bp 60–80 °C). In a typtical experiment 35 mg of this fraction was dissolved in a mixture of 10% CH_2Cl_2 and 90% hexane. A small amount of insoluble material (~3 mg) was filtered off, and portions up to 2 mL of this solution were injected into a HPLC instrument (P = 240 bar; D = 19 mL/min). A first fraction was collected after a retention time of 8.5 min, and a second after 11 min. The solvent was removed at reduced pressure, and both fractions were characterized. Fraction 1 contained 8 mg of oT_4C_2 and fraction 2 contained 21 mg of $(oT_2CH)_2$. The experiment was repeated on larger amounts to characterize both compounds fully, resulting in 15% yield of oT_4C_2 and 40% yield of $(oT_2CH)_2$.

Fraction 1 (oT_4C_2): mp 227–229 °C; UV (cyclohexane) λ_{max} 215 nm (ϵ 37 100), 243 (23 800); 297 (14 300) [the bands at 243 and 297 nm are characteristic of tetraarylethenes (tetraphenylethene,[23] 239 (26 800), 309 (15 300); tetramesitylethene,[27] 257 (26 300), 311 (14 100); tetrakis(2,6-dimethyl-4-methoxyphenyl)ethene,[27] 261 (36 300), 323 (20 900))]; mass spectrum (only one significant peak, the parent peak at m/e 388), m/e 388 (100), 389 (33.16), 390 (5.46), calculated 389 (33.61), 390 (5.36); ^{1}H NMR (90 MHz, CD_2Cl_2, 30 °C, Me_4Si) 1.98 ppm (12 H, broad signal with a high field shoulder, CH_3), 6.97 (16 H, broad signal, arom); ^{1}H NMR (270 MHz, CD_2Cl_2, Me_4Si, methyl region) 30 °C, two unequal signals at 1.981 and 1.941 ppm; −75 °C, 2.072, 1.975, 1.931, 1.919, 1.911, 1.852; ^{13}C NMR (67.89 MHz, CD_2Cl_2, Me_4S, −40 °C, methyl region) eight singlets at 21.83, 21.66, 21.44, 20.89, 20.75, 20.68, 20.37, 20.05 ppm due to different rotamers (see text); 124.8–125.4 (six overlapping peaks (C_p; TPE[16,17] C_p, 126.4)), 126.8–133.6 (14 overlapping peaks (C_o + C_m; TPE[16,17] C_o, 131.8, and C_m, 127.6), 136.2–137.1 (5 overlapping peaks, C's bound to CH_3, C_1 in toluene,[50] 137.8), 141–143.6 (10 overlapping peaks (C_{ipso} + C_α), TPE[16,17], C_{ipso}, 143.7, C_α, 141.0). Anal. Calcd for $C_{30}H_{28}$: C, 92.72; H, 7.28. Found: C, 92.53; H, 7.47.

Fraction 2 ($oT_2CH)_2$: mp 259–260 °C; UV (cyclohexane) λ_{max} 210 nm (ϵ 40 400), 232 (s) (15 100); mass spectrum (base peak at m/e 195 due to the stable di-o-tolylmethylradical cation, peaks at m/e 388–390 are observed but with a distribution different from that of oT_4C_2), m/e 388 (100), 389 (61.18), 390 (16.78); ^{1}H NMR (90 MHz, CD_2Cl_2, Me_4Si, 30 °C) 1.94 ppm (s, CH_3, 12 H), 5.11 (s, CH, 2 H), 6.94–7.27 (m, H_{arom}, 16 H). Anal. Calcd for $C_{30}H_{30}$: C, 92.24; H, 7.76. Found: C, 91.36; H, 8.02.

Resolution Enhancement. The Lorentz–Gauss transformation[39,41] consists of a multiplication of the original free induction decay (FID) being a sum of exponentially decaying functions

$$\sum_k a_k e^{-t/T_2^k} e^{i\omega_k t}$$

by a function of the form C $\exp(At - Bt^2)$. In an ideal transformation, A is choosen such that $A = 1/T_2^l$, the original line width of line l. B is related to the Gaussian line width, and C is a scaling factor. The result of the multiplication for such a line is that only the factors $a_l e^{i\omega_l t} e^{-Bt^2}$ are left. Fourier transformation will then produce pure Gaussian lines with line widths $\sigma_l \simeq B^{1/2}$. For a line with a short T_2^j (broad lines), a residual exponential factor $a_j e^{(A_j - 1/T_2^j)t}$ with $[A_l - (1/T_2^j)] < 0$ will lead to a reduction of its intensity relative to the ideally enhanced line. Increasing the value of A such that $A_j - 1/T_2^j = 0$ to obtain Gaussian line shape for line j will overenhance the line l since for this line now an exponential factor $e^{(A_j - 1/T_2^j)t}$ with $A_j - 1/T_2^l > 0$ remains, which increases its intensity with respect to the broader line k. In normal spectra the spread in T_2 values is usually very small, giving only minor intensity deformations. During coalescence phenomena extremely broad lines are present that will be eliminated almost completely by the resolution-enhancement routine.

Instruments. UV spectra were recorded on a Perkin-Elmer Model 402 instrument. HPLC separations were performed on a Du Pont 830 Liquid Chromatograph instrument coupled to a Du Pont UV spectrophotometer (λ = 254 nm) and a Du Pont scriptor. Mass spectra were recorded on an MS 902 S AEI spectrometer. The column was a Lichrosorb Si 60-7, particle size 7 μm, number of theoretical plates 16 645. ^{1}H NMR spectra were recorded on a 90-MHz Bruker WH instrument; ^{1}H and ^{13}C spectra were obtained on a 270-MHz Bruker HX instrument (^{13}C frequency 67.89 MHz). Temperatures in NMR experiments were determined with a thermocouple. Elemental analysis was performed by the section of analytical research of Janssen Pharmaceutica, Belgium.

Acknowledgment. We thank Drs. J. Brocas, C. Hoogzand, and K. Jurkschat for helpful discussions. The assistance of Dr. M. Malinowski is kindly acknowledged. We thank also F. Resseler and M. Desmet for recording the NMR and mass spectra, respectively. R.D. acknowledges the Belgian IWONL for a predoctoral grant, and H.P. thanks the Belgian NFWO for financial support. Di-o-tolyl ketone was provided by Dr. C. Hoogzand and prepared by Ir. C. Adriaenssens. They are gratefully acknowledged.

Registry No. Di-o-tolyl ketone, 1018-97-9; tetra-o-tolylethene, 85407-51-8; 1,1,2,2-tetra-o-tolylethane, 32313-73-8.

Supplementary Material Available: NMR spectra for oT_4C_2 at various temperatures, isomerization schemes for oT_4C_2, magnitization exchange pattern of mode M_{2t}, and graph of possible dynamic behavior of isomer I_4 (13 pages). Ordering information is given on any current masthead page.

(50) E. Breitmaier and W. Voelter, "^{13}C NMR Spectroscopy, Monographs in Modern Chemistry 5", Verlag Chemie, Weinheim, West Germany, 1978, p 185.

Diaryldichlorocarbonyl Ylides Derived from Dichlorocarbene and Aromatic Ketones

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Received October 10, 1982

The thermal decomposition of phenyl(bromodichloromethyl)mercury (4) in the presence of benzophenone (2) in dry benzene at 80 °C resulted in α-chlorodiphenylacetyl chloride (6) as the only major initial product together with small amounts of dichlorodiphenylmethane (5) and carbon monoxide. Analogous products were observed from fluorenone (3). Dimethyl acetylenedicarboxylate (15) failed to trap the presumed intermediate dihalocarbonyl ylide from either ketone. Attempts to explain the difference in behavior between dihalocarbonyl ylides derived from benzaldehydes and diaryl ketones suggest that in the latter case a twist in the plane of the ylide caused by endo,endo interactions of a chlorine and an aromatic ring leads to rapid closure to oxirane 11 followed by rearrangement to acid chloride 6. Alternative explanations are also explored.

Although one of the recognized modes of reaction for carbonyl ylides is electrocyclic ring closure to the corresponding oxiranes,[1] this process has been shown to be insignificant for dihaloarylcarbonyl ylides 1 generated from

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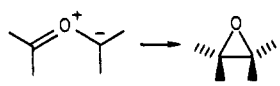
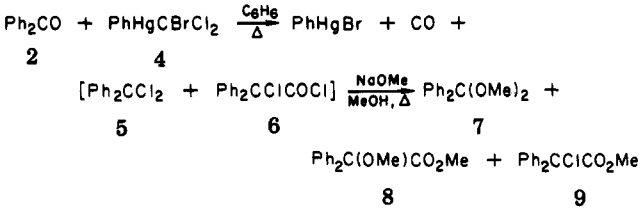


aromatic aldehydes and dihalocarbenes in benzene.[2,3] For such ylides halogen migration followed by loss of CO, or cycloaddition of the ylide with the aldehyde[2] or with an added electrophilic dipolarophile[3] is the dominant reactions as shown in Scheme I.

As a means toward understanding better how steric effects might influence pathways available for carbonyl ylide reactions, we now report on the reactions of benzophenone (**2**)[4] and fluorenone (**3**) with phenyl(bromodichloromethyl)mercury (**4**) in which electrocyclic ring closure of the intermediate carbonyl ylide appears to be the principal feature of the process.

Results and Discussion

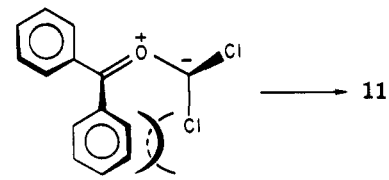
When an excess of ketone **2** was heated with mercurial **4** in benzene at 80 °C (inert atmosphere) for 4.5 h (adequate to ensure complete decomposition of the mercurial),



the major products after treatment of the reaction mixture with sodium methoxide in methanol at reflux were esters **8** and **9** derived from initially formed α-chlorodiphenylacetyl chloride (**6**).[5] A small amount of carbon monoxide and a comparable amount of acetal **7** derived from dichloride **5** were also noted. A control experiment in which ketone **2** and acid chloride **6** were heated in benzene with phenylmercuric bromide gave only unreacted starting materials. Results are summarized in Table I.

Possible routes to explain the dominant formation of acid chloride **6** are outlined in Scheme II.

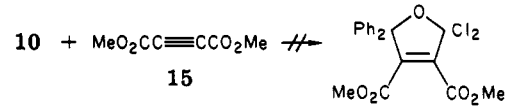
With reference to path a, steric interference between the endo groups[6] of ylide **10** force the structure to be twisted from a preferred planar configuration.[1a,8] Because the allowed thermal electrocyclic closure of ylide **10** to oxirane **11** requires conrotatory motion that corresponds to the twist shown in structure **10a**, ring closure of this ylide



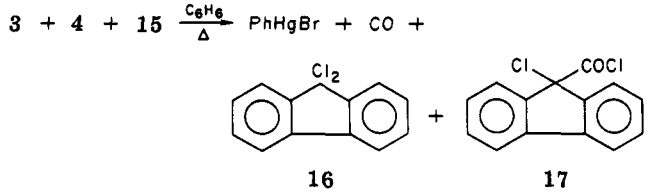
10a

would be expected to be greatly accelerated when compared to closure of a carbonyl ylide in which at least one endo group is hydrogen. In view of the propensity of dichlorooxiranes to rearrange to acid chlorides,[9] a rapid transformation of **11** to **6** would be anticipated.

Path b of Scheme II is analogous to the process shown to occur when benzaldehydes react with dihalocarbenes[2] (path b, Scheme I) except for the last step, which leads to acid chloride **6**. However, molecular models indicate that the cycloaddition of ylide **10** with benzophenone to give dioxolane **13** should be sterically unfavorable. In fact we have observed that the inclusion of dimethyl acetylenedicarboxylate (**15**) during the reaction of ketone **2** with mercurial **4** did not result in the carbonyl ylide being trapped by this agent even though such trapping was the dominant reaction for the ylides derived from benzaldehydes[3] (path c of Scheme I). Because acetylene **15** offers less steric inhibition toward cycloaddition with ylide **10** than would be anticipated from benzophenone, path



b of Scheme II seems highly improbable. This conclusion gains further support from the observation that fluorenone (**3**) in which the aromatic rings are coplanar (in contrast to benzophenone), but which must also form a twisted dichlorocarbonyl ylide, gave results identical with those of benzophenone. Products **16** and **17** are analogous to **5** and **6**, and no product was detected that involved the cycloaddition of acetylene **15** to an intermediate ylide.



16 **17**

With reference to path c of Scheme II, intermediates analogous to carbene **12** have been postulated to explain the formation of CO and benzal halides in the reaction of benzaldehydes with dihalocarbenes (path a, Scheme I).[2] However, in the latter study, even comparatively electron-rich benzaldehydes such as *p*-methoxybenzaldehyde and mesitaldehyde failed to exhibit acid chloride products analogous to **6**. These observations together with the known propensity of alkoxyhalocarbenes to break down with loss of CO[10] make path c of Scheme II a less likely explanation of the observed chemistry than path a.

Experimental Section

Elemental analyses were performed by the Department of Medicinal Chemistry at the University of Kansas or by Chema-

(1) (a) Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504. (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572 and references cited therein.

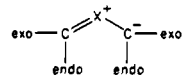
(2) Martin, C. W.; Lund, P. R.; Rapp, E.; Landgrebe, J. A. *J. Org. Chem.* **1978**, *43*, 1071.

(3) Gill, H. S.; Landgrebe, J. A. *J. Org. Chem.* **1983**, *48*, 1051.

(4) Martin, C. W.; Landgrebe, J. A. *J. Chem. Soc.* **1971**, 15.

(5) The 4.8:1 ratio of esters **8** and **9** was the same as that produced when an authentic sample of acid chloride **6** was subjected to identical treatment. Treatment of the reaction mixture from **2** and **4** with methanol and pyridine at 0 °C, conditions used in studying the reactions of substituted benzaldehydes with mercurial **4**,[2] resulted in ester **9** together with small (and comparable) amounts of carbon monoxide and dichloride **5**.

(6) The following convention is used for planar ylides with the general structure shown.[7]



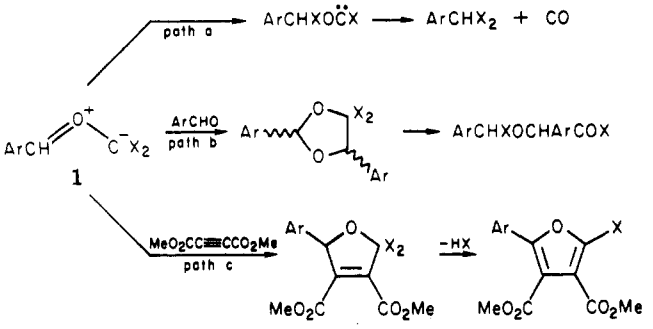
(7) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572.

(8) It should be noted that lack of planarity also exists between the two aromatic rings because of steric interactions of the nearest ortho hydrogens.

(9) McDonald, R. N. *Mech. Mol. Migr.* **1971**, *3*, 67.

(10) (a) Skell, P. S.; Starer, I. *J. Am. Chem. Soc.* **1959**, *81*, 4117. (b) *Ibid.* **1962**, *84*, 3962. (c) Sanderson, W. A.; Mosher, S. H. *Ibid.* **1961**, *83*, 5033. (d) Landgrebe, J. A. *Tetrahedron Lett.* **1965**, 105. (e) Skell, P. S.; Reichenbacher, P. H. *J. Am. Chem. Soc.* **1968**, *90*, 2309.

Scheme I



Scheme II

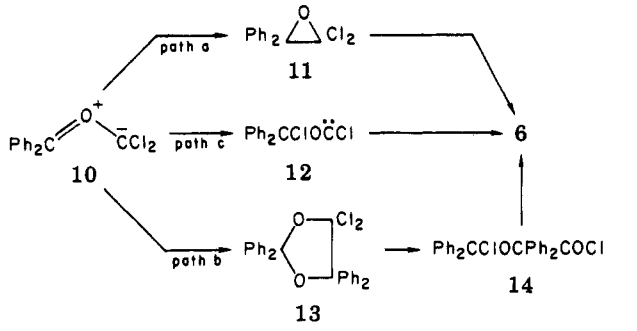


Table I. Summary of Selected Data for Reaction of Ph_2CO with $PhHgCBrCl_2$[a]

$(Ph_2CO)_0$ / $(PhHgCBrCl_2)_0$	solv vol, mL	yield of CO[b] esters 8 + 9, %		no. of runs
3-5	30-40	10 ± 2	46 ± 6	3
1.7	90-115	5[c]	28 ± 3	2

[a] Reactions done with 66 mmol of mercurial 4 in benzene for 4.5 h at 80 °C. [b] An equimolar amount of dichloride 5 was detected as acetal 7. [c] Determined in one run.

lytics, Inc., Tempe, AZ. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were obtained with either a Varian EM-360 or A-60 spectrometer. Precise m/e values were determined by peak matching with a Varian MAT CH-5 mass spectrometer interfaced with a PDP-8A computer. Other mass spectral data including GC–MS with a 25-m OV-101 capillary column were determined with a Riber R10-10 quadrupole mass spectrometer interfaced with a PDP-8A computer. Infrared data were recorded with a Beckman IR-8 spectrophotometer. A Perkin-Elmer Sigma 3B chromatograph equipped with a 25-m OV-101 capillary column and a flame ionization detector, and attached to a Hewlett-Packard 3390A recording integrator, was used for GC analyses. Thin-layer chromatograms were run on plastic sheets coated with silica gel 60F-254 (E. Merck). Flash chromatography was done with 32–63 μm silica gel (Woelm). All glassware and syringe needles were assembled hot and cooled under dry argon.

Reagent-grade benzene was dried with calcium hydride, distilled, and stored over 5-Å molecular sieves.

Phenyl(bromodichloromethyl)mercury (4) was prepared by the method of Seyferth and Lambert[11] in 65–70% yield; mp (109–110 °C dec (lit. [11] mp 108–111 °C dec). The mercurial was refrigerated. Benzophenone was recrystallized from petroleum ether (bp 35–60 °C) and dried over phosphorus pentaoxide in vacuo. Fluorenone was recrystallized from hexane/benzene and dried in the same manner.

Dimethyoxydiphenylmethane (7) was prepared in 96% yield from dichlorodiphenylmethane by the procedure of Mackenzie.[12] The product was recrystallized from ether: mp 105–108 °C (lit.[12] mp 106.5–107 °C); ^1H NMR (CCl_4) δ 7.34–7.51, 7.08–7.29 (m, 10 H, Ph), 3.04 (s, 6 H, OMe); IR (CCl_4) 3080, 3055, 2960, 2850, 1210, 1092, 1060, 990, 698 cm^{-1}.

Methyl α-Chlorodiphenylacetate (9). α-Chlorodiphenylacetyl chloride (1.93 g, 7.28 mmol) and methanol (4 mL) were dissolved in benzene (50 mL) and allowed to stand for 5.5 h at 25 °C followed by concentration of the solution and isolation of product ester by distillation (0.98 g, 3.76 mmol, 51.6%): bp 166 °C (1.8 torr); ^1H NMR (CCl_4) δ 7.31 (m, 10 H, Ph), 3.69 (s, 3 H, CO_2Me); IR (CCl_4) 3120 (sh), 3090, 3050, 3020 (sh), 2970, 1740, 1590, 1490, 1450, 1435 cm^{-1} in addition to others at lower wave numbers.

Anal. Calcd for $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.02. Found: C, 68.89; H, 4.88.

Methyl α-Methoxydiphenylacetate (8) was prepared from α-chlorodiphenylacetyl chloride by treatment with excess sodium methoxide in methanol at reflux for 3 h. The crude product was purified by column chromatography (Silicar CC-7, hexane/benzene mixtures); ^1H NMR (CCl_4) δ 7.05–7.50 (m, 10 H, Ph), 3.62 (s, 3 H CO_2Me), 3.10 (s, 3 H, OMe); IR (CCl_4) 1740 cm^{-1} (C=O).

9,9-Dichlorofluorene (16) was prepared by heating 9-fluorenone (5.0 g, 27.7 mmol) and phosphorus pentachloride (6.9 g, 33.3 mmol) at 110 °C (N_2) for 3 h followed by removal of phosphorus oxychloride at 1.5 torr, extraction of the residue with benzene, and evaporation of the solvent. Recrystallization of the crude product from diethyl ether gave white rhombic crystals (3.7 g, 15.7 mmol, 56.7%): mp 103–104 °C (lit.[13] mp 103 °C); ^1H NMR ($CDCl_3$) δ 7.0–7.8 (m, similar in appearance to fluorenone); MS (70 eV), m/e (rel intensity) 234 (M^+, 6.8), 199 (100), 163 (27.6). Precise m/e calcd for $C_{13}H_8Cl_2$, 234.000; found, 233.998 ± 0.001.

9-Hydroxyfluorene-9-carboxylic acid was prepared by the method of Standinger[14] to give a white solid (hot water), which was dried at 110 °C in vacuo, mp 162 °C (lit.[14] mp 166 °C).

9-Chlorofluorene-9-carbonyl chloride (17) was prepared from 9-hydroxyfluorenecarboxylic acid by the general procedure of Krapcho.[15] The product was purified by three recrystallizations from hexane to give a white solid: mp 114–115 °C (lit.[15] mp 111–113 °C); ^1H NMR ($CDCl_3$) δ 7.0–7.8 (m, similar in appearance to fluorenone); IR (CCl_4) 3020–3090 (w), 1812 (s), 1780 (s), 1600 (w), 1463 (w), 1450 (m), 1016 (m), 700 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.7 (s, C=O), 142.5, 140.7, (s, Ar) 131.2, 128.8, 125.6, 121.1 (d, Ar), CCl not unambiguously identified; MS (70 eV), m/e (rel intensity) 262 (M^+, 9.1), 199 (100), 163 (31.9). Precise m/e calcd for $C_{14}H_8OCl_2$, 261.995; found, 261.994 ± 0.002.

Anal. Calcd for $C_{14}H_8OCl_2$: C, 63.91; H, 3.06. Found: C, 63.78; H, 3.28.

Treatment of Benzophenone with Phenyl(bromodichloromethyl)mercury. The reaction was carried out in a manner analogous to that with benzaldehyde to produce phenylmercuric bromide, carbon monoxide, and various other products.[2] After filtration, the filtrate was divided, half being subjected to treatment with methanol and pyridine as described previously[2] and half being subjected to treatment with excess sodium methoxide in methanol at reflux for 4.5 h. The reaction mixture from sodium methoxide treatment was added to excess water, extracted with benzene, and the extracts dried ($MgSO_4$) and concentrated prior to analysis. The amount of dimethoxydiphenylmethane and of methyl α-methoxydiphenylacetate was determined from the OCH_3 (ether) peak of each compound. The area of the OCH_3 ether peak of the latter compound was subtracted from the CO_2CH_3 protons in the δ 3.50–3.70 region to determine the amount of methyl α-chlorodiphenylacetate.

Treatment of Benzophenone with α-Chlorodiphenylacetyl Chloride and Phenylmercuric Bromide. A mixture of benzophenone (16.4 g, 90.7 mmol), α-chlorodiphenylacetyl chloride (5.4 g, 20 mmol), and phenylmercuric bromide (19.7 g, 55 mmol) in benzene (115 mL) was heated at 80 °C for 4 h. The observed volume change of ≤9 mL corresponds to <0.03% yield of carbon monoxide (based on mercurial). Filtration resulted in phenylmercuric bromide (19.3 g, 98%), mp 276–278.5 °C.

(11) Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1969**, *16*, 21.
(12) Mackenzie, J. E. *J. Chem. Soc.* **1896**, *69*, 987.
(13) Smedley, I. *J. Chem. Soc.* **1905**, *87*, 1251.
(14) Standinger, H. *Chem. Ber.* **1906**, *39*, 3062.
(15) Krapcho, J. U.S. Patent 3 329 717, 1967; *Chem. Abstr.* **1967**, *67*, 116256p.

Portions of the filtrate were treated with methanol and pyridine and with sodium methoxide in methanol ass described in the general procedure. Absorptions in the NMR spectrum of a sample from the former procedure show only methyl α-chlorodiphenylacetate (outside of the phenyl region) while those of a sample from the latter procedure show only a mixture of methyl α-chlorodiphenylacetate and methyl α-methoxydiphenylacetate.

Treatment of Diaryl Ketones with Phenyl(bromodichloromethyl)mercury in the Presence of Dimethyl Acetylenedicarboxylate. A mixture of phenyl(bromodichloromethyl)mercury (2.0 g, 4.59 mmol), dimethyl acetylenedicarboxylate (1.9 g, 13.4 mmol), diaryl ketone (13.4 mmol), and dry benzene (15 mL) was heated at 80 °C under argon for 15–19 h. The progress of the reaction was monitored by TLC (ethyl acetate/hexane, 1:39) and GC (25-m OV-101 capillary). The reaction mixture was filtered through sintered glass (positive argon pressure), and the collected phenylmercuric bromide was washed with benzene. The benzene washings and filtrate were combined and examined by capillary GC.

The products from benzophenone were shown to be dichlorodiphenylmethane and α-chlorodiphenylacetyl chloride (area ratio 1:3) by careful comparison of capillary GC retention times with authentic samples. Treatment of the product mixture with dry methanol for 30 min at 25 °C converted the acid chloride to methyl α-chlorodiphenylacetate.

The products from fluorenone were shown to be 9,9-dichlorofluorene (very small amount) and 9-chlorofluorene-9-carbonyl chloride by careful comparison of capillary GC retention times with authentic samples.

Acknowledgment. We are grateful for a predoctoral fellowship for C.W.M. from the National Institutes of Health, a postdoctoral fellowship for H.S.G. from the Department of Chemistry and the College of Liberal Arts and Sciences of the University of Kansas, and for support from the General Research Fund of the University of Kansas. We thank Dr. Charles Judson and Robert Drake for providing mass spectrometer and ^{13}C NMR services and NIH-USPHS for Grants GM 27430, RR 07037, and RR 3603 for purchase of the instrumentation used.

Registry No. 2, 119-61-9; 3, 486-25-9; 4, 3294-58-4; 5, 2051-90-3; 6, 2902-98-9; 7, 2235-01-0; 8, 51552-62-6; 9, 54311-64-7; 10, 85422-07-7; 16, 25023-01-2; 17, 5101-06-4.

Notes

Resolution of *d,l*-2,3-Dibromobutane by Entrapment in Brucine Crystals. Refutation of a Contrary Report

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Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received October 4, 1982

Resolution of racemates of compounds lacking reactive functional groups (hydrocarbons, alkyl halides, etc.) has been difficult. We mentioned briefly in 1973 that the resolution of *d,l*-2,3-dibromobutane into both dextro- and levorotatory components could be effected with brucine since the dextrorotatory component was incorporated into the suspended solid brucine.[1] Since then we have learned from Professor S. Wilen[2] that he has used this method to obtain (+) and (−) fractions from a number of bromochlorofluoralkanes. As the original report is buried in a footnote to other work and as Chemical Abstracts searches failed to bring the method to light, we would like to call attention to this procedure by providing further confirmation. This has become important since contrary claims have been published:[4] "In our hands, contrary to these interesting claims, only *trans*-2-bromo-2-butene, the elimination product, and the active (−)-2,3-dibromobutane could be obtained from either the distillation or the brucine trapped material."

Winstein and Lucas[3] had applied brucine to *d,l*-2,3-dibromobutane to effect a kinetic resolution through destruction of the dextrorotatory component, presumably by dehydrohalogenation, leading to a sample with $[\alpha]_D$ −2.5°. There are numerous analogous examples in the literature employing this method, preferential destruction of one enantiomer. The method we describe has resulted in separation of both (+) and (−) samples, the former with $[\alpha]^{20}_D$ +26.4° (>70% of the maximum value). Isolation of both enantiomers as well as a high mass balance makes clear the fact (confirmed by the findings of Wilen) that interaction of alkyl halides with brucine is not a kinetic resolution by asymmetric destruction but rather is a preferential entrapment of one enantiomer.

This method is equally effective in resolving the antipodes of the *erythro*- and *threo*-2-bromo-3-chlorobutanes.[1]

Tanner and co-workers reported[4] a failure to reproduce these findings. However, a reading of their experiments indicates reaction times of 48, 70, 76 and 112 h instead of the 3 h we employed, resulting in a duplication of the earlier reported results of Lucas et al., which produced only (−)-2,3-dibromobutane and 2-bromo-2-butene.

Thus, with short reaction times resolution by preferential entrapment in the brucine crystals is the resolving process; with long contact times preferential dehydrohalogenation of dextrorotatory component occurs.[3,4]

Experimental Section

A slurry of brucine and *d,l*-2,3-dibromobutane (0.5:1.0 molar ratio) was agitated for 3 h at room temperature, after which the volatiles were removed by high-vacuum pumping to yield a levorotatory fraction. The solid residue was treated with aqueous acid and extracted to recover the dextrorotatory fraction. From 28.7 g of *d,l* dibromide there were recovered the following amounts of volatiles: 18.7 g, α_{365} −23.6°; 7.4 g, α_{365} +48.7°. This procedure was applied again with good effect to the dextrorotatory fraction, yielding 4.0 g of volatile fractions (α_{365} +18.8°) and 1.8 g of volatile fractions on acid release from the solids (α_{365} +90.2°). A third

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(2) Private communication: Prof. S. Wilen, The City College of The City University of New York, New York, NY 10031.

(3) Winstein, S.; Lucas, H. J. *J. Am. Chem. Soc.* **1939**, *61*, 1576, 2843. See also: Lucas, H. J.; Gould, C. W. *Ibid.* **1942**, *64*, 601. Winstein, S.; Buckles, R. E. *Ibid.* **1942**, *64*, 2780.

(4) Tanner, D. D.; Blackburn, E. V.; Kosugi, Y.; Ruo, T. C. S. *J. Am. Chem. Soc.* **1977**, *99*, 2722.

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