Recrystallization from ethanol gave colorless plates: mp 207–208°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 257, 292, 301 mμ (ϵ 16,900, 3130, 3050); $\nu_{\max}^{\mathrm{KBr}}$ 1780 (C═O), 1769 (C═O), 1736 (C═O), 1592 cm^{-1} (C═C); mass spectrum *m/e* 590 (M$^+$, 8Cl), 488 [M$^+$ – $(CH_3CO)_2O$], 460 [M$^+$ – CO – $(CH_3CO)_2O$].

Anal. Calcd for $C_{16}H_6Cl_8O_7$: C, 32.36; H, 1.02; Cl, 47.75. Found: C, 32.37; H, 1.15; Cl, 47.76.

2,3′,4′-Trihydroxy-2′,3,4,5,5′,6,6′-heptachlorodiphenyl Ether.—Zinc dust (10 g) was added with stirring to a solution of **1** (10 g) in acetic acid (100 ml). The mixture was heated for 1 hr and poured into water after removal of the catalyst. The resulting crystals were collected and recrystallized from benzene to give colorless prisms, mp 180° (lit.[4] mp 181–182°), yield 7 g.

2,3′,4′-Triacetoxy-2′,3,4,5,5′,6,6′-heptachlorodiphenyl Ether. A.—Spirocyclohexenedione **1** (10 g) was dissolved in acetic anhydride (100 ml). The mixture was treated with zinc dust until the solution became colorless. After a few drops of sulfuric acid was added, the mixture was heated for 30 min on a water bath. The mixture was poured into water to give colorless prisms (6 g), mp 147–148° (lit.[4] mp 144°).

Anal. Calcd for $C_{18}H_9Cl_7O_7$: C, 36.92; H, 1.55; Cl, 42.39. Found: C, 36.97; H, 1.52; Cl, 42.35.

B.—Acetylation of 2,3′,4′-trihydroxy-2′,3,4,5,5′,6,6′-heptachlorodiphenyl ether (3 g) with acetic anhydride and sulfuric acid gave the colorless triacetate (2 g), mp 147–148°.

Spiro[2′,3′,4,5,5′,5′,6,7-octachloro-4′-hydroxy-1,3-benzodioxole-2,1′-[2]cyclopentene]-4′-carboxylic Acid (**6**).—Spirocyclohexenedione **1** (10 g) was heated on a water bath with 10% aqueous sodium hydroxide (10 ml) and dioxane (50 ml) for 2 hr. The mixture was poured into water and the resulting crystals were collected by filtration to yield 9 g of the crude material. Recrystallization of this compound from chloroform gave colorless prisms (**6**): mp 188° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3370, 2900 (OH), 1741 (C═O), 1636 cm^{-1} (C═C). Its molecular weight by a potentiometric titration with 0.1 *N* sodium hydroxide was 500.0 (theoretical 527.8) and it was a monobasic acid, pK_a' 3.55 in 10% ethanol solution. The pK_a' value was assumed to be the pH of half-neutralization.

Anal. Calcd for $C_{12}H_2Cl_8O_5 \cdot H_2O$: C, 27.31; H, 0.76; Cl, 53.74. Found: C, 27.54; H, 1.31; Cl, 53.62.

Spiro[2′,3′,4,5,5′,5′,6,7-octachloro-4′-hydroxy-1,3-benzodioxole-2,1′-[2]cyclopentene]-4′-carboxylic Acid Ethyl Ester (**7**). **A.**—Esterification of **6** (5 g) with ethanol and sulfuric acid gave 2 g of its ester (**7**): mp 176–177°; $\nu_{\max}^{\mathrm{KBr}}$ 3350 (OH), 1740 (C═O), 1638 cm^{-1} (C═C).

B.—To the solution of **1** (5 g) in ethanol (40 ml) was added hydrochloric acid (5 ml). The mixture was heated on a water bath for 2 hr and poured into water. The resulting crystals were collected, dried and recrystallized from ethanol to give colorless prisms, mp 176–177°, yield 2.5 g. This compound was identified as ethyl ester **7** of **6** by mixture melting point and infrared spectrum.

Anal. Calcd for $C_{14}H_6Cl_8O_5$: C, 31.26; H, 1.12; Cl, 52.73. Found: C, 31.07; H, 1.31; Cl, 52.59.

Hexachloro-3-cyclohexene-1,2-dione hydrate (**9**) was prepared by the method indicated by Zincke and Küster.[2] Chlorine was passed through a solution of pyrocatechol (20 g) in acetic acid (400 ml) under cooling. The reaction mixture was poured into water. The resulting precipitate was collected by filtration and recrystallized from ethanol to obtain colorless prisms (**9**, 39 g): mp 90–92° (lit.[2] mp 93–94°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 269 mμ (ϵ 8500); $\nu_{\max}^{\mathrm{KBr}}$ 1723 cm^{-1}.

Anhydrous Form (**8**).—The acetic acid was removed from the above reaction mixture *in vacuo* and the red residue was distilled to give a yellow liquid (**8**): bp 114–116° (0.35 mm) [lit.[2] bp 170° (18 mm)]; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 269 mμ (ϵ 8830); $\nu_{\max}$ 1778, 1720 cm^{-1}.

1-Hydroxy-2,3,4,4,5,5-hexachloro-2-cyclohexene-1-carboxylic acid was produced by the method reported by Prins.[6] A solution of **8** (12.7 g) in acetic acid (25 ml) was added with stirring to a 0.15-mol solution (40 ml) of sodium carbonate. The acid was set free by adding a mixture of acetic acid (25 ml) and hydrochloric acid (12 ml). The mixture was poured into water and the precipitate was filtered to afford colorless plates (8 g): mp 112–113° (lit.[2] mp 111°); $\nu_{\max}^{\mathrm{KBr}}$ 1730 cm^{-1} (C═O).

Registry No.—**1**, 19254-91-2; **2**, 19254-92-3; **3**, 19294-05-4; **4**, 19294-06-5; **5**, 19294-07-6; **6**, 19254-90-1; **7**, 19254-93-4; **8**, 19254-94-5; **9**, 19254-95-6.

The Thermolysis of Bromodifluoroacetic Anhydride

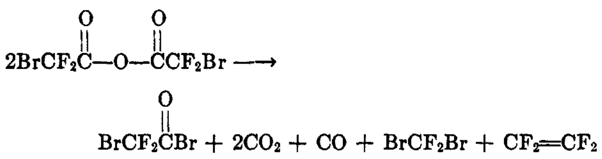
GEORGE A. L. GANT

Physical Chemistry Section, Chemical Research Department, Dow Corning Corporation, Midland, Michigan

Received May 31, 1968

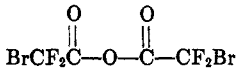
The thermal decomposition of fluorinated carboxylic acid anhydrides has been of interest for several years.[1,2] Kirshenbaum, *et al.*,[2] in a detailed study of the action of heat on the silver salts of perfluorocarboxylic acids, reports qualitative data on the thermolysis of perfluorobutyric anhydride. The reactions were carried out at autogenous pressures at 400–435° for 3 hr. The anhydride in the presence of Ag_2O gave the coupled product, C_6F_{14}. When, however, the thermolysis was attempted using a perfluoroanhydride *without* Ag_2O very little coupled product was realized.

In our studies, we have found that the thermolysis of bromodifluoroacetic anhydride proceeds almost quantitatively in the absence of an added catalyst (*i.e.*, Ag_2O), as represented by eq 1.



$$2\mathrm{BrCF_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CF_2Br} \longrightarrow \mathrm{BrCF_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Br} + 2\mathrm{CO_2} + \mathrm{CO} + \mathrm{BrCF_2Br} + \mathrm{CF_2{=}CF_2} \quad (1)$$

The coupled products in Kirshenbaum's work were stable, isolable compounds but, in the case of bromodifluoroacetic anhydride, the coupled product, $BrCF_2CF_2Br$, is unstable at high temperatures (*i.e.*, 300°). An independent experiment has confirmed the presence of Br_2 + polyperfluoroethylene and perhaps $CF_2{=}CF_2$, from the thermolysis of $BrCF_2CF_2Br$ under the same experimental conditions used in the thermolysis of



$$\mathrm{BrCF_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}CF_2Br}$$

Experimental Section

A. Apparatus.—The thermolysis system consisted of an airtight, heated vertical Vycor tube loosely packed with glass wool. The reactant entered the system through an addition funnel and was flushed down with anhydrous nitrogen. The products from the thermolysis were trapped in cold traps at –70°.

B. Procedure.—In a typical run, the Vycor tube and glass wool was heated to 150° for 2 hr under a stream of nitrogen. The temperature was then increased to 300° and bromodifluoroacetic anhydride (100 g, 0.30 mol) was allowed to enter slowly into the reaction zone.

The material condensing in the traps was then distilled through a 6-in. Vigreux column. Based on eq 1, a 76% yield (25 g) of $BrCF_2Br$, bp 23° (lit.[3] bp 20–25°), and 92% yield (33 g) of $BrCF_2C({=}O)Br$, bp 71°, was isolated. Infrared spectroscopy (CCl_4) shows two absorptions in the carbonyl region at 5.55 (strong) and 5.68 μ (weak) for $BrCF_2C({=}O)Br$. These bands are in accord with the spectra of known acid halides.[4] ^{19}F nmr shows a single at 59.1 ppm (relative to $CFCl_3$) and mass spectrometry gives a fragmentation pattern consistent with

---

(1) R. N. Haszeldine, British Patent 747,893 (1956).

(2) A. D. Kirshenbaum, A. G. Streng and M. Hauptschein, *J. Amer. Chem. Soc.*, **75**, 3141 (1953).

(3) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p 48.

(4) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 45.

$BrCF_2C(=O)Br$, with the molecular ion at 236 ($C_2Br_2F_2O$) and the most abundant *m/e* at 129 $(CF_2Br)^+$. The properties of the ethyl ester of $BrCF_2C(=O)Br$ were identical with a sample of authentic $BrCF_2C(=O)CH_2CH_3$ prepared from the corresponding acid and ethanol.[5]

Dibromodifluoromethane was identified mass spectrally with a molecular ion (CF_2Br_2) at 208 and the most intense *m/e* at 191 $(CFBr_2)^+$.

Carbon dioxide and carbon monoxide were identified mass spectrally when the decomposition was performed in such a way as to intercept the effluent gases from the thermolysis by an AEI mass spectrometer.

Registry No.—Bromodifluoroacetic anhydride, 7601-98-1.

Acknowledgments.—The author wishes to thank Mr. R. Gohlke for interpreting the mass spectral data and Dr. Y. Kim for his timely suggestions.

---

[5] G. A. Grindahl, W. X. Bajzer, and O. R. Pierce, *J. Org. Chem.*, **32**, 603 (1967).

O *vs.* C Alkylation of Ethyl Acetoacetate

W. J. LE NOBLE AND H. FRANK MORRIS

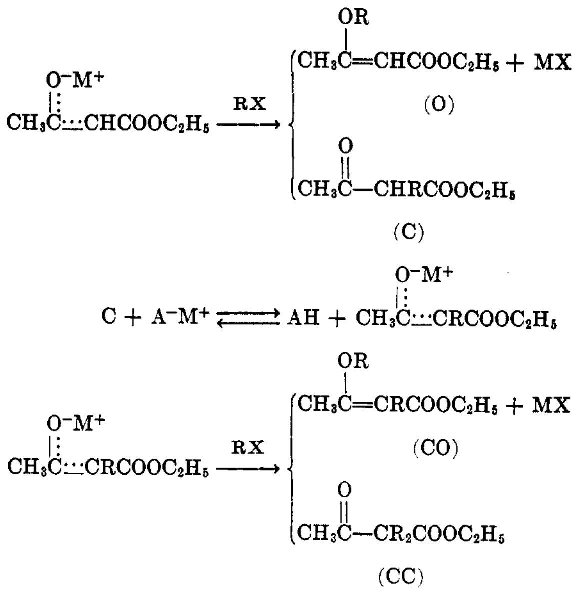
Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790

Received September 25, 1968

Following a number of isolated instances of O alkylation of ethyl acetoacetate,[1] several reports of the fairly general applicability of this reaction have appeared by now.[2-4] These studies have revealed that the O/C-alkylation ratio is remarkably dependent on the structure of the alkyl group, the solvent, the temperature and the cation; however, a more detailed investigation of these effects was hampered by the fact that the over-all yields are often rather poor. A recent communication concerning this reaction in hexamethylphosphoramide[5] (HMPA) prompts us to report our own results obtained with this solvent. We have found that the use of HMPA allows not only better yields, but also the highest O/C ratios yet observed. This reaction is therefore useful for studies of ambident anion behavior as well as for synthetic purposes. The alkylation of ethyl acetoacetate is described in Scheme I.

In most cases, the reaction was carried out at about 100°; the anion was generated by the addition of ethyl acetoacetate to an ethoxide salt followed by the careful removal of ethanol, and the dissolution of the remaining solid in HMPA. The alkylating agent was in each case injected slowly under the surface of the solution so as to minimize evaporation losses. The products could be readily separated from the starting material, the solvent and added water by means of extractions with *n*-pentane. The analysis of the four products could be carried out completely by means of either vpc or nmr, as detailed in the Experimental Section. The two methods agreed closely in each instance. Table I shows some of the results of the alkylation of the potassium salt of ethyl acetoacetate in HMPA. The reason for the improved yields is not known; however, alkylation and reduction of DMSO by alkylating agents are known reactions.[6] Of equal interest is the fact that the O/C ratios are a great deal higher in HMPA. This ratio increases along the series acetone < acetonitrile < DMSO ≈ dimethylformamide (DMF) ≈ dimethylacetamide ≈ N-methylpyrrolidone < HMPA (data in part from ref 3). A similar sequence (tetrahydrofuran (THF) < ethylene glycol dimethyl ether (glyme) < DMSO ≈ DMF) has been observed[7] in several alkylation reactions of sodium β-naphthoxide. It has been pointed out that the dielectric constants (in parentheses) of these solvents increase roughly in the same order: THF (7) ≈ glyme (7) < DMSO (45) ≈ DMF (37), and acetone (21) < acetonitrile (39) ≈ dimethylacetamide (37). However, the dielectric constant of HMPA is only equal to 30.[8] It is furthermore observed[3,4] that a rise in temperature causes an increase in O/C ratio although the dielectric constant rapidly declines with increasing temperature; we therefore prefer to think of these trends as a correlation with solvent basicity. Such basicity can be defined and measured in a number of ways. One of these is the downfield shift in parts per million of the proton signal of chloroform in infinite dilution in the solvent of interest, as compared to that in cyclohexane. This measure is used here because most of the appropriate data are available: THF, 0.80; acetone, 0.94; DMF, 1.30; DMSO, 1.34; HMPA, 2.03. To the limited extent then that data involving aprotic solvents are available, the O/C ratio appears to correlate

SCHEME I



---

[1] (a) G. D. Lander, *J. Chem. Soc.*, 729 (1900); (b) J. L. Simonsen and R. Storey, *ibid.*, 2106 (1909); (c) C. D. Hurd and K. Wilkinson, *J. Amer. Chem. Soc.*, **70**, 739 (1948); (d) S. J. Rhoads, R. W. Hasbrouck, C. Pryde, and R. W. Holder, *Tetrahedron Lett.*, 669 (1963); (e) K. R. Brower, R. L. Ernst, and J. S. Chen, *J. Phys. Chem.*, **68**, 3814 (1964).

[2] S. T. Yoffe, K. V. Vatsuro, E. E. Kugutcheva, and M. I. Kabachnik, *Tetrahedron Lett.*, 593 (1965).

[3] G. Brieger and W. M. Pelletier, *ibid.*, 3555 (1965).

[4] W. J. le Noble and J. E. Puerta, *ibid.*, 1087 (1966).

[5] A. L. Kurz, I. P. Beletskaya, A. Macias, and O. A. Reutov, *ibid.*, 3679 (1968).

[6] For a recent review of the properties of DMSO, see D. Martin, A. Weise, and H. J. Niclas, *Angew. Chem. Intern. Ed. Engl.*, **6**, 318 (1967).

[7] N. Kornblum, R. Seltzer, and P. Haberfield, *J. Amer. Chem. Soc.*, **85**, 1148 (1963).

[8] For an up-to-date review of the properties of HMPA, see H. Normant, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1046 (1967).