Syntheses of Phenylketene Acetals *via* α-Bromophenylacetaldehyde Acetals

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Four known phenylketene acetals (dimethyl, diethyl, dimethylene, and trimethylene acetals) and eight new analogs (di-*n*-propyl, diisopropyl, di-*sec*-butyl, divinyl, methyl ethyl, methyl *sec*-butyl, and methyl *t*-amyl acetals, and 3-ethoxy-1H-benzopyran) have been conveniently synthesized by dehydrobromination of α-bromophenylacetaldehyde acetals. The wide scope of this preparative method is contrasted with the relatively limited applicability of syntheses for phenylketene acetals by way of ortho esters. Reactions leading to the intermediate α-bromophenylacetaldehyde acetals and β-alkoxystyrenes have been further developed and extended.

To further a detailed mechanistic investigation of the photochemical behavior of phenylketene acetals,[2] we needed a set of diverse representatives of these compounds and sought to utilize known synthetic routes to obtain them.

The first of two principal methods for preparing phenylketene acetals, involving pyrolysis of alkyl orthophenylacetates,[3-5] is known to have several shortcomings. Since the pyrolysis of the ortho ester may be incomplete[6] or the product may decompose under the pyrolytic conditions,[7] the product obtained may be contaminated with ortho ester or normal ester or both, and is difficult to purify. These ortho esters are sensitive to moisture[8] and are hard to purify; some types of orthophenylacetates are extremely difficult to prepare. Thus, although others have claimed syntheses of orthophenylacetates substituted with two isopropyl groups,[9] we have been unable to obtain tri-*sec*-butyl and di-*sec*-butylmethyl orthophenylacetates[10] following a published procedure.[9] The method is inapplicable for preparations of mixed acetals, such as phenylketene methyl ethyl acetal; yet, in spite of these limitations, the ortho ester method has been almost invariably used for syntheses of simple phenylketene acetals in recent years.[6,11]

The second principal method for synthesizing phenylketene acetals, through dehydrobromination of α-bromophenylacetaldehyde acetals, was first described[12] in 1948 but has received comparatively little attention since that time. The method was reported[12] to give products in good yield and high purity, and seemed to offer important advantages through greater convenience and versatility, relative to the ortho ester method. The starting materials are easily available and stored, the reactions are simple to run, and the method may be adapted for preparing mixed acetals. This approach has now been exploited and considerably extended, giving the results described below.

Results and Discussion

Phenylketene Acetals.—Dehydrobromination of α-bromophenylacetaldehyde acetals with potassium *t*-butoxide in *t*-butyl alcohol generally proceeds smoothly and in good yield. The results obtained with this method and the properties of the 12 phenylketene acetals prepared are summarized in Table I. Eight of these 12 acetals are new compounds.

The freshly distilled primary (**1a**–**1c**, **2a**), primary–secondary (**2b**), vinyl (**1f**), and cyclic acetals (**3a**–**3c**) were at least 95% pure as judged by nmr spectroscopy or by vpc analyses. The other acetals were obtained in only 70–80% pure condition, as estimated by ultraviolet or nmr spectroscopic criteria.

Phenylketene acetals decompose rapidly when exposed to the atmosphere, as evidenced by their loss of characteristic spectral properties, reduction of refractive indexes, and discoloration. Elemental analytical data secured for the acetals **1c**, **2a**, and **2b** were not within the normally accepted limits; carbon and hydrogen percentages were uniformly low. Hence the boiling points and refractive indices in Table I should not be taken as physical constants truly characteristic of analytically pure phenylketene acetals.

In the ultraviolet the alkyl phenylketene acetals **1** and **2** have $\lambda_{\max}^{\text{cyclohexane}}$ 265 mμ (ϵ 16,000–17,000), the cyclic acetals **3a** and **3b** have $\lambda_{\max}$ 265 mμ (ϵ 18,000–19,500), and 3-ethoxy-1H-benzopyran (**3c**) has $\lambda_{\max}$ 283 mμ (ϵ 9500).

The phenylketene acetals have a characteristic singlet in nmr spectra for the lone vinyl hydrogen at τ 4.9 to 5.6. In the mixed acetals, absorptions corresponding to both geometrical isomers are observed; in the ethyl methyl acetal, for example, methyl singlets are seen at τ 6.35 and 6.45 and vinyl proton singlets at 5.45 and 5.50. These nmr parameters are not sufficient evidence to formulate this particular mixed acetal as **2a** rather than as a mixture of the dimethyl and diethyl acetals **1a**, and **1b**, for in the dimethyl acetal the methyl singlets appear at τ 6.35 and 6.45. The distinction is easily made by mass spectrometry or by vpc: the mixed acetal **2a** shows a parent ion peak at m/e 178 and has a vpc retention time distinct from those for the acetals **1a** and **1b**.

Attempts to prepare the diallyl and dibenzyl acetals of phenylketene from the corresponding α-bromophenylacetaldehyde acetals were unsuccessful. This failure is probably caused by the instability of the two phenylketene acetals, rather than by a limitation in the synthetic method. McElvain and co-workers[13] isolated rearranged products in their attempts to prepare ketene diallyl and dibenzyl acetals. Attempts to prepare ketene diallyl acetal yielded only allyl 4-

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(1) National Science Foundation Cooperative Graduate Fellow, 1963–1966.

(2) J. E. Baldwin and L. E. Walker, *J. Am. Chem. Soc.*, **88**, 3769, 4191 (1966).

(3) S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949).

(4) S. M. McElvain and W. R. Davie, *J. Am. Chem. Soc.*, **73**, 1400 (1951).

(5) S. M. McElvain and J. T. Venerable, *ibid.*, **72**, 1661 (1950).

(6) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

(7) S. M. McElvain and C. L. Stevens, *ibid.*, **68**, 1917 (1946).

(8) H. Staudinger and G. Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922).

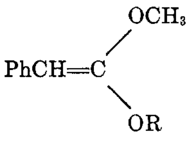
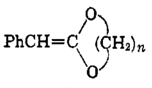
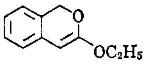
(9) P. P. T. Sah, S. Y. Ma, and C. H. Kao, *J. Chem. Soc.*, 305 (1931).

(10) L. E. Walker, unpublished.

(11) *Inter alia*, S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81** 2579 (1959); M. F. Dull and P. G. Abend, *ibid.*, **81**, 2588 (1959).

(12) S. M. McElvain and M. J. Curry, *ibid.*, **70**, 3781 (1948)

TABLE I
YIELDS AND PROPERTIES OF PHENYLKETENE ACETALS

Structure		R or *n*	Yield, %	Bp, °C	Pressure, mm	$n^{20}D$
$PhCH{=}C(OR)_2$ 1	**1a**	Me[a]	74–85	64–66	0.3	1.5655
	1b	Et[b]	55–80	75–77	0.2	1.5408
	1c	*n*-Pr	45–70	98–101	0.4	1.5289
	1d	*i*-Pr	30	78–82	0.3	1.5217
	1e	*sec*-Bu	21	93–96	0.4	1.5128
	1f	Vinyl	15	72–76	0.4	1.5592
 $PhCH{=}C(OCH_3)(OR)$ 2	**2a**	Et[c]	55–70	70–72	0.2	1.5522
	2b	*sec*-Bu	40–50	88–89	0.5	1.5373
	2c	*t*-Amyl	16	89–95	0.4	1.5278
 3	**3a**	3[d]	65–80	94–96	0.2	*e*
	3b	2[f]	75	118–121	0.2	1.6062
 3c	**3c**		15–40	76–81	0.3	1.5681

[a] Lit.[12] bp 81–82° (1.0 mm), $n^{25}D$ 1.5620. [b] Lit.[1] bp 86–88° (0.2 mm), $n^{20}D$ 1.5385. [c] Contains 3–5% of **1b**. [d] Lit.[12] bp 124–126° (0.6 mm), mp 25–27°. [e] Mp 35–37°. [f] Lit.[12] bp 108–112° (0.8 mm), $n^{25}D$ 1.6075.

pentenoate while attempts to prepare ketene dibenzyl acetal gave only benzyl *o*-tolylacetate.[13] The ketene acetals were probably formed but underwent Claisen rearrangement to give the observed products. The cyclic phenylketene-type acetal, 3-ethoxy-1H-benzopyran, could be prepared by the normal method. Apparently the position of the cyclic benzyl group prevents the molecule from assuming the geometry required for the Claisen rearrangement, thus making the compound isolable.

α-Bromophenylacetaldehyde Acetals.—The wide applicability of this synthetic approach to phenylketene acetals is in part a consequence of the ready accessibility of the α-bromophenylacetaldehyde acetals, which can be prepared by the general methods outlined in eq 1–5.

$$\underset{4}{PhCH{=}CHOAc} \xrightarrow{Br_2} \xrightarrow{ROH} \underset{5}{PhCHBrCH(OR)_2} \qquad (1)$$

$$\underset{6}{PhCH{=}CHOR} \xrightarrow{Br_2} \xrightarrow{ROH} \underset{5}{PhCHBrCH(OR)_2} \qquad (2)$$

$$\underset{6}{PhCH{=}CHOR} \xrightarrow{Br_2} \xrightarrow{NaOMe} \underset{7}{PhCHBrCH(OMe)OR} \qquad (3)$$

$$\underset{5}{PhCHBrCH(OR)_2} \xrightarrow{R'OH} \underset{8}{PhCHBrCH(OR')_2} \qquad (4)$$

$$\underset{9}{PhCBr{=}CHOR} \xrightarrow{ROH} 5 \qquad (5)$$

The reaction of eq 1 was first utilized for the preparation of α-bromophenylacetaldehyde dimethylacetal.[14] Jacobs and Scott later showed[15] that a styryl ether (**6**) would undergo the reaction of eq 2. Suitable variations of the latter method (eq 3) have made it possible to prepare reasonably pure mixed acetals of type **7**. McElvain and Curry[12] first reported the exchange reaction (eq 4) for the preparation of cyclic acetals from the corresponding methyl derivative.

The conversion of phenylacetaldehyde to styryl acetate by a standard method[14] provides a mixture of *trans* and *cis* isomers; the nmr spectrum of the mixture of acetates shows two AB patterns with coupling constants of 13 (*trans*-vinyl hydrogens) and 7 cps (*cis* hydrogens) in a ratio of integrated intensities of approximately 4:1. The requisite styryl alkyl ethers (**6**, methods 2 and 3) are easily prepared from phenylacetylene and the appropriate sodium alkoxide in the alcohol. The use of β-bromostyrene in place of phenylacetylene gave an equally acceptable yield of **6** for the one case where it was tried. Previously, this method had been applied for the preparation of **6** with primary R groups.[15–18] The method, however, has given satisfactory results for secondary and tertiary R groups. The only limitations of the method are associated with the insolubility of sodium in the alcohol. Of the simple alcohols up to five carbons tried, *t*-butyl was the only one that failed to give an acceptable yield. This failure was attributed to the low solubility of sodium in the alcohol. *t*-Amyl alcohol, on the other hand, dissolved a much larger quantity of sodium and gave a 27% yield of the corresponding **6**. 1H-Benzopyran, a cyclic β-alkoxystyrene, was prepared from isocoumarin[19] by a literature method[20] rather than from the unknown *o*-(hydroxymethyl)-phenylacetylene. The properties, yields, and reaction conditions for the preparation of the β-alkoxystyrenes are given in Table II. The two vinyl protons in these intermediates absorbed at τ 4.9 and 3.9–4.05 in the nmr, and split one another with $J \simeq 7$ cps; a

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(13) S. M. McElvain, H. I. Anthes, and S. H. Shapiro, *J. Am. Chem. Soc.*, **64**, 2525 (1942).

(14) P. Z. Bedoukian, *ibid.*, **66**, 1325 (1944).

(15) T. L. Jacobs and W. R. Scott, Jr., *ibid.*, **75**, 5500 (1953).

(16) W. S. Emerson, *Chem. Rev.*, **45**, 183 (1949).

(17) C. Moureu, *Bull. Soc. Chim. France*, [3] **31**, 526 (1904).

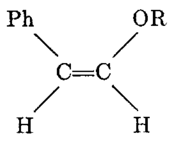
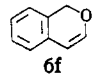
(18) C. Durfaisse and R. Chaux, *ibid.*, [4] **39**, 905 (1926).

(19) H. W. Johnston, C. E. Kaslow, A. Langsjoen, and R. L. Shriner, *J. Org. Chem.*, **13**, 477 (1948).

(20) J. N. Chatterjea, *Chem. Ber.*, **91**, 2636 (1958).

TABLE II

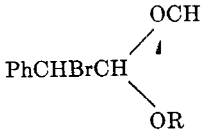
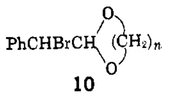
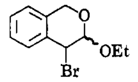
YIELDS AND PROPERTIES OF *cis*-β-ALKOXYSTYRENES

Structure		R	Yield, %	Bp, °C	Pressure, mm	n^{20}D	Na/ROH,[a] g/100 ml	Reflux time, hr
 **6**	**6a**	Me[b]	65–75	44	0.3	1.5662	13	24
	6b	Et[c]	70–85	52	0.3	1.5520	10	24
				43	0.1			
	6b	Et[d]	75–85	60–62	0.4	1.5522	13–16	40
				57–59	0.2			
	6c	*i*-Pr	70	54–55	0.25	1.5400	7	48
	6d	*sec*-Bu[e]	70–90	60–62	0.2	1.5352	6–10	15–25
				70–73	0.5			
	6e	*t*-Amyl	27	75–79	0.4	1.5330	3	32
 **6f**	**6f**	*f*	50–60	93–95	17	1.5765		

[a] For the methyl, ethyl, and isopropyl cases, 8–10 g of sodium was used per 0.1 mole of phenylacetylene (or β-bromostyrene). For the *sec*-butyl and *t*-amyl cases, 3–7 g of sodium was used per 0.1 mole of phenylacetylene. [b] Lit.[17] bp 210–213°, $n^{15.5}$D 1.5647. [c] Lit.[18] bp 108–109° (15 mm), n^{20}D 1.5544. [d] β-Bromostyrene was used in place of phenylacetylene. [e] Carbon and hydrogen analytical values for **6d** were low. *Anal.* Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 80.99; H, 9.05. [f] Prepared from isocoumarin; lit.[20] bp 140° (115 mm), n^{20}D 1.5818.

TABLE III

YIELDS AND PROPERTIES OF α-BROMOPHENYLACETALDEHYDE ACETALS

Structure		R or *n*	Yield, %	Bp, °C	Pressure, mm	n^{20}D	Method[a]
PhCHBrCH(OR)$_2$ **5**	**5a**	Me[b]	55–85	84–86	0.4	1.5390	1, 2
	5b	Et	70–75	96	0.3	1.5193	1, 2
	5c	*n*-Pr	75–80	108–110	0.4	1.5080	1, 4 + 5
	5d	*i*-Pr	70	98–104	0.4	1.5098	2, 4 + 5
	5e	*sec*-Bu	50–75	115–118	0.3	1.5060	2, 4
	5f	CH_2CH_2Cl	50–55	168–174	0.6–0.7	1.5472	1, 5
	5g	Allyl	73	118–121	0.4	1.5365	1
	5h	Benzyl	69	Mp 84–85			4
 PhCHBrCH(OCH$_3$)(OR) **7**	**7a**	Et	55–80	91–93	0.4	1.5284	3
	7b	*sec*-Bu	70–75	104–108	0.4–0.5	1.5188	3
	7c	*t*-Amyl	64	117–122	0.5	1.5185	3
 **10**	**10a**	3[c]	85	104–107	0.2	1.5665	4
	10b	2[d]	76	112–118	0.5–0.6	1.5662	4
 **10c**	**10c**[e]		60–65	103–104	0.5	1.5638	3

[a] Numbers refer to text equations. [b] Lit. bp 133–135° (10 mm), n^{25}D 1.5395;[12] bp 110–114° (1.7 mm), n^{25}D 1.5390.[14] [c] Recrystallized from 50% ethanol; mp 46–48° [lit.[12] bp 120–125° (0.8 mm), n^{25}D 1.5602, mp 46–48°]. [d] Lit.[12] bp 162–165° (9 mm), n^{25}D 1.5628. [e] Carbon and hydrogen analytical values for **10c** were low. *Anal.* Calcd for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.09. Found: C, 50.79; H, 4.95.

spin–spin interaction of this magnitude is consistent with a *cis* stereochemistry for the vinyl hydrogens.[21]

The bromo ethers of type **9** are sometimes formed either from an incomplete preparation or from a distillation of **5** under acidic conditions. Fortunately, compounds of type **9** can be converted to **5** (eq 5) by treating with an alcohol in the presence of acid.

Fourteen α-bromophenylacetaldehyde acetals have been obtained by one or more of the five methods. Eleven of these are new compounds. The method, yield, and physical properties of the α-bromophenylacetaldehyde acetals prepared for this work are summarized in Table III. Analytical data for some of the new compounds are given in Table IV.

Pure α-bromophenylacetaldehyde acetals (**5**, **7**, and **10**) are colorless liquids or solids having faint pleasant odors. The ultraviolet spectra of the pure compounds in 95% ethanol show only the weak absorption of the phenyl group in the 250-mμ region. The nmr spectra of the bromo acetals in carbon tetrachloride show the two protons geminal and vicinal to the bromine at τ 5.2–5.4. The two alkyl groups in the acetals are nonequivalent and give rise to the anticipated spectral complications. In the dimethyl acetal **5a** for example, methyl singlets are observed at τ 6.65 and 6.85.

The α-bromophenylacetaldehyde acetals of structure **7** are mixtures of two *dl* pairs of diastereoisomers. The two protons geminal and vicinal to bromine in the dimethyl bromo acetal **5a** are observed in the nmr spectrum as two AB doublets, centered at τ 5.2 and 5.4;

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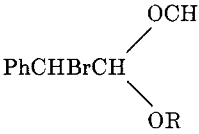
[21] This stereochemistry is in accord with a previous assignment: S. I. Miller, *J. Am. Chem. Soc.* **78**, 6091 (1956).

TABLE IV

ANALYTICAL RESULTS FOR NEW α-BROMOPHENYLACETALDEHYDE ACETALS

Structure		R	Formula	Calcd, %			Found, %		
				C	H	Br	C	H	Br
PhCHBrCH(OR)$_2$ **5**	**5b**	Et	$C_{12}H_{17}BrO_2$			29.25			29.51
	5d	*i*-Pr	$C_{14}H_{21}BrO_2$	55.83	7.03	26.53	56.16	7.02	26.39
	5e	*sec*-Bu	$C_{16}H_{25}BrO_2$	58.36	7.65	24.27	58.80	7.64	23.99
	5f	CH$_2$CH$_2$Cl	$C_{12}H_{15}BrCl_2O_2$			44.07[a]			42.76[a]
	5g	Allyl	$C_{14}H_{17}BrO_2$	56.58	5.77	26.88	56.44	5.66	27.65
 $PhCHBrCH\begin{matrix}OCH_3\\OR\end{matrix}$ **7**	**7a**	Et	$C_{11}H_{15}BrO_2$	50.98	5.83	30.84	51.46	5.81	31.41
	7b	*sec*-Bu	$C_{13}H_{19}BrO_2$	54.37	6.67	27.82	54.74	6.55	27.57

[a] Bromine plus chlorine.

in the diethyl bromo acetal **5b**, these two protons appear only as a sharp singlet at 5.25. The mixed acetal **7a** shows in this region of the spectrum a broad singlet centered at τ 5.2. The nmr data confirm the presence of two isomers in **5a**, and demonstrate that the bromo acetal **7a** is indeed a methyl ethyl bromo acetal, not a mixture of **5a** and **5b**. Neither the pair of diastereomers of structure **7** nor the pair of geometrical isomers of structure **2** was separated.

On standing at room temperature or on distillation using either a long column or an acidic flask, the α-bromophenylacetaldehyde acetals lose 1 equiv of an alcohol to give α-bromo-β-alkoxystyrenes (**9**). As the bulk of the alkyl groups increases, the ease with which alcohol is eliminated from the bromo acetals is enhanced; the di-*sec*-butyl bromo acetal eliminates *sec*-butyl alcohol more readily than the dimethyl bromo acetal loses methanol, and so forth. The α-bromo-β-alkoxystyrenes (**9**) appear deep yellow and have strong absorptions in the 250-mμ region and a strong band near 1600 cm^{-1} in the infrared, higher refractive indices than the α-bromo acetals, and very irritating odors. To avoid formation of the α-bromo-β-alkoxystyrenes, the α-bromophenylacetaldehyde acetals must be stored in a freezer, distilled only with a short, base-washed distillation head, and distilled from potassium carbonate or, better, from calcium hydride. Even when great care is taken, a significant amount of the bromostyryl ether may be formed in certain cases. Fortunately, the reaction may be reversed and the α-bromophenylacetaldehyde acetal can be recovered.

Experimental Section[22]

***cis*-β-Alkoxystyrenes** were prepared following procedures for the known compounds in this series. Sodium was dissolved in the appropriate alcohol at reflux, in the ratio indicated in Table II. Normally much of the sodium alkoxide crystallized when the solution was cooled; occasionally not all of the alkoxide was soluble in the hot solution. To the cool solution or mixture was added phenylacetylene or β-bromostyrene. The resultant mixture was heated at reflux vigorously for the time indicated in Table II. The mixture was cooled, treated with water (in small portions at first), and extracted with ether. The ethereal solution was washed with water, dried over magnesium sulfate, filtered, and concentrated to leave a yellow or brown oil. Vacuum distillation through a 15-cm Vigreux column afforded the *cis*-β-alkoxystrene. The products obtained with this general method had the boiling points and refractive indices indicated in Table II.

1H-Benzopyran was prepared from isocoumarin[19] by the two-step procedure of Chatterjea.[20] The crude intermediate *o*-(hydroxymethyl)phenylacetaldehyde was used directly for the preparation of the 1H-benzopyran. Since this cyclic ether is reported to decompose on standing at room temperature,[20] it was used immediately after preparation.

α-Bromophenylacetaldehyde Acetals. A. From Styryl Acetate.—The preparations of α-bromophenylacetaldehyde, dimethyl, diethyl, di-*n*-propyl, diallyl, and di-β-chloroethyl acetals from styryl acetate were accomplished using Bedoukian's procedure[14] for the dimethyl acetal. A magnetic stirrer was employed during the addition of the bromine and during the 2-day reaction period.

The normal work-up procedure for a product mixture consists of diluting the reaction mixture with ether, washing the ethereal extract with dilute potassium carbonate solution, drying over anhydrous potassium carbonate, concentrating under vacuum at room temperature, and distilling from either potassium carbonate or a potassium carbonate–calcium hydride mixture using a short-path distillation head.

The α-bromophenylacetaldehyde di-β-chloroethyl acetal obtained was contaminated with the corresponding α-bromo-β-alkoxystyrene. The pure acetal was obtained as indicated below.

B. From *cis*-β-Alkoxystyrenes.—The conversions of *cis*-β-alkoxystyrenes to the corresponding α-bromophenylacetaldehyde acetals were carried out by adapting the procedure of Jacobs and Scott[15] for the dimethyl acetal. To a stirred solution of the alkoxystyrene in absolute ether cooled to −30° was added dropwise 1 equiv of bromine over a 5-min period. A mixture of 1 equiv of potassium carbonate in the appropriate alcohol was then added to the cooled mixture. The mixture was stirred at room temperature for 1–2 days and then worked up in the usual way (*cf.* part A). This method has been applied for the preparation of the dimethyl, diethyl, diisopropyl, and di-*sec*-butyl acetals in good yields.

α-Bromophenylacetaldehyde Mixed Acetals.—A solution of the appropriate β-alkoxystyrene (0.15 mole) in 100 ml of absolute ether was cooled to −30° using a 50% ethanol–water–Dry Ice bath. The solution was stirred and treated with 1 equiv of bromine. To the resulting light yellow to colorless solution was then added over a 0.5-hr period a suspension containing 0.15 mole of sodium methoxide in 100 ml of methanol. The mixture was stirred for 30 min at −30°, treated with dilute potassium carbonate solution, and diluted with ether. The ethereal solution was washed with cold potassium carbonate solution and dried over potassium carbonate and magnesium sulfate. Filtration and concentration over potassium carbonate at or below room temperature yielded a colorless oil. This was distilled from the potassium carbonate and added calcium hydride to afford the pure product. This procedure has given the methyl ethyl, methyl *sec*-butyl-, and methyl *t*-amyl acetals.

For the preparation of 4-bromo-3-ethoxy-1H-3,4-dihydrobenzopyran from 1H-benzopyran, an ethanolic potassium carbonate suspension was added to the intermediate dibromide; the resulting mixture was allowed to stand overnight and then worked up in the normal fashion.

C. From α-Bromophenylacetaldehyde Dimethylacetal.—The procedure of McElvain and Curry[12] was used to prepare the trimethylene and dimethylene acetals **10a** and **10b**. A modifica-

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[22] Analyses were by J. Nemeth and associates, Urbana, Ill. Nuclear magnetic resonance and infrared spectra were obtained on Varian A-60 and on Perkin-Elmer Model 21 or 521 spectrometers by O. Norton and associates. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer, purchased with funds provided by the Research Board of the University of Illinois.

tion of the procedure was used to synthesize **α-bromophenylacetaldehyde dibenzylacetal.** An equimolar mixture of α-bromophenylacetaldehyde dimethylacetal and benzyl alcohol containing a few drops of concentrated sulfuric acid was placed in a flask equipped with a short-path distillation apparatus. The mixture was heated at 60–70° at 35 mm for 2.25 hr. During this time an 80% yield of methanol collected in the cold receiving flask. The contents of the reaction flask solidified on cooling. The solid was taken up in a large volume of carbon tetrachloride and washed with dilute potassium carbonate solution, dried over potassium carbonate, filtered, and concentrated under vacuum to yield an off-white solid. One recrystallization from absolute ethanol afforded a crystalline solid, mp 84–85°, in 69% yield.

D. **From α-Bromo-β-alkoxystyrenes.**—Some of the α-bromophenylacetaldehyde acetals obtained contained varying amounts of the corresponding α-bromo-β-alkoxystyrenes. Such an impure product was dissolved in the appropriate alcohol and treated with a few drops of concentrated sulfuric acid. The resulting mixture was allowed to stand for 2 to 7 days followed by the usual work-up. The product thus obtained was free of the styryl impurity.

E. **From Mixtures of Various Compounds.**—A bottle containing 100 ml of an alcohol and a few drops of concentrated sulfuric acid was maintained into which forerun fractions from distillations of various α-bromophenylacetaldehyde acetals and fractions of the mixed acetals containing the α-bromo-β-alkoxystyrenes were placed. After a period of 1 to 12 weeks, the alcoholic solution was heated under a 15-cm Vigreux column until about 70% of the alcohol had distilled. A fresh quantity of the alcohol was added and the mixture was allowed to stand at room temperature for 1 to 2 weeks. After this time the normal work-up was employed to yield the product. This method was used for preparing the di-*n*-propyl-, diisopropyl-, and di-*sec*-butylacetals.

Synthesis of Phenylketene Acetals.—The general procedure employed for synthesizing the diprimary, primary–secondary, and cyclic acetals was essentially that used by McElvain and Curry[12] for preparation of some of these phenylketene acetals. A solution of potassium *t*-butoxide was prepared by dissolving 1.7 g (0.044 mole) of potassium in 36 ml of *t*-butyl alcohol. The appropriate α-bromophenylacetaldehyde acetal (0.04 mole) was added and the mixture was heated under a Vigreux column equipped with a short-path distillation apparatus at such a rate that most of the *t*-butyl alcohol distilled over a 2- to 4-hr period. The last of the *t*-butyl alcohol was removed at reduced pressure and the product was distilled rapidly at 0.1 to 1.0 mm using only the short-path distillation apparatus. Slow redistilllation from calcium hydride gave the pure product. The purity of most of the phenylketene acetals was estimated by vpc analyses on a 1.5-m Apiezon L column at 180–190°.

For disecondary or primary–tertiary acetals, a 4–15-hr reflux period was employed. The crude products obtained were contaminated with varying amounts of the normal and ortho esters, starting material, and α-bromo-β-alkoxystyrenes. Further distillation yielded 70–80% pure material.

3-Ethoxy-1H-benzopyran was prepared as were the diprimary and primary–secondary acetals except that a shorter heating time (0.5 to 1 hr) was employed.

Excess potassium *t*-butoxide (3.1 equiv) and a 16–23-hr-reflux period were used for the preparation of **phenylketene divinyl acetal.** The crude product (49%) obtained contained significant amounts of various partially dehydrobrominated products. The divinyl acetal was easily separated in pure conditions by distillation (15% yield).

Two attempts were made to prepare phenylketene diallyl acetal. The normal procedure gave some product lacking the characteristic strong ultraviolet absorption appropriate to a phenylketene acetal. In the second attempt, the bromo compound was stirred with a potassium *t*-butoxide solution at room temperature. No increase in absorption at 265 mμ was observed.

No phenylketene dibenzyl acetal was obtained when the appropriate α-bromo acetal was treated with a potassium *t*-butoxide solution both at 25 and 60° as determined by ultraviolet monitoring.

Catalytic Hydrogenation. II. A New, Convenient Technique for Laboratory Hydrogenations. A Simple, Automatic Device for Atmospheric Pressure Hydrogenations

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The rapid, *in situ* preparation of highly active hydrogenation catalysts by the reduction of platinum metal salts with sodium borohydride has been combined with a convenient automatic hydrogen generator based on sodium borohydride to provide a new highly convenient procedure for laboratory-scale hydrogenations. The utility of the new platinum-on-carbon catalyst and the applicability of the new hydrogenation technique have been explored over a wide range of representative hydrogenation problems. It is concluded that the new technique possesses a number of significant advantages for laboratory-scale hydrogenations.

For nearly one-half century the low-pressure hydrogenator has been a valuable tool to the synthetic organic chemist. For all its virtues, however, the low-pressure hydrogenator in its usual form—hydrogen reservoir, control valves, heavy-walled glass reaction bottle and shaker—possesses a number of disadvantages. (1) It requires a reasonably permanent set-up with a consequent loss of laboratory space for other purposes. (2) The apparatus requires a hydrogen cylinder and often a purification train for the gas. (3) The apparatus operates with pressure in a glass bottle and with a consequent danger from fast internal pressure build-ups during exothermic reactions. (4) It is not well suited for following quantitatively the hydrogen uptake, and, since the pressure changes during the reaction, really meaningful rate data cannot be obtained. (5) It is relatively inconvenient to cool the shaking reaction vessel, making difficult hydrogenations at reduced temperatures. (6) Finally, in its usual form, the apparatus possesses a quite limited capacity.

In the course of a study of the new hydrogenation catalysts, readily produced by the reaction of sodium borohydride with platinum salts,[1] we developed a new, convenient technique for low-pressure hydrogenations.[2,3] This technique utilized the acidic hydrolysis of sodium borohydride solutions to produce hydrogen as required to maintain the pressure at the desired level. This allowed the entire quantity of hydrogen for 1 mole of olefin to be stored in as little as 100 ml of solution. To utilize fully this new, convenient method of hydrogen supply, a simple glass apparatus assembled

(1) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1494 (1962).

(2) C. A. Brown and H. C. Brown, *ibid.*, **84**, 1495 (1962).

(3) H. C. Brown and C. A. Brown, *Tetrahedron*, in press.