. Chem.*, **28**, 3564 (1963).

(7) P. R. Jones and P. J. Desio, *ibid.*, **30**, 4293 (1965).

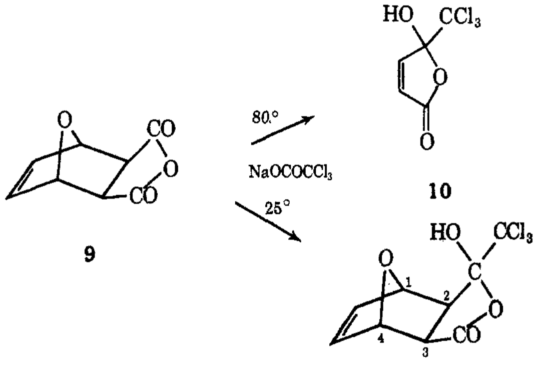
(8) J. H. Boothe, S. Kushner, J. Petisi, and J. H. Williams, *J. Am. Chem. Soc.*, **75**, 3261 (1953).



7 8

Reaction of sodium trichloroacetate with the furan-maleic anhydride Diels–Alder adduct **9** in refluxing dimethoxyethane afforded only lactol **10**, a compound which may be obtained directly by trichloromethylation of maleic anhydride.[2] Reaction at room temperature, on the other hand, afforded a 0.37% yield of the expected lactol **11** (see Scheme I). Since lactol **11** readily sublimes without dissociation by reverse Diels–Alder reaction, formation of lactol **10** must have arisen through trichloromethylation of maleic anhydride produced by rapid dissociation of the furan–maleic anhydride adduct **9**.[9]

SCHEME I



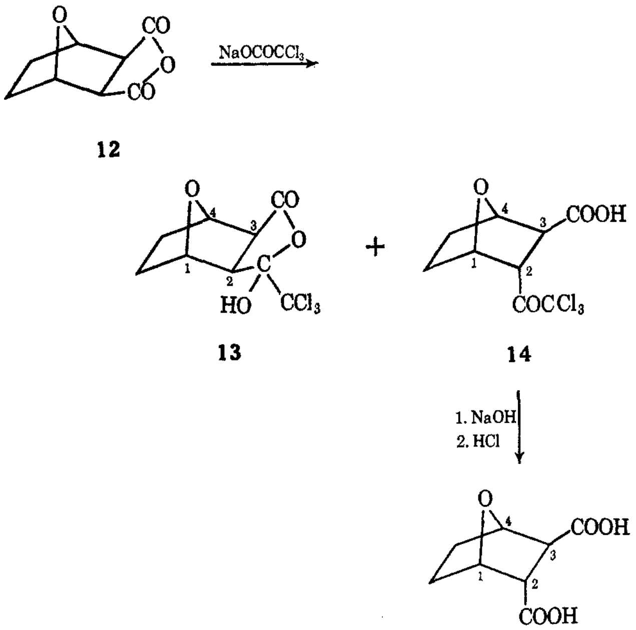
9 10 11

The lactol structure **11** is consistent with the infrared spectrum, which shows hydroxyl and lactol carbonyl peaks (Table I). In the nmr spectrum (Table II) protons H_2 and H_3 give a simple AB pattern, since a bridgehead proton is not strongly coupled with an adjacent *endo* proton due to the dihedral angle between them being close to 90°. For the same reason, protons H_1 and H_4 appear as doublets, the splitting being caused by the H_5 and H_6 protons only. In making the specific line assignments in this and succeeding cases, the lower field line for a pair of similar protons was always assigned to the proton nearer the trichloromethyl group in accordance with the increased deshielding expected at these locations.

Reaction of sodium trichloroacetate with the dihydro adduct **12** afforded a 76% yield of a crystalline solid, from which two isomeric trichloromethyl compounds were separated. From the infrared spectra of the two isomers, the principal component appeared to be a keto acid, and the minor component a lactol. The lactol was quite unstable and isomerized readily to the keto acid in hot benzene, ethanol, or acetic acid. The infrared and nmr spectra of the lactol were consistent with structure **13**, expected from a normal trichloromethylation reaction. The infrared spectrum showed the typical hydroxyl and the lactol carbonyl bands. The nmr spectrum exhibited two doublets having an AB pattern (J_{AB} = 8 cps) consistent with an *endo–cis* configuration of H_2 and H_3. The lower field doublet was assigned to H_2, the proton nearer the trichloroacetyl group.

The keto acid structure of the primary product was revealed by the presence of the ketone and acid carbonyl peaks in the infrared. It was unlikely that the keto acid was the chain tautomer of lactol **13**, in view of the high stability of the lactol ring when the participating groups are fixed in an eclipsed configuration. Since titration of the keto acid with 2 equiv of base afforded the *trans* dibasic acid **15**, epimerization of one of the groups must have occurred to place the carboxyl and trichloroacetyl groups in the *trans* arrangement. The nmr spectrum is consistent only with the *exo*-carboxy-*endo*-trichloroacetyl structure **14** (Scheme II). The assignment of the line at τ 5.72 to the H_2 proton and the line at 6.96 to the H_3 proton, is consistent with the downfield shift of proton H_2, α to the trichloroacetyl group. The nature of the splitting establishes the configuration of the groups. Proton H_2, in showing a triplet, is coupled with both H_3 and the bridegehead proton H_1, and must be *exo*. Proton H_3, on the other hand, gives a doublet and must be an *endo* proton, coupled with H_2, but not with the bridgehead proton H_4, because of the 90° dihedral angle.[10] Although epimerization of the trichloroacetyl group has not been observed before in these reactions, such an occurrence is not unexpected and reflects the high activity of the proton α to the trichloroacetyl group and α to the *oxa* bridge.

SCHEME II



12 13 14 15

Reaction of sodium trichloroacetate with quinolinic anhydride (**16**) should provide two trichloromethylation products, **17** and **18**, from attack at each of the two nonequivalent carbonyl groups (Scheme III). Frac-

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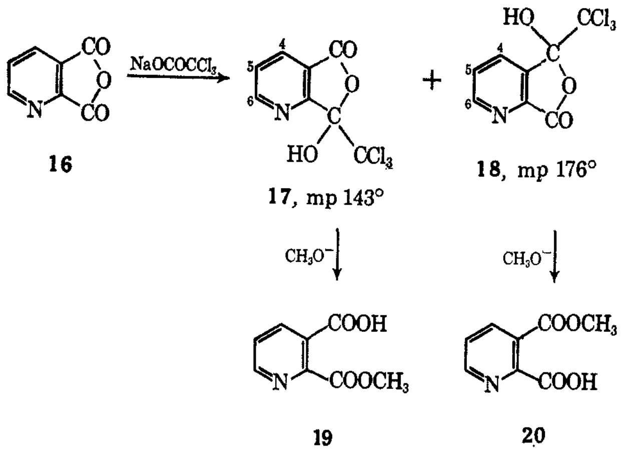
(9) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948).

(10) W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, Jr., *ibid.*, **80**, 2533 (1958); E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

Scheme III



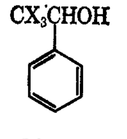
tional crystallization of the reaction mixture afforded two isomeric trichloromethylation products, mp 143 and 176°, in about a 5:1 ratio. Both isomers have the lactol structure, as indicated by hydroxy and lactol carbonyl peaks in the infrared.

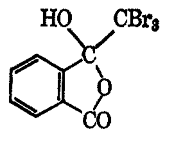
Structural assignments of the lactols **17** and **18** can be made on the basis of the particular half-ester formed on titration with 2 equiv of sodium methoxide. The reaction of base with the lactols proceeds in two stages: neutralization of the acidic proton by the first equivalent of base, and displacement of the trichloromethyl group by the second equivalent.[2] Infrared spectroscopy showed that the first-stage neutralization was accompanied by ring opening of the lactol to give the keto acid salt. The attack of the second equivalent must then occur at the trichloromethyl ketone site. Thus, in the titration of lactols **17** and **18** with methoxide, the position of the carbomethoxy group of the product would indicate the position originally occupied by the trichloromethyl group. The isomer melting at 143° gave methyl 3-carboxypyridine-2-carboxylate (**19**), and was assigned structure **17**. The isomer melting at 176° gave methyl 2-carboxypyridine-3-carboxylate (**20**), and was assigned structure **18**.

The nmr spectra of lactones **17** and **18** confirm the structural assignments. Both isomers exhibit an AMX pattern for the H_6, H_4, and H_5 protons, listed in order of increasing field strength and in accordance with their increasing electron density. The primary difference between the spectra of **17** and **18** is the shift in position of one of the three lines, the one assigned to H_4. This result is consistent with the assignment of H_4 to the middle line, since H_4, being closest to the lactol ring, would be most affected by the structural change. The H_4 line of **18** is downfield from that of **17** because of greater deshielding by the trichloromethyl group.

Reaction with sodium trichloroacetate is also an effective means for the trichloromethylation of aldehydes.[11] Benzaldehyde afforded a 30% yield of 2,2,2-trichloro-1-phenylethanol (**21**) while 2-ethylhexanal gave a 47% yield of 1,1,1-trichloro-3-ethyl-2-heptanol, along with some of the starting aldehydes. Acid chlorides also undergo the reaction and a 20% yield of 1,1,1-trichloro-2-propanone was obtained from acetyl chloride. Reaction with methyl iodide caused the displacement of the iodide ion with the formation of 1,1,1-trichloroethane in about 2.5% yield.

Decomposition of sodium tribromoacetate in the presence of phthalic anhydride afforded tribromomethyl lactol **23** in 54% yield. A carbonyl peak at 1750 cm^{-1} (Nujol) indicated strong intramolecular hydrogen bonding between the lactol carbonyl and the hydroxyl groups.[12] In solution, hydrogen bonding is of little importance and the carbonyl assumes its normal frequency at 1820 cm^{-1}. Reaction of sodium tribromoacetate with benzaldehyde afforded tribromomethylcarbinol **22**, which, being difficult to purity, was isolated and characterized as the acetate.


21, X=Cl
22, X=Br


23

Reaction of sodium trifluoroacetate with phthalic anhydride and several other anhydrides failed to provide any trifluorinated products. The reactions were carried out not only in refluxing dimethoxyethane, but also in diglyme at 180°. Although severe etching of the glassware occurred, very little carbon dioxide was evolved under either set of conditions.

The rates of decomposition of sodium trichloro- and tribromoacetate are markedly enhanced by the presence of the anhydride. This effect is clearly illustrated by the immediate exothermic reaction occurring when sodium tribromoacetate is mixed with phthalic anhydride in DME solution at room temperature. Carbon dioxide is rapidly evolved and the reaction is essentially complete in about 20 min. Preliminary measurements of the rate of decomposition of sodium trichloro- and tribromoacetate (Table III) clearly show the acceleration caused by the anhydride. The remarkable speed of the process suggests a transition state involving the trihaloacetate ion itself rather than the trihalomethyl anion intermediate arising from the thermal decomposition of the trihaloacetate. Further work in this area is contemplated.

Table III

Effect of Conditions on the Rate of Decomposition of Sodium Trihaloacetates

				% decompn after			
Trihaloacetate	Solvent	Catalyst	Temp, °C	0.25 hr	0.5 hr	1 hr	2.5 hr
NaOCOCCl$_3$	Heptane	None	95	0	...	..	0
NaOCOCCl$_3$	DME	None	80	25	52	71	75
NaOCOCCl$_3$	DME	Pth anh[a]	80	64	89	94	94
NaOCOCCl$_3$	DME	None	24	...	...	..	15
NaOCOCCl$_3$	DME	Pth anh	24	...	...	..	56
NaOCOCBr$_3$	Heptane	None	85	...	...	..	10
NaOCOCBr$_3$	DME	None	85	43	80	82	83
NaOCOCBr$_3$	DME	Pth anh	85	84	84	84	84
NaOCOCBr$_3$	DME	None	25	...	...	..	48
NaOCOCBr$_3$	DME	Pth anh	25	...	...	..	81
NaOCOCBr$_3$	DME	Benzald[b]	25	...	...	..	80

[a] Phthalic anhydride. [b] Benzaldehyde.

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[11] W. M. Wagner, H. Kloosterziel, and S. Van der Ven, *Rec. Trav. Chim.*, **80**, 740 (1961).

[12] P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **77**, 5598 (1955).

TABLE IV

TRIHALOMETHYLATION PRODUCTS OF ANHYDRIDES

Product	Anhydride, mole	Yield, %	Mp, °C	Formula	Calcd, %			Found, %		
					C	H	Cl	C	H	Cl
1	0.13	75	185–186	$C_{10}H_{11}Cl_3O_3$	42.10	3.90	37.00	42.40	4.08	37.20
2[a]	0.20	78	111–111.5	$C_9H_{11}Cl_3O_3$	39.69	3.94	38.78	39.91	4.10	38.83
3	0.10	59	237–239	$C_9HCl_7O_3$	26.70	0.25	61.24	27.00	0.30	61.21
4	0.10	50	253–255	$C_{11}H_5Cl_3O_7$	37.16	1.42	29.92	37.32	1.68	29.88
5[b]	0.50	...	52.5–53.5	$C_{10}H_3Cl_9O_3$	24.44	0.61	65.20	25.68	0.66	63.64
6[c]	...	78[a]	153.5–154	$C_{11}H_5Cl_9O_3$	26.10	1.00	63.45	25.94	1.06	63.40
10[d]	0.25	4.6	...	...	...	...	...	...	...	...
11[e]	0.10	0.37	125	$C_9H_7Cl_3O_4$	37.83	2.48	37.26	38.13	2.61	36.95
13[f]	0.12	76	157	$C_9H_9Cl_3O_4$	37.53	3.16	37.07	37.65	3.18	37.21
14[f,g]			166.5–167.5	$C_9H_9Cl_3O_4$	37.53	3.16	37.07	37.53	3.20	36.90
17[h]	0.05	24	142–143	$C_8H_4Cl_3NO_3$[i]	35.75	1.49	39.65	35.90	1.45	33.92
18[h]		4.4	176.5–177	$C_8H_4Cl_3NO_3$[i]	35.75	1.49	39.65	35.88	1.52	39.82
23	0.10	54	162.5–163	$C_9H_5Br_3O_3$	26.96	1.25	59.80[j]	27.30	1.30	59.92[j]

[a] Basic hydrolysis gave *cis*-cyclohexane-1,2-dicarboxylic acid, mp 191–192°, lit. mp 191°: O. Diels and K. Alder, *Ann.*, **460,** 98 (1928). [b] Isolated and purified by sublimation from considerable amounts of tarry products. [c] Prepared by treatment of lactol **5** with hot methanol–sulfuric acid. [d] Infrared spectrum identical with that of an authentic sample; see ref 2. Reaction conditions, 10 min at 80°, then 24 at 25°. [e] Reaction conditions, 24 hr at 25°. Recrystallized from chloroform–hexane. [f] Washing a mixture of **13** and **14** with cold glacial acetic acid left a fairly pure fraction of lactol **13**. Keto acid **14** was isolated as the least soluble fraction on crystallization of a mixture of **13** and **14** from ethanol–water. Lactol **13** isomerizes in solution to keto acid **14**. [g] Titration with 2 equiv of base gave *trans* diacid **15**, as white crystals from chloroform, mp 179–180° (lit.[9] mp 180°). [h] Lactols **17** and **18** were separated by fractional crystallization from benzene. [i] *Anal.* Calcd for N: 5.22. Found: 5.20 for **17**, 5.21 for **18**. [j] Analysis for Br.

The various trichloromethyl keto acids and lactols are capable of undergoing ring–chain tautomerism.[2] The extent to which the tautomers exist in solution is qualitatively indicated by their infrared spectra (Table I). The solution spectra of lactols **1**, **4**, **5**, **11**, **17**, and **18** are lacking in ketone or acid carbonyl bands of the open chain forms; hence, in these cases, the cyclic tautomers are greatly favored. The lactol appears to be particularly stable when the trichloroacetyl and the carboxyl groups are held in a fixed eclipsed configuration. Keto acid **2** cyclizes to a small extent in chloroform solution, as evidenced by the appearance of weak infrared bands for the hydroxyl and lactol carbonyl groups. The low intensities of the bands indicate that the extent of cyclization in the cyclohexane case is somewhat less than that of the previously reported cyclohexene derivative,[2] thus reflecting the greater energy required for the *cis* groups of cyclohexene to assume coplanarity. Keto acid **14** shows no evidence of a ring tautomer in solution consistent with a high stability of the keto acid form when the *trans* groups are held rigidly out of coplanarity.

Experimental Section[13]

Materials.—The sodium trihaloacetates were dried in a vacuum oven at 100° over phosphorous pentoxide. Dimethoxyethane (DME) was dried over calcium hydride and distilled. The anhydrides, except for the following, and other reagents were obtained from commercial sources.[14] *endo,cis*-Bicyclo[2.2.1]-heptane-2,3-dicarboxylic anhydride was prepared by catalytic hydrogenation of the cyclopentadiene–maleic anhydride Diels–Alder adduct as white crystals, mp 167–170° (lit.[15] mp 167.5–168°). Cyclohexane-1,2-dicarboxylic anhydride was prepared by catalytic hydrogenation of 4-cyclohexene-1,2-dicarboxylic anhydride as white crystals, mp 30–32° (lit.[16] mp 32°). *exo,cis*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**9**) was prepared by the Diels–Alder reaction of furan and maleic anhydride as white crystals, mp 123–124° (lit.[9] mp 125°). Catalytic hydrogenation afforded *exo,cis*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (**12**) as white crystals, mp 115° (lit.[9] mp 116–117°). Tetraphenyldihydrophthalic anhydride was prepared by the Diels–Alder condensation of tetraphenylcyclopentadienone and maleic anhydride as white crystals, mp 237–241° (lit.[17] mp 235–240°). Dehydrogenation with bromine afforded tetraphenylphthalic anhydride as tan crystals, mp 288–289° (lit.[17] mp 289–290°).

Preparation of Sodium Trihaloacetates.—The sodium trihaloacetates were prepared by neutralizing a methanolic solution of the trihaloacetic acid with sodium methoxide followed by evaporation of the solvent and drying.[2]

The salt was also prepared by an alternate procedure, which involved the slow addition of an ether solution of trichloroacetic acid to an ether suspension of sodium hydride, while cooling in a Dry Ice–carbon tetrachloride bath. The sodium salt precipitated and was removed by filtration and dried.

Reaction of Sodium Trihaloacetate with Anhydrides.—Sodium trihaloacetate and the anhydride, in 1:1 molar ratio, were allowed to react in dimethoxyethane (DME) solution as described previously.[2] The reactions were quite rapid and at 80° were complete within 2 hr as indicated by a decrease in the evolution of carbon dioxide. At 25°, 12–24 hr was usually required. In some cases the salt of the keto acid precipitated, and, when this occurred, the best method for obtaining the product was to collect the salt by filtration, dissolve it in water, and acidify. The keto acid or lactol precipitated and was collected and purified. If the salt did not precipitate from the reaction mixture, the reaction mixture was diluted with water, acidified, and extracted with ether. The products were crystallized, in most cases, from benzene, hexane, or mixtures of the two. Yields, melting points, and analytical data of the trichloromethyl and tribromomethyl products are given in Table IV. Reactions of sodium trifluoroacetate with phthalic anhydride in DME at 80° and Diglyme at 180° failed to provide any trifluoromethylated products.

Reaction of Sodium Trichloroacetate with Tetraphenyl-1,2-dihydrophthalic Anhydride.—A mixture of 22.7 g (0.05 mole) of the anhydride and 9.28 g (0.05 mole) of sodium trichloroacetate in 150 ml of DME was stirred and heated under reflux for 3 hr. A white solid was removed by filtration and was partially dissolved in water. The insoluble portion was recrystallized from

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(13) Melting points and boiling points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., Clark Microanalytical Laboratory, Urbana, Ill., and Olefin Research and Development Laboratory, Union Carbide Corp., South Charleston, W. Va. Infrared spectra were run on the Beckman IR-4 and IR-5 and on the Perkin Elmer 137 and 137-G spectrophotometers. The vapor phase chromatographs employed were the F & M Model 500 and the Beckman GC-2. The nmr spectra were recorded on the Varian HA-60 instrument with tetramethylsilane as the internal standard.

(14) Chlorendic anhydride was kindly supplied by Velsicol Chemical Corp., Chicago, Ill.

(15) M. S. Morgan, R. S. Tipson, A. Lowy, and W. E. Baldwin, *J. Am. Chem. Soc.*, **66,** 404 (1944).

(16) E. F. Jenkins and E. J. Costello, *ibid.*, **68,** 2733 (1946).

(17) O. Grummitt in "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 807.

chloroform to give 7.3 g of white crystals of tetraphenylphthalic anhydride, mp 287–288° (lit.[17] mp 289–290°). Acidification of the aqueous filtrate with dilute hydrochloric acid gave an additional 0.8 g for a total yield of 8.1 g (36%). The DME filtrate was concentrated to an oily solid. Extraction of the solid with methanol followed by evaporation afforded 13.5 g (59%) of unreacted starting material.

Reaction of Lactols 17 and 18 with Sodium Methoxide.—A solution of 0.2156 g (0.803 mmole) of the mp 176° isomer in 10 ml of methanol at 0° was titrated with 1.606 mmoles of sodium methoxide. The solution was acidified with dilute sulfuric acid and the methanol was evaporated under a stream of dry air. A white, oily solid separated and was dissolved in a mixture of ethyl acetate and chloroform. Evaporation of the extract gave 0.121 g (83%) of methyl 2-carboxypyridine-3-carboxylate (**20**) as white crystals, mp 102–105° (lit.[18] mp 106°).

Similar treatment of the lower melting isomer (mp 143°) gave an 80% yield of methyl 3-carboxypyridine-2-carboxylate (**19**), mp 120–122° (lit.[18] mp 123°).

Reaction of a Trichloromethyl Lactol with Base.—About 0.5 g of the trichloromethyl lactol from phthalic anhydride[2] was dissolved in a small amount of ethanol and titrated with sodium methoxide solution. At various stages during the titration the infrared spectrum was recorded. Initially, the spectrum showed only the single sharp peak of the lactol carbonyl at 1780 cm^{-1}. Over the course of the titration the intensity of the 1780-cm^{-1} peak decreased and two new peaks, one at 1720 (ketone) and the other at 1590 (carboxylate anion) appeared and gradually increased in intensity. These results indicate that the neutralization is accompanied by a ring opening to the keto acid salt.

Reaction of Sodium Trichloroacetate with Aldehydes.—A mixture of 26.5 g (0.25 mole) of benzaldehyde, 52.0 g (0.28 mole) of sodium trichloroacetate, and 100 ml of DME was stirred at room temperature for 80 hr. The reaction mixture was diluted with water and extracted with ethyl ether. The ether was removed by distillation and the residue was distilled under reduced pressure to give 10 g of benzaldehyde and 16.6 g (29.5%) of 1,1,1-trichloromethylphenylcarbinol (**21**): bp 106–108° (1.0 mm) and 146–147° (25 mm), n^{20}D 1.5673 [lit.[19] bp 158–160° (26 mm), n^{20}D 1.5673].

From a similar reaction between 12.8 g (0.1 mole) of 2-ethylhexanol and 20.4 g (0.11 mole) of sodium trichloroacetate was obtained 11.8 g (47.5%) of 1,1,1-trichloro-3-ethylheptan-2-ol, bp 87–88° (0.5 mm), along with some unreacted starting material. The infrared spectrum of the product was identical with that of an authentic sample prepared by the reaction of 2-ethylhexanol with chloroform.[20]

Reaction of Sodium Trichloroacetate with Acetyl Chloride.—A mixture of 19.6 g (0.25 mole) of acetyl chloride, 56.0 g (0.30 mole) of sodium trichloroacetate, and 200 ml of DME was heated under reflux for 40 min. The reaction mixture was diluted with water and extracted with ethyl ether. The ether extracts were washed with 5% sodium bicarbonate solution, then with water, and dried over magnesium sulfate. The solvent was evaporated and the remaining material (26 g) was distilled under reduced pressure to yield 8.6 g (21.3%) of 1,1,1-trichloroacetone, bp 52–56° (43.6 mm), n^{20}D 1.4590 [lit. bp 56–58° (40 mm)[2] and 57° (48 mm),[21] n^{20}D 1.4586[2]]. The infrared spectrum of the product was identical with that of an authentic sample of 1,1,1-trichloroacetone.

Reaction of Sodium Tribromoacetate with Benzaldehyde.—A solution of 20 g (0.063 mole) of DME was stirred at room temperature for 24 hr. The reaction mixture was added to 200 ml of water and extracted with ether. Evaporation of the ether afforded 7 g of an oil which exhibited infrared bands for both alcohol and ketone groups. Since crystallization proved difficult, the oil was heated under reflux with acetic anhydride for 3 hr. Upon addition of water, an oil separated, which, on crystallization from cyclohexane, gave 3.7 g (15.4%) of the acetate of tribromomethylphenylcarbinol as white crystals, mp 139–140° (lit.[22] mp 140°).

Anal. Calcd for $C_{10}H_9Br_3O_2$: C, 29.95; H, 2.24; Br, 59.78. Found: C, 30.20; H, 2.24; Br, 59.90.

Reaction of Sodium Trichloroacetate with Methyl Iodide.—A solution of 35.4 g (0.25 mole) of methyl iodide, 51.9 g (0.28 mole) of sodium trichloroacetate, and 100 ml of anhydrous DME was heated under reflux for 2 hr, at which time the evolution of carbon dioxide had ceased. The reaction mixture was cooled to room temperature, diluted with water, and extracted with ether. The ether extracts were combined, washed with water, and dried over magnesium sulfate. Evaporation of the ether left 19 g of material. A vpc analysis of the ether distillate showed that it contained 3 g of methyl iodide. The residue was distilled under reduced pressure (25 mm) at a kettle temperature of 110°. In the cold trap 6 g of material was collected. By vpc analysis the product was shown to consist of 1 g of methyl iodide, 4 g of DME, and 0.8 g (2.4%) of 1,1,1-trichloroethane.

In the identification of 1,1,1-trichloroethane, the material from the cold trap was analyzed by vpc on a 2-ft F & M silicone rubber column at 60°, a 12-ft 20% Montan Wax column at 100°, and a 4-ft 20% silicone rubber column at 75°. In each case, a peak homogeneous with that of an authentic sample of 1,1,1-trichloroethane was observed. A sample of the material producing this peak was collected by preparative-scale vpc. The infrared spectrum was identical with that of an authentic sample of 1,1,1-trichloroethane.

Rate Studies of the Decomposition of Sodium Trihaloacetates.—The sodium trihaloacetate (0.01 mole) in 50 ml of DME or heptane was allowed to decompose at room temperature or at the reflux temperature of the solvent. Similar experiments in which an equivalent amount (0.01 mole) of phthalic anhydride, or in one case, benzaldehyde, was present were also performed. The carbon dioxide evolved was trapped in standard barium hydroxide solution, and measured through titration of aliquots of the solution, after removal of the barium carbonate. The yields of carbon dioxide evolved under the various experimental conditions are reported in Table III as per cent of the theoretical amount.

Acknowledgment.—The use of the research facilities of Union Carbide Corp., South Charleston, W. Va., by K. E. A. and D. E. B. is gratefully appreciated. We thank the West Virginia University Cancer Research Committee and the American Cancer Society for partial support of this work. We appreciate the help of Mr. Robert R. Smith for recording the nmr spectra and Mr. Ronald F. Bargiband for the infrared studies of the lactol ring opening reaction with base.

Registry No.—**1**, 13135-95-0; **2**, 13135-96-1; **3**, 13135-97-2; **4**, 13135-98-3; **5**, 13135-99-4; **6**, 13136-00-0; **11**, 13136-01-1; **13**, 13136-02-2; **14**, 13136-03-3; **15**, 13136-04-4; **17**, 13136-05-5; **18**, 13136-06-6; **21**, 2000-43-3; **23**, 13136-07-7; sodium trichloroacetate, 650-51-1; sodium tribromoacetate, 1184-87-8; acetyl chloride, 75-36-5; benzaldehyde, 100-52-7; acetate of tribromomethylphenylcarbinol, 13136-09-9; methyl iodide, 74-88-4; 1,1,1-trichloroethane, 71-55-6.

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