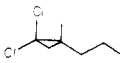
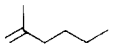
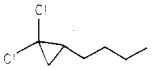
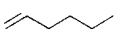
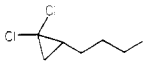
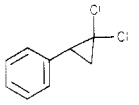
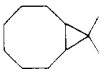
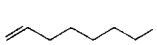
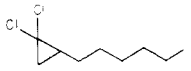
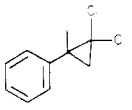
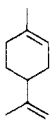
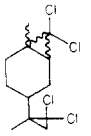
Table I. Dichlorocarbene Addition to Alkenes

reactant	product	time, %	isolated yield, %
		0.7	74
		1.8	80
		1.0	96
		3.0	93
		3.0	62
		1.0 16.0 20.0	96 31 [a] 38 [b]
		5.0	99
		6.5	81
		1.5	97
		3.0	95

[a] Mechanical stirring only. [b] Ultrasonic irradiation only.

Table II. Relative Reactivities toward Dichlorocarbene Addition

alkene	NaOH/$CHCl_3$ [a] (sonication and stirring), 30-40 °C	$KOC(CH_3)_3$/$CHCl_3$, [b] -15 °C
2,3-dimethyl-2-butene	57.2	53.7
2-methyl-1-pentene	4.2	
cyclohexene	1.0	1.0
1-hexene	0.2	0.2

[a] Reaction of 5 mmol of alkene plus 5.0 mmol of cyclohexene (reference standard) with 0.5 mmol of NaOH in 20 mL of $CHCl_3$. [b] See ref 6.

7 spectrometers, respectively. Product mixtures were analyzed by GLC on a Hewlett Packard Model 5830 A flame-ionization instrument (2 ft × 0.125 in. UCW-982 on Chromosorb W column). Ultrasound was produced with a L&R T-9 (Sargent Welch) bath-type sonicator (45 kHz, 35 W).

General Procedure for Preparation of Dichlorocyclopropanes. Procedures similar to that used for the conversion of styrene to 1,1-dichloro-2-phenylcyclopropane were followed for all of the reactions described in Table I. A mixture of powdered NaOH (0.8 g, 20 mmol) and styrene (0.21 g, 2.0 mmol) dissolved in 20 mL of chloroform was placed in a 100-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer (standard 4-cm curved Teflon blade). The flask was immersed in a sonic cleaner and was positioned approximately 0.5 in. above the floor of the cleaning bath. The mixture was then simultaneously stirred and irradiated with ultrasound for 1.5 h (the temperature of the bath never exceeded 40 °C). Analysis of the liquid phase (GLC) indicated the complete disappearance of styrene. The contents was then centrifuged and the organic layer separated. After chloroform was removed under reduced pressure, the residue was dissolved in ether, washed with water, dried ($MgSO_4$), and distilled (Kugelrohr) to give 0.36 g (95%) of 1,1-dichloro-2-phenylcyclopropane having an IR and NMR spectrum which was identical with that of an authentic sample.

Registry No. 2,3-Dimethyl-2-butene, 563-79-1; 2-methyl-1-pentene, 763-29-1; 2-methyl-1-hexene, 6094-02-6; cyclohexene, 110-83-8; 1-hexene, 592-41-6; styrene, 100-42-5; cyclooctene, 931-88-4; 1-octene, 111-66-0; α-methyl styrene, 98-83-9; 1-methyl-4-(1-methylethenyl)-cyclohexene, 138-86-3; 1,1-dichloro-2,2,3,3-tetramethylcyclopropane, 3141-45-5; 1-(1-methyl-2,2-dichlorocyclopropyl)propane, 52259-98-0; 1-(1-methyl-2,2-dichlorocyclopropyl)butane, 80822-57-7; 7,7-dichlorobicyclo[4.1.0]heptane, 823-69-8; 1-(2,2-dichlorocyclopropyl)-butane, 3722-08-5; 1,1-dichloro-2-phenylcyclopropane, 2415-80-7; 9,9-dichlorobicyclo[6.1.0]nonane, 6498-44-8; 1-(2,2-dichlorocyclopropyl)hexane, 5685-42-7; 1,1-dichloro-2-methyl-2-phenylcyclopropane, 3591-42-2; 4-(1-methyl-2,2-dichlorocyclopropyl)-7,7-dichloro-1-methylbicyclo[4.1.0]heptane, 37608-28-9; dichlorocarbene, 1605-72-7.

N-Bromosaccharin: Benzylic and α-Carbonylic Bromination

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Received December 17, 1980

N-Bromosaccharin (NBSac) has been used as a brominating agent with cyclohexene[1] and diphenylmethane;[2] the former only gave the addition derivative, while the latter was brominated in the benzylic position; no yield was reported. We previously reported a new method of NBSac preparation[3] where it had been obtained with excellent yield. Now that a suitable NBSac synthesis is available, we herein report its ability as a brominating agent at the benzylic and α-carbonylic positions.

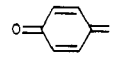
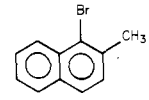
Benzylic Substitution (Table I). The toluene (1) bromination yields obtained corresponded to a 1:1 reactant molar ratio. When this ratio was increased 10% in NBSac, benzal bromide was afforded and a similar result was obtained when those reactants were irradiated with a sunlamp. Reflux or irradiation with a sunlamp dramatically reduced the reaction time. When radical initiators were added, the yields were increased perceptibly. Similar findings were observed in the bromination of diphenylmethane (2). When the bromination reaction was carried out with 2-methylnaphthalene (3), 2-(bromomethyl)-naphthalene (A) and 1-bromo-2-methylnaphthalene (B) were obtained. These results are in agreement with the literature[4] where *N*-bromosuccinimide (NBS) was used as the brominating agent under Ziegler conditions; 63% of A and 35% of B were obtained.

α-Carbonyl Substitution (Table II). Cyclohexanone (4) by bromination should afford 2-bromocyclohexanone,

(1) Ziegler, K.; Spath, A.; Schumann, W.; Winkelman, E. *Justus Liebigs Ann. Chem.* **1942**, *551*, 80-110.
(2) Fondovila, M. E.; Schroder, P. M. *Rev. Fac. Cien. Quím., Univ. Nac. La Plata*, **1960**, *33*, 33; *Chem. Abstr.* **1963**, *58*, 5655h.
(3) Sánchez, E. I.; Fumarola, M. J. *Synthesis* **1976**, 736.
(4) Chapman, N. S.; Williams, J. F. *J. Chem Soc.* **1952**, 5044.

0022-3263/82/1947-1588$01.25/0

Table I. Benzylic Bromination

substrate	conditions	rctn time, h	added matl	NBSac % yield[a] MBD[b]	side products	unreacted substrate	NBS % yield[a] MBD[b]
toluene	dark, room temp	8		0		100	
toluene	dark, 80 °C	2	PhC(O)OO(O)CPh (5%)	72		28	75
toluene	room light, 80 °C	0.3		76		24	0
toluene	100-W lamp, room temp	5	AIBN (5%)	80 (75)[c]		20	82
toluene	100-W lamp, room temp	6		72		28	3
toluene	100-W lamp, 80 °C	0.3		76		24	7
toluene	100-W lamp, 80 °C	0.3	 (10%)	0		100	0
toluene	sunlamp, room temp	0.25		76	$PhCHBr_2$ 18	6	73
diphenylmethane	100-W lamp, room temp	5		75		25	73
diphenylmethane	sunlamp, room temp	0.25		85 (70)[c]		15	80
2-methylnaphthalene	100-W lamp, room temp	8.5		60	 35 (20)[c]	5	65
2-methylnaphthalene	100-W lamp, 80 °C	0.3		63 (50)[c]		2	62

[a] Evaluated by ^1H NMR spectroscopy from crude reaction; the yields of products are based on starting substrate. [b] Monobromo derivative. [c] Isolated yields.

Table II. α-Carbonylic Bromination

substrate	conditions	rctn time, h	added matl	NBSac % yield[a] MBD[b]	side products	unreacted substrate	NBS % yield[a] MBD[b]
cyclohexanone	dark, room temp	8		0		100	0
cyclohexanone	dark, 80 °C	2.25	PhC(O)OO(O)CPh (5%)	67		33	50
cyclohexanone	100-W lamp, room temp	6		73	*d*, 15	12	68
cyclohexanone	100-W lamp, 80 °C	1.5		84	*d*, 9.5	6.5	75
cyclohexanone	sunlamp, room temp	0.5		91 (75)[c]	*d*, 5	4	85
α-phenylacetophenone	100-W lamp, room temp	5		85		15	71
α-phenylacetophenone	100-W lamp, 80 °C	1		92 (79)[c]		8	83
acetophenone	100-W lamp, 80 °C	48		20		80	21
acetophenone	sunlamp, room temp	48		25		75	25

[a] Evaluated by ^1H NMR spectroscopy from crude reaction; the yields of products are based on starting substrate. [b] Monobromo derivative. [c] Isolated yields. [d] 2-Cyclohexenone.

but through hydrogen bromide elimination, the latter afforded 2-cyclohexenone in a ratio proportional to the photostimulation period. When this reaction was carried out in darkness, the dehydrobromination was negligible. On the other hand, an excellent yield of α-phenylphenacyl bromide (desyl bromide) was obtained in the α-phenylacetophenone (**5**) bromination. This result may be explained by the high activity of the methylene group due both to its benzylic and α-carbonylic position. Acetophenone (**6**) afforded a low yield of phenacyl bromide, which was similar to the results obtained by other authors[5,6] in the bromination of several methyl vinyl and methyl aryl ketones with NBS.

As shown in Tables I and II, the yield of the substitution derivative was negligible without irradiation, heating, or

(5) Ward, C. F. *J. Chem. Soc.* **1923**, *123*, 2207.
(6) Orazi, O. O.; Meseri, J. *Anal. Asoc. Quim. Argentina* **1950**, *38*, 300.

Table III. Competitive Bromination Reactions[a] with 1 and 2

halogenating agent	conditions, rctn time, added matl	% yield[b] benzyl bromide	% yield[b] benzhydryl bromide
NBSac	80 °C, 150-W lamp, 45 min, PhC(O)OO(O)CPh (5%)	34.25	65.75
NBS		35.00	65.00

[a] NBSac or NBS, 0.0015 mol; 1, 0.002 mol; 2, 0.001 mol in 10 mL of dry CCl_4. [b] Evaluated by ^1H NMR spectroscopy from crude reactions.

radical initiator, but it was increased dramatically by means of visible or ultraviolet irradiation or in the prescence of a radical initiator [azobis(isobutyronitrile), benzoyl peroxide] and was negligible again in the presence of a radical scavenger (*p*-quinone). These observations clearly indicate that the substitution product is formed by a chain sequence. We believe that this process involves the bromine molecule like the Goldfinger[7] mechanism.

$$Br\cdot + RH \rightarrow BrH + R\cdot \quad (1)$$

$$BrH + NBSac \rightarrow Br_2 + HNSac \quad (2)$$

$$Br_2 + R\cdot \rightarrow BrR + Br\cdot \quad (3)$$

This is supported by the following: (a) free bromine formation was observed after several minutes of reaction, which was evident by both its typical red-yellow color and a weak absorption at 406 nm in the UV spectra, (b) inhibition of the reaction by addition of silver acetate.[8] This salt reacts with the hydrogen bromide formed in the abstraction step (1) blocking the subsequent bromine molecule formation (2). This was proved by the appearance in the ^1H NMR spectra of the acetic acid proton absorption. It was shown that this acid was not formed by the acid–base reaction of silver acetate and insoluble saccharin since a mixture of these two compounds boiled together in carbon tetrachloride and irradiated with a 100-W lamp for 6 h did not form acetic acid as measured by ^1H NMR. It might be thought that the inhibition of the reaction was due to the consumption of the NBSac by the silver acetate, but we observed that they did not react under our experimental conditions. In addition, competitive reactions between NBSac and NBS with a mixture of toluene and diphenylmethane gave similar results. This would also suggest that both reactions take place by the same mechanism (Table III).

In general, NBSac showed to be an excellent brominating agent in both benzylic and α-carbonylic positions. As it is shown in Tables I and II, NBS produces slightly lower yields than NBSac only with the carbonylic compounds. Besides, a few comparable results were obtained by using NBS in this type of bromination.[9]

Experimental Section

General Procedures. The ^1H NMR spectra were recorded with a Varian T-60 spectrometer with Me_4Si as an internal standard. The IR spectra were recorded on a Beckman IR-8 spectrophotometer and the UV spectra on a Beckman DBG spectrophotometer. Thin-layer chromatography was carried out on silica gel G with $CHCl_3$ as eluent. Gas chromatographic analyses were performed on a Hewlett-Packard F&M 776 equipped with a flame-ionization detector and a 5 ft × 6 mm o.d. stainless-steel column packed with 10% Apiezon "L" on Chrom CLA (100/200 mesh). The sunlamp was a Philips UV 300 W (low limit, 280 nm) placed 10 cm from the reaction vessel.

General Bromination Procedure. The substrate was added to a suspension of dry crude NBSac in 10 mL of dry CCl_4 as solvent, generally the concentration of NBSac was 0.1 M and the molar ratio NBSac/reactant was 1:1. The reactions were carried out under nitrogen and stirred with a magnetic stirrer. Their progress was monitored with potassium iodide–starch paper test and/or iodometry. Then they were cooled, and the insoluble saccharin was filtered off with suction (95% recovery). The crude solutions were analyzed by thin-layer or gas chromatography and directly evaluated by ^1H NMR spectroscopy. The products of the more representative reactions were separated by vacuum fractional distillation or by preparative thin-layer chromatography. The yields of the products so obtained are shown in parentheses in Tables I and II. Their structures were determined by spectroscopic comparisons of their spectra with those of authentic samples. Experimental conditions are indicated in the tables.

Acknowledgment. Part of this investigation was made possible by Grant 7161/75 from the National Council of Scientific and Technical Research.

Registry No. 1, 108-88-3; 2, 101-81-5; 3, 91-57-6; 4, 108-94-1; 5, 451-40-1; 6, 98-86-2; benzyl bromide, 100-39-0; α,α-dibromotoluene, 618-31-5; benzhydryl bromide, 776-74-9; 2-(bromomethyl)-naphthalene, 939-26-4; 1-bromo-2-methylnaphthalene, 2586-62-1; 2-bromocyclohexanone, 822-85-5; 2-cyclohexenone, 930-68-7; α-phenylphenacyl bromide, 1484-50-0; phenacyl bromide, 70-11-1; *N*-bromosaccharin, 35812-01-2.

(7) Adam, J.; Gosselain, P. A.; Goldfinger, P. *Nature (London)* **1953**, *171*, 704.
(8) Beebe, T. R.; Howard, F. M. *J. Am. Chem. Soc.* **1969**, *91*, 3379.
(9) (a) Buu-Hoi Ng. Ph. *Justus Liebigs Ann. Chem.* **1944**, *556*, 1. (b) Schmid, H.; Karrer, P. *Helv. Chim. Acta* **1946**, *29*, 573. (c) Incremona, J. H.; Martin, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 627.

Regiospecific Synthesis of Arylfurans Employing a Nickel(II)–Phosphine Complex as a Catalyst in the Homolytic Cross-Coupling of Grignard Reagents to Halofurans[1]

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Received November 17, 1981

In developing a new pyridazine antihypertensive,[2] we required a general regiospecific synthesis of 2-(*o*-alkoxyphenyl)furans. The commonly reported syntheses of arylfurans (i.e., **3a–f**) require generation of aryl radicals in the presence of furan. These radicals may be generated by aprotic diazotization of aromatic amines with alkyl-nitrites[3] or by decomposition of *N*-nitrosoacetanilides,[5,7c] (phenylazo)triphenylmethane,[6] or aromatic diazonium

(1) Jones, S. J.; Pridgen, L. N., presented in part at the 28th Congress of the International Union of Pure and Applied Chemistry, Aug 1981, Vancouver, British Columbia, Canada.
(2) Coates, W. J.; Roe, A. M.; Slater, R. A.; Taylor, E. M. U.S. Patent 4 053 601, 1977.
(3) (a) Fisera, L.; Kovac, J.; Komanova, E. *Tetrahedron* **1974**, *30*, 4123. (b) Ayres, D. C.; Smith, J. R. *J. Chem. Soc.* **1968**, 2737.
(4) (a) Mathur, K. B. L.; Mehra, H. S. *J. Chem. Soc.* **1961**, 2576. (b) Freund, W. *Ibid.* **1952**, 3068.
(5) Grieve, W. S.; Hey, D. H. *J. Chem. Soc.* **1934**, 1797.
(6) Hey, D. H. *J. Chem. Soc.* **1934**, 1966.

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