The Synthesis of Some 3′,2″-Dioxamethylene-Bridged *p*-Quaterphenyls and Related Compounds[1a]

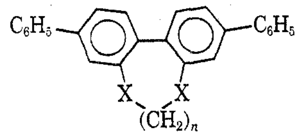
J. ERNEST SIMPSON,[1b] GUIDO H. DAUB,*[1c] AND F. NEWTON HAYES[1d]

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, and Biomedical Research Group, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

Received August 17, 1973

The synthesis of some *p*-quaterphenyls with $-O(CH_2)_nO-$ bridges across the 3′ and 2″ positions having $n = 1$, 2, 3, and 4 is reported. These compounds have been evaluated as liquid scintillator solutes, the results of which are being reported elsewhere. Attempts to prepare analogous compounds with $-NH(CH_2)_nNH-$ bridges across the 3′ and 2″ positions generally were unsuccessful; however, some products related to these are reported. The synthesis of the bridged *p*-quaterphenyls having –O– or –NH– across the 3′ and 2″ positions is also reported.

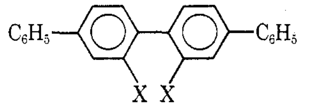
Earlier work by Taber[2] on the effect of noncoplanarity of some bridged *p*-quaterphenyls on the scintillator efficiency of the compounds prompted the synthesis of the following compounds for further studies.



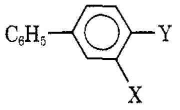
1, X = -O- **2**, X = -NH-
1a, $n = 1$ **2a**, $n = 1$
1b, $n = 2$ **2b**, $n = 2$
1c, $n = 3$ **2c**, $n = 3$
1d, $n = 4$ **2d**, $n = 4$

We are reporting the synthesis of the compounds **1a–d** along with attempts to prepare the compounds **2a–d** and certain other related compounds. The dioxepin **1a**, dioxocin **1b**, dioxonin **1c**, and dioxecin **1d** were each obtained from 2″,3′-dihydroxy-*p*-quaterphenyl (**3**) by reaction of the appropriate dihalide with **3** in DMF containing potassium carbonate.[3] Depending on the desired number of methylene groups in the bridge, either methylene iodide, 1,2-dibromoethane, 1,3-dibromopropane, or 1,4-dibromobutane was used to yield the respective bridged diethers **1a–d**.

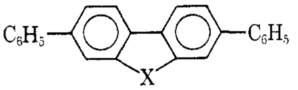
The 2″,3′-dihydroxy-*p*-quaterphenyl (**3**) was synthesized in several steps starting with commercially available 4-nitrobiphenyl (**4**), which was converted to 2-nitro-5-phenylphenol (**5**) by treatment with potassium hydroxide in diphenyl ether at 95° under an oxygen atmosphere. The yields in this hydroxylation step were quite good, running as high as 80%. Other procedures, such as using potassium hydroxide and toluene or benzene[4] without the oxygen atmosphere, were less successful, the yields generally being less than 20%.



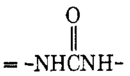
3, X = OH
9, X = OCH_3
12, X = NO_2
13, X = NH_2
15, X = NHTs

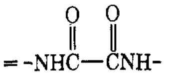


5, X = OH; Y = NO_2
6, X = OCH_3; Y = NO_2
7, X = OCH_3; Y = NH_2
8, X = OCH_3; Y = I
10, X = NO_2; Y = NH_2
11, X = NO_2; Y = I



14, X = O
17, X = NH

18, X =

$-NH\overset{O}{\overset{\|}{C}}NH-$

19, X =

$-NH\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}NH-$

Treatment of crude **5** with dimethyl sulfate and potassium carbonate[5] in anhydrous toluene gave the methyl ether **6** in an 87% yield. Reduction of **6** with Raney nickel and hydrazine[6] afforded a 68% yield of 3-methoxy-4-biphenylamine (**7**). Diazotization of **7** with sodium nitrite and hydrochloric acid followed by treatment of the resulting diazonium salt with potassium iodide resulted in an 81% yield of 4-iodo-3-methoxybiphenyl (**8**). Treatment of **8** with copper bronze at 200° afforded a 54% yield of 2″,3′-dimethoxy-*p*-quaterphenyl (**9**), which was cleaved to the desired **3** in 96% yield by refluxing with 57% hydriodic acid in glacial acetic acid. Thus, **3** was prepared in an overall yield of about 20% from 4-nitrobiphenyl (**4**).

Attempts to synthesize the analogous diazepine **2a**, diazocine **2b**, diazonine **2c**, and diazecine **2d** failed; however, several key intermediates and related compounds also of interest to us were prepared as discussed below.

3-Nitro-4-biphenylamine (**10**) prepared from 4-nitrobiphenyl (**4**) by modification of the procedure described by Campbell, Anderson, and Gilmore,[7] was diazotized and treated with potassium iodide to give a 55% yield of 4-iodo-3-nitrobiphenyl (**11**). Ullmann coupling of **11** afforded 2″,3′-dinitro-*p*-quaterphenyl (**12**), which was reduced with hydrazine in the presence of Raney nickel[8] to 2″,3′-diamino-*p*-quaterphenyl (**13**) in 77% overall yield.

Initially it was hoped that diazotization of **13** and treatment of the diazonium salt with water would yield 2″,3′-dihydroxy-*p*-quaterphenyl (**3**); however, the

---

(1) (a) From the dissertation presented by J. Ernest Simpson to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation was supported in part by a Research Grant from the Division of Biology and Medicine of the U. S. Atomic Energy Commission, Contract No. AT-(29-2)915. (b) Graduate Research Assistant, June 1963–Aug 1967. (c) University of New Mexico. (d) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. L. Taber, G. H. Daub, F. N. Hayes, and D. G. Ott, *J. Heterocycl. Chem.*, **2**, 181 (1965).

(3) J. E. Simpson, G. H. Daub, and F. N. Hayes, *J. Org. Chem.*, **38**, 1771 (1973).

(4) J. C. Colbert, W. Meigs, and R. L. Jenkins, *J. Amer. Chem. Soc.*, **59**, 1122 (1937).

(5) B. B. Day, *J. Sci. Ind. Res. (India)*, **3**, 338 (1945); *Chem. Abstr.*, **39**, 4597[9] (1945).

(6) D. Balcom and A. Furst, *J. Amer. Chem. Soc.*, **75**, 4334 (1953).

(7) N. Campbell, W. Anderson, and J. Gilmore, *J. Chem. Soc.*, 446 (1940).

(8) R. E. Moore and A. Furst, *J. Org. Chem.*, **23**, 1504 (1958).

major product isolated in 31% yield proved to be 3,7-diphenyldibenzofuran (**14**). Attempts to cleave **14** to yield 2″,3′-dihydroxy-*p*-quaterphenyl (**3**) proved futile.

Stetter[9] has reported the synthesis of some biphenyl derivatives similar to **2a–d** by treatment of the ditosyl derivative of 2,2′-diaminobiphenyl with dihalides of the type $Br(CH_2)_nBr$ where $n = 2$, 3, 4, and 5 in *n*-butyl alcohol containing sodium *n*-butoxide. The resulting bridged biphenyl was then hydrolyzed to the corresponding biphenyl with the $-NH(CH_2)_nNH-$ bridge across the 2 and 2′ positions.

In an effort to use Stetter's procedure for the synthesis of **2a–d**, the ditosyl derivative of **13** was prepared by addition of *p*-toluenesulfonyl chloride to a solution of **13** in anhydrous pyridine, affording a 96% yield of *N*,*N*′-ditosyl-2″,3′-diamino-*p*-quaterphenyl (**15**). However, treatment of **15** with sodium, *n*-butyl alcohol, and an appropriate dibromoalkane failed to give any of the desired bridged compounds. Other bases, such as sodium hydride, potassium carbonate, and potassium metal, were tried as well as different solvents, such as *N*,*N*-dimethylformamide, dimethyl sulfoxide, and *n*-amyl alcohol, but without success; however, in one case a 10% yield of the *N*,*N*′-ditosyl derivative (**16**) of 3,11-diphenyl-6,7,8,9-tetrahydro-5*H*-dibenzo[*f*,*h*][1,5]diazonine (**2c**) was obtained using *N*,*N*-dimethylformamide and potassium carbonate.

Attempts to remove the tosyl groups from **16** using sodium metal and *n*-amyl alcohol or using concentrated hydrobromic acid and phenol failed to give any of the desired **2c**, only starting material being recovered. Attempts to make the desired bridged compounds using the diamine **13** in a manner similar to that used for the analogous oxygen compounds **1** also failed.

Attention was then turned to some different approaches to the synthesis of **2a–d** and 3,7-diphenylcarbazole (**17**), which would be the nitrogen analog of 3,7-diphenyldibenzofuran (**14**). The carbazole **17** was indeed prepared in 75% yield by heating the diamine **13** with phosphoric acid.[10]

One approach to synthesis of **2a** might be through reduction of the corresponding compound with a carbonyl function at the 6 position. With this in mind 3,9-diphenyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*d*,*f*][1,3]diazepine (**18**) was prepared by treatment of the diamine **13** with urea[11] at 200°, affording a 91% yield of **18**. Attempts to reduce **18** with lithium aluminum hydride to the desired diazepine **2a** failed, yielding only recovered starting material.

A similar approach to **2b** was made by preparing 3,10-diphenyl-6,7-dioxo-5,6,7,8-tetrahydrodibenzo[*e*,*g*][1,4]diazocine (**19**) in 82% yield by treatment of the diamine **13** with oxalyl chloride in anhydrous toluene. However, reduction of **19** with lithium aluminum hydride failed to give anything but recovered starting material. Further studies on the synthesis of **2a–d** were abandoned.

Experimental Section[12]

2-Nitro-5-phenylphenol (**5**).—A mixture of 120 ml of diphenyl ether and 170 g of KOH, after mixing in a warm blender, was added to 67.2 g of 4-nitrobiphenyl, mp 113–114°. After stirring in an atmosphere of oxygen at 95° for 28 hr, benzene and water were added to the brick-red mixture. A bright orange solid (70 g) was collected by filtration and dissolved in 1.5 l. of water. Acidification gave 58 g (80%) of **5**, mp 103–104° (lit.[4] mp 103–103.3°).

3-Methoxy-4-nitrobiphenyl (**6**).—A 58-g (0.27 mol) portion of the crude 2-nitro-5-phenylphenol (**5**), mp 103–104°, was dissolved in 1 l. of dry toluene and 37.6 g (0.272 mol) of anhydrous potassium carbonate was added. To this mixture a solution of 41.9 g (0.33 mol) of dimethyl sulfate in 50 ml of dry toluene was added dropwise over 0.5 hr with the temperature maintained between 70 and 90°. The reaction mixture was heated on a steam bath for 24 hr, after which time the mixture had turned to a light orange slurry. The toluene layer was washed with 5% sodium hydroxide and then water. After drying over anhydrous sodium sulfate, the toluene solution was chromatographed through an alumina column (Woelm neutral, activity grade 1 alumina). Removal of the toluene from the eluates gave a light yellow oil which solidified upon cooling, and was recrystallized once from 95% ethanol affording 53.8 g (87% yield) of light yellow solid, mp 62–63.5°. Repeated crystallization from 95% ethanol gave an analytical sample of **6** as light yellow rods, mp 62–63.5°.

Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84. Found: C, 68.03; H, 4.99.

3-Methoxy-4-biphenylamine (**7**).—A 54-g (0.235 mol) portion of 3-methoxy-4-nitrobiphenyl (**6**), mp 62–63.5°, was dissolved in 1 l. of 95% ethanol, and 3–4 teaspoons of fresh Raney nickel mud[13] were added; a solution of 144 ml of anhydrous hydrazine in 75 ml of ethanol was added to this mixture at such a rate so as to maintain gentle reflux. When addition of the hydrazine was complete, the mixture was refluxed on a steam bath for 3 hr, after which the Raney nickel was removed by filtration. The solvent was removed using a rotary evaporator and replaced by dry ether Concentrated HCl (35 ml) was added to the ether solution and the amine hydrochloride separated. After filtering, the solid hydrochloride was dissolved in hot water and filtered, and the cooled aqueous solution was made basic with 10% sodium hydroxide, whereupon the free amine separated. The free amine was filtered, washed well with water, and dried. Recrystallization from cyclohexane afforded 32 g (68% yield) of **7** as tan plates, mp 74–76°. The acetyl derivative of **7** was prepared and recrystallized twice from cyclohexane, giving an analytical sample of 2-methoxy-4-phenylacetanilide, mp 117.5–118.5°.

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27. Found: C, 74.49; H, 6.34.

4-Iodo-3-methoxybiphenyl (**8**).—A mixture of 32.4 g (0.162 mol) of 3-methoxy-4-biphenylamine (**7**), mp 74–76°, 300 ml of water, and 42 ml of concentrated hydrochloric acid was cooled to 0° and a solution of 11.8 g (0.170 mol) of sodium nitrite in 100 ml of water was added dropwise with stirring over 1.5 hr with the temperature being maintained at 0–2°. After stirring for an additional 1 hr at 2–3°, the excess sodium nitrite was destroyed with sulfamic acid and the diazonium salt was decomposed by the addition of a solution of 134 g (0.81 mol) of potassium iodide in 100 ml of water. The pasty mixture was stirred at 5–10° for 0.75 hr and at room temperature for 1.0 hr. Considerable foaming was encountered, and, after all of the nitrogen had been expelled, the dark brown, oily product was extracted with benzene. The benzene layer was washed successively with 10% aqueous sodium bisulfite, 10% aqueous sodium hydroxide, and water. The benzene solution was dried (potassium carbonate) and chromatographed (Woelm, neutral, activity grade 1 alumina). The benzene was removed from the eluates, and the iodo compound **8** was obtained as a viscous, light yellow oil which was sufficiently pure for the next step. Crystallization from 95% ethanol gave 40.8 g (81% yield), mp 48–50°. Repeated crystallization from 95% ethanol gave an analytical sample of **8** as colorless needles, mp 51–52.5°.

Anal. Calcd for $C_{13}H_{11}OI$: C, 50.34; H, 3.58. Found: C, 50.75; H, 3.82.

2″,3′-Dimethoxy-*p*-quaterphenyl (**9**).—4-Iodo-3-methoxybiphenyl (**8**), 4.4 g (0.014 mol), was heated at 190–210°, and 3.16 g (0.050 mol) of copper bronze (O. Hommel Co., Pittsburgh, Pa.,

---

(9) H. Stetter, *Chem. Ber.*, **86**, 380 (1953).

(10) E. Tauber, *Chem. Ber.*, **26**, 1703 (1893).

(11) St. von Niementowski, *Chem. Ber.*, **34**, 3325 (1901).

(12) All melting points were taken in Pyrex capillary tubes in a Hoover-Thomas melting point apparatus and are uncorrected.

(13) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper Chromium Oxide and Nickel," The University of Wisconsin Press, Madison, Wis., 1937.

5743) was added in small portions over 1.5 hr. The reaction mixture was stirred (dry nitrogen) during the addition and for an additional 4 hr. The reaction mixture was cooled and extracted with hot benzene, and the benzene solution was filtered and chromatographed (Woelm, neutral, activity grade 1 alumina). After removal of the benzene, 1.4 g (54% yield) of fluorescent solid, mp 160–163°, was obtained. Repeated crystallization from ethyl acetate gave an analytical sample of **9** as colorless plates, mp 162.5–163.5°.

Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.48; H, 6.28.

2'',3'-Dihydroxy-*p*-quaterphenyl (3).—A mixture of 2.5 g (6.8 mmol) of 2'',3'-dimethoxy-*p*-quaterphenyl (**9**), mp 161.5–163°, 64 ml of 57% hydriodic acid, and 32 ml of glacial acetic acid was refluxed and vigorously agitated for 24 hr, after which time the reaction mixture was poured into ice water. The precipitated solid was collected and dried, affording 2.2 g (96% yield) of colorless product, mp 231–233°. Two recrystallizations from toluene gave an analytical sample of **3**, mp 232–233°.

Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.87; H, 5.32.

3,9-Diphenyldibenzo[*d,f*][1,3]dioxepin (1a).—A mixture of 1.5 g (4.5 mmol) of 2'',3'-dihydroxy-*p*-quaterphenyl (**3**), mp 231–233°, and 1.35 g (9.77 mmol) of anhydrous potassium carbonate in 100 ml of dry *N,N*-dimethylformamide was warmed to 80° and a solution of 1.25 g (4.65 mmol) of methylene iodide in 50 ml of dry *N,N*-dimethylformamide was added with stirring over 2.5 hr.[3] The reaction mixture was heated for an additional 22 hr at 80–90° and was then poured into water and extracted with benzene. The benzene layer was washed twice with 5% sodium hydroxide and water, dried (potassium carbonate), and chromatographed (Woelm neutral, activity grade 1 alumina). Concentration of the eluates yielded a colorless solid which upon recrystallization from cyclohexane afforded 0.7 g (44% yield) of **1a** as colorless needles, mp 147.5–149°. Repeated crystallization from cyclohexane gave an analytical sample, mp 148–149°.

Anal. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.64; H, 5.08.

3,10-Diphenyl-6,7-dihydrodibenzo[*e,g*][1,4]dioxocin (1b).—The procedure used was essentially the same as that used for **1a** (except that 1,2-dibrpomoethane replaced the methylene iodide), resulting in a 36% yield of a colorless solid, mp 235–236.5°. An analytical sample of **1b**, mp 235.8–236.8°, was obtained by repeated crystallization fom benzene.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.81; H, 5.60.

3,11-Diphenyl-7,8-dihydro-6*H*-dibenzo[*f,h*][1,5]dioxonin (1c).—The procedure used was essentially the same as that used for **1a** (but using 1,3-dibromopropane), resulting in a 49% yield of colorless solid, mp 218–220°. Recrystallization from a cyclohexane–benzene solvent pair led to a more insoluble crystalline form, mp 224.5–225.5°, and a more soluble form, mp 218–220°. Repeated crystallization from cyclohexane–benzene yielded analytical samples of both types of melting points, 219–220.5 and 224.5–225.5°. A sample of solid, mp 219–220.5°, was melted, allowed to cool, and remelted, mp 224–224.5°. Thin layer chromatography indicated that both samples were pure and the same. A mixture melting point (222–225°) was taken.

Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found (mp 219–220.5°): C, 85.73; H, 5.69. Found (mp 224.5–225.5°): C, 85.84; H, 5.97.

3,12-Diphenyl-6,7,8,9-tetrahydrodibenzo[*g,i*][1,6]dioxecin (1d).—The procedure used was the same as that described for **1a** (using 1,4-dibromobutane), resulting in a 66% yield of colorless solid, mp 185.7–186.5°. Repeated crystallization from a cyclohexane–benzene solvent pair gave an analytical sample of **1d**, mp 186.0–186.5°.

Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.54; H, 6.10.

4-Iodo-3-nitrobiphenyl (11).—Concentrated sulfuric acid (75 ml) was cooled to 5° and to this was added gradually 11.7 g (0.170 mol) of sodium nitrite. The resulting solution was warmed to 70° on a steam bath and then cooled to 10°, at which time a hot solution of 33 g (0.154 mol) of 3-nitro-4-biphenylamine (**10**), mp 169–171°, in 600 ml of glacial acetic acid was added with stirring over a 2-hr period, the temperature being maintained between 10 and 15°. The resulting diazonium salt was decomposed by the addition of a solution of 80 g (0.48 mol) of potassium iodide in 80 ml of water over a 15-min period below 15°. Stirring was continued for 16 hr at room temperature, after which time the reaction mixture was diluted with water, and sodium bisulfite was added to reduce any free iodine. The aqueous mixture was extracted with benzene and the benzene layer was washed four times with 75 ml of 10% sodium hydroxide and finally several times with water. After drying (magnesium sulfate), the benzene layer was concentrated and cyclohexane was added to produce a 10:1 ratio of cyclohexane to benzene. This solution was chromatographed (Woelm, neutral, activity grade 1 alumina) and the column was eluted with solutions of increasing benzene concentration. After the solvent was removed from the eluates, the resulting crude yellow solid was recrystallized from methanol, affording 27.7 g (55% yield) of **11** as yellow rods, mp 73–75°. Repeated crystallization gave an analytical sample of **11**, mp 74.5–75° (reported[14] mp 74°).

2'',3'-Dinitro-*p*-quaterphenyl (12).—A Pyrex test tube was charged with 4.67 g (0.0143 mol) of **11**, mp 73–75°, and heated to 190° in a Wood's metal bath. To this melt 2.7 g (0.046 mol) of copper bronze (Hommel 5743) was added with stirring in small portions over 30 min, keeping the reaction temperature between 190 and 205°. The initially fluid reaction mixture gradually solidified with addition of the copper bronze and after an additional 30 min the reaction mixture had turned to a powdery solid. The reaction mixture was cooled and extracted with 200 ml of hot toluene in three portions, and the toluene solution was filtered to remove the excess copper bronze. Concentration of the filtrate afforded 2.36 g (83% yield) of a light-sensitive yellow solid, mp 238.0–239.5°. Repeated crystallization from toluene gave a pure sample of **12**, mp 239.5–241.0° (reported[14] mp 242°).

2'',3'-Diamino-*p*-quaterphenyl (13).—To a stirred mixture of 8.69 g (0.0219 mol) of **12**, mp 238.0–239.5°, and two teaspoons of freshly prepared Raney nickel mud[13] in 950 ml of 95% ethanol was added dropwise 39 ml of 95% hydrazine over a period of 1 hr. The reaction mixture was kept under gentle reflux by warming on a steam bath during the addition of the hydrazine and for an additional 4 hr, after which time the reaction mixture was diluted with 500 ml of ice water. The reaction mixture was filtered and the precipitate was extracted with 300 ml of DMF and filtered to remove the Raney nickel. The filtrate was added to 500 ml of water, whereupon a white solid separated. This crude product was collected, washed well with water, and air dried. The solid was recrystallized from toluene containing a small amount of DMF to give 6.9 g (93% yield) of **13** as colorless plates, mp 225–227°. Repeated crystallization from toluene gave an analytical sample, mp 225.8–227.0° (reported[14] mp 217°).

Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99. Found: C, 85.89; H, 5.85.

3,7-Diphenyldibenzofuran (14).—A slurry of 1.68 g (5.0 mmol) of **13**, mp 225–227.0°, in 20 ml of glacial acetic acid was added dropwise to a stirred solution of 0.69 g (10.0 mmol) of sodium nitrite in 5 ml of concentrated sulfuric acid while the temperature was kept between 5 and 12°. After the addition period, the reaction mixture was stirred at 10° for an additional 30 min; 50 ml of water was then added, whereupon the reaction mixture turned to a clear red color. The solution was heated on a steam bath for 10 hr with nitrogen being evolved and a brown solid separating The crude product was filtered, and three recrystallizations from benzene (Norit) afforded 0.5 g (31% yield) of **14** as light pink plates, mp 247.5–249° (reported[15] mp 248°).

3,7-Diphenylcarbazole (17).—The synthesis of **17** was accomplished by heating 1.0 g (3.0 mmol) of **13**, mp 225.5–227.0°, with 3 ml of concentrated phosphoric acid at 190–200° for 3–4 hr. The crude product was recrystallized three times from DMF, affording 0.72 g (75% yield) of an analytical sample of **17**, mp 349.5–351.5°, as fine, colorless needles.

Anal. Calcd for $C_{24}H_{17}N$: C, 90.25; H, 5.37; N, 4.39. Found: C, 90.25; H, 5.64; N, 4.28.

3,9-Diphenyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*d,f*][1,3]diazepine (18).—An intimate mixture of 0.34 g (1.0 mmol) of **13**, mp 225.5–227.0°, and 0.06 g (1.0 mmol) of urea was heated to a melt at 200°. A solid reformed after a minute during which time ammonia was evolved, and after heating for several minutes more, the reaction mixture was cooled. The solid material was

---

(14) H. O. Wirth, R. Mueller, and W. Kern, *Makromol. Chem.*, **77**, 90 (1964).

(15) H. O. Wirth, G. Waese, and W. Kern, *Makromol. Chem.*, **86**, 139 (1965).

taken up in hot DMF, filtered, and water was added to precipitate the crude product which was collected, affording 0.33 g (91% yield) of a colorless solid, mp 389–391°. Repeated crystallization from DMF–water solvent pair gave an analytical sample of **18**, mp 390–392°.

Anal. Calcd for $C_{25}H_{18}N_2O$: C, 83.13; H, 5.01. Found: C, 82.91; H, 5.02.

An attempt to reduce **18** using lithium aluminum hydride in anhydrous diglyme yielded only unreduced **18** and none of the desired **2a**.

3,10-Diphenyl-6,7-dioxo-5,6,7,8-tetrahydrodibenzo[*e*,*g*][1,4]-diazocine (19).—Two grams (6.0 mmol) of **13**, mp 225.0–227.0°, was dissolved in 250 ml of anhydrous toluene and to this refluxing solution 0.93 ml (7.5 mmol) of oxalyl chloride in 100 ml of anhydrous toluene was added dropwise with stirring. A colorless solid separated immediately. After refluxing for an additional 30 min, the reaction mixture was cooled, filtered, washed with toluene, and dried at 125° for 24 hr. The product proved to be insoluble in several solvents, and was finally triturated with hot DMF and filtered. This process was repeated twice, affording 1.9 g (82% yield) of **19** as a colorless powder, mp above 400°.

Anal. Calcd for $C_{26}H_{18}N_2O_2$: C, 79.99; H, 4.64. Found: C, 79.65; H, 4.26.

Lithium aluminum hydride reduction of **19** in anhydrous diglyme yielded only recovered **19** and none of the desired reduction product **2b**.

Registry No.—**1a**, 42447-99-4; **1b**, 42448-00-0; **1c**, 42448-01-1; **1d**, 42448-02-2; **3**, 42448-03-3; **5**, 18062-89-0; **6**, 42271-42-1; **7**, 42271-43-2; **7** acetyl derivative, 42271-44-3; **8**, 42271-45-4; **9**, 42271-46-5; **10**, 4085-18-1; **11**, 2499-68-5; **12**, 2499-69-6; **13**, 2499-76-5; **17**, 42448-04-4; **18**, 42448-05-5; **19**, 42448-06-6; diphenyl ether, 101-84-8; 4-nitrobiphenyl, 92-93-3; methylene iodide, 75-11-6; 1,2-dibromoethane, 106-93-4; 1,3-dibromopropane, 109-64-8; 1,4-dibromobutane, 110-52-1.

A New Ring Expansion Reaction. V. The Decomposition of the Magnesium Salts of Various 1-(1-Bromo-1-methylethyl)-1-cycloalkanols. Electrophilic Addition to Isopropylidenecycloalkanes

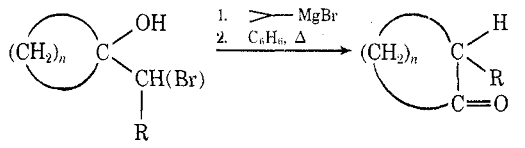
ANTHONY J. SISTI* AND M. MEYERS

Department of Chemistry, Adelphi University, Garden City, New York 11530

Received June 11, 1973

The synthesis of some 2,2-dimethylcycloalkanones is described. They were prepared from the decomposition of the magnesium salts of various halohydrins by a ring-enlargement procedure previously described. The necessary halohydrins were prepared from an electrophilic addition reaction with aqueous NBS and the isopropylidenecycloalkanes. The reasons for the observed selective orientation of the bromo and hydroxyl groups are discussed.

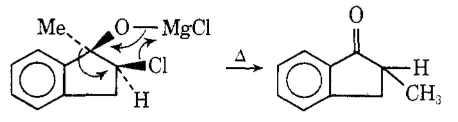
Preliminary papers[1] have reported a new ring-enlargement procedure[2] entailing the decomposition of the magnesium salts of appropriate halohydrins (eq 1).



(1)

R = CH_3 and C_6H_5; n = 4, 5, 6, and 7

Our results were in accord with those of Geissman and Akawie,[3] who extensively studied the reaction producing ketones *via* the decomposition of the magnesium salts of halohydrins. They observed that primary halides rearrange only when a good migrating group is involved but that secondary and tertiary halides rearrange regardless of the migrating group. From their stereochemical studies, they concluded that the halo and hydroxyl groups must be cis (or be able to attain the cis conformation in nonrigid systems) to effect the rearrangement. Trans isomers lead to extensive decomposition, making an epoxide intermediate for the reaction unlikely and leaving as most plausible a pinacol-type mechanism (eq 2).



(2)

This paper describes the synthesis of various 2,2-dimethylcycloalkanones by the new ring-enlargement procedure,[1] as starting materials for which we required halohydrins of the type depicted in **1**. In a preliminary communication,[4] we reported that isopropylidenecyclopentane, when treated with aqueous *N*-bromosuccinimide (NBS), yielded **1** (n = 4), the structural assignment for which was confirmed by the conversion of its magnesium salt to 2,2-dimethylcyclohexanone[5] in 54% overall yield. Additional confirmation has now been furnished by examination of the nmr spectrum, which reveals, from the location of the methyl signal (τ 8.2), that the bromine is indeed attached to the exocyclic carbon atom.[6] It was also reported[4] that isopropylidenecyclohexane, when treated with aqueous NBS, gave a halohydrin **2** *isomeric* with **1** (n = 5). The structure **2** was verified by decomposition of the magnesium salt, which yielded only 1-acetyl-1-methylcyclohexane in 66% overall yield. Further

---

[1] A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968); **35**, 2670 (1970).

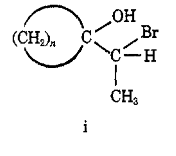
[2] For an excellent recent review, see C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

[3] T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.* **73**, 1993 (1951).

[4] A. J. Sisti, *Tetrahedron Lett.*, 3305 (1970).

[5] The vpc revealed the presence of a 5–10% contaminant, presumably methyl 1-methylcyclopentyl ketone based upon the same retention time as that of an authentic sample [A. J. Sisti and A. C. Vitale, *J. Org. Chem.*, **37** 4090 (1972)] and the nmr spectrum (τ 8.0 and 8.8, two small sharp singlets) It is presumed that the ketone arose from the rearrangement of small amounts of the corresponding epoxide and/or small amounts of the magnesium salt of the halohydrin isomeric with **1** (n = 4).

[6] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 136. Model compounds i show the nmr methyl signal at τ 8.3 (doublet); see A. J. Sisti, *J. Org. Chem.*, **35**, 2670 (1970).



i