The volume of filtrate was 550 cc. Analysis of the filtrate on a F & M Model 500 gas chromatograph using a Porapak Q column showed that only a trace of butyraldehyde was present.

Registry No.—**1**, 17648-03-2; **2**, 2106-03-5; **3**, 21016-05-7; **4**, 23861-68-9; **5**, 25158-10-5; **6**, 25109-60-8; **7**, 25158-11-6; **8**, 25109-61-9; **9**, 23861-69-0; **10**, 23861-74-7; **11**, 23861-70-3; **12**, 25109-64-2; **13**, 25109-65-3; **14**, 25109-66-4; **15**, 25109-67-5; **16**, 25109-68-6.

Acknowledgments.—Appreciation is expressed to Professor F. Ramirez for timely suggestions and assistance in the preparation of this manuscript, Mr. J. Kobliska for microanalysis, Dr. J. Gove for nmr interpretations, Dr. T. Mead for mass spectra data, and Mr. J. Morath for vapor phase chromatographic analysis.

Molecular Rearrangements. X.[1] The Boron Trifluoride Etherate Catalyzed Rearrangements of *trans*-2,3-Diphenyl-2,3-epoxypropionitrile and Its *p*- and *p'*-Methyl Derivatives

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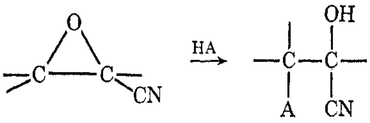
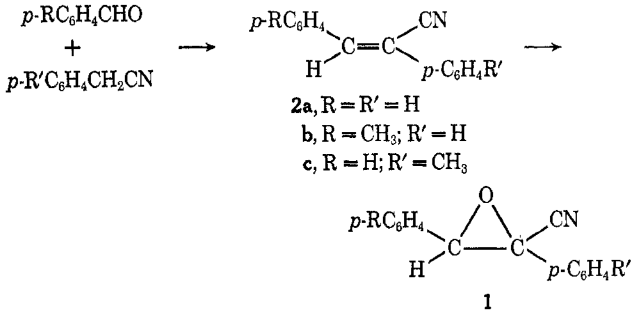
The syntheses of *trans*-2,3-diphenyl- (**1a**), *trans*-2-phenyl-3-(*p*-tolyl)- (**1b**), and *trans*-3-phenyl-2-(*p*-tolyl)-2,3-epoxypropionitrile (**1c**) are presented. Boron trifluoride etherate catalyzed rearrangement of **1a** and **1c** leads exclusively to the product of phenyl migration, α-cyanodiphenylacetaldehyde (**6**) and α-cyanophenyl-*p*-tolylacetaldehyde (**5**), respectively, while **1b** yields 47% **5** and 53% phenyl-*p*-tolylpyruvonitrile (**7a**), the products of *p*-tolyl and phenyl migration, respectively. Treatment of **7a** with base yields the stable enol form, **7b**. The catalyzed rearrangements of **1a**–**1c** are discussed in terms of a stepwise, ionic mechanism. Thermally, **1b** and **1c** produce *trans* → *cis* isomerization only.

There have been several reported studies of the rearrangements of α-cyano epoxides.[3] Cyano group migration has been observed in the formation of α-cyano ketones in a few cases where the intermediate α-cyano epoxide has been produced by treatment of an α-halocyanohydrin with base. Acid (protonic or Lewis) promoted rearrangements of α-cyano epoxides generally lead to α-substituted cyanohydrins as the products. In our general study of the chemistry of α-electronegatively substituted epoxides we have investigated the thermal and boron trifluoride etherate catalyzed rearrangements of *trans*-2,3-diphenyl-2,3-epoxypropionitrile (**1a**), *trans*-2-phenyl-3-(*p*-tolyl)-2,3-epoxypropionitrle (**1b**), and *trans*-3-phenyl-2-(*p*-tolyl)-2,3-epoxypropionitrile (**1c**). These substrates were chosen because of our previous success in demonstrating exclusive chlorine migration from the intermediate α-chloro epoxides in the epoxidation of *trans*-α-chlorostilbenes.[4]



Synthesis of 2,3-Diaryl-2,3-epoxypropionitriles.—The synthetic approach to **1a**–**c** involved the preparation of the *trans*-α,β-diarylacrylonitriles (**2**) followed by base catalyzed peroxidation. The *trans*-α,β-diarylacrylonitriles (**2a**–**c**) were readily prepared by the condensation of the appropriate arylacetonitrile and arylcarboxaldehyde in the presence of sodium ethoxide.[5] The *trans* configuration was assigned to these products on the basis of the observed ultraviolet spectra compared with those of *cis*- and *trans*-α,β-diphenylacrylonitrile (**2a**) previously reported[6] (Table I).



2a, R = R' = H
b, R = CH$_3$; R' = H
c, R = H; R' = CH$_3$

1

TABLE I
OBSERVED ULTRAVIOLET SPECTRA OF *cis*- AND *trans*-α,β-DIARYLACRYLONITRILES

	cis, λ_{max} (log ε)	*trans*, λ_{max} (log ε)
2a	224 (4.36), 295 (4.22)[6]	227 (4.27), 312 (4.41)[6]
2b		232 (4.13), 317 (4.40)
2c		229 (4.21), 317 (4.39)

Of the two literature methods for synthesizing **1a**, (1) treatment of desyl chloride with sodium cyanide in ethanol[7] and (2) basic peroxidation of **2a** with *t*-butyl hydroperoxide in the presence of benzyltrimethylammonium hydroxide,[8] the latter method was chosen since only *trans* isomer **1a** was obtained and in good yield. Applying this procedure to **2a**–**c** gave **1a**–**c** in

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[1] For paper IX in this series, see R. N. McDonald and R. N. Steppel, *J. Org. Chem.*, **35**, 1250 (1970).

[2] Taken from the M. S. Thesis of D. G. Hill, 1969. A portion of these results were communicated in *Chem. Commun.*, 671 (1969).

[3] For a review of this and related rearrangements of α-substituted epoxides, see R. N. McDonald in "Mechanisms of Molecular Migrations," Vol 3, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., in press.

[4] R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, **85**, 4004 (1963).

[5] (a) A. Bistrzycki and E. Stelling, *Ber.*, **34**, 3089 (1901); (b) K. Hohenlohe-Oeringen, *Monatsh. Chem.*, **89**, 484 (1958); (c) S. Wawzonek and E. M. Smolin, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 715.

[6] C. F. Codington and E. Mostig, *J. Org. Chem.*, **17**, 1027 (1952).

[7] E. P. Kohler and F. W. Brown, *J. Amer. Chem. Soc.*, **55**, 4299 (1933).

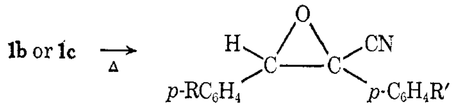
[8] G. B. Payne and A. H. Williams, *J. Org. Chem.*, **26**, 651 (1961).

good yields. The *trans* configurations of **1a–c** were based on the comparison of the spectral data given in Table II.

TABLE II
COMPARISON OF SOME INFRARED AND NMR ABSORPTIONS FOR 2,3-DIARYL-2,3-EPOXYPROPIONITRILES

		Epoxide ring		
	ν (CN), μ	ν_{sym}, μ	ν_{asym}, μ	τ (H_a)
1a	4.47	7.87	11.30	5.98
1b	4.47	7.88	11.35	6.05
1c	4.40	7.90	11.45	6.02
3b	4.45	8.48	11.16	5.32

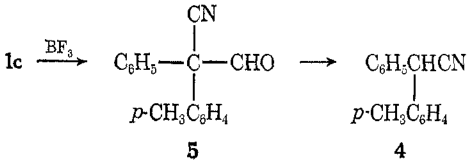
Attempted Thermal Rearrangement of 2,3-Diaryl-2,3-epoxypropionitriles.—α-Cyano epoxides **1b** and **1c** were each separately heated to 200° under full vacuum and passed through a 200-mm glass column filled with Pyrex helices heated to 350°. After four successive passes the nmr spectra of the product indicated that 40% of the starting material had been altered. The infrared and nmr spectra of the pure product gave conclusive evidence that only *trans* to *cis* isomerization had occurred in this thermolysis (see Table II). A similar isomerization had been observed when **1a** was photolyzed for short periods of time.[9]



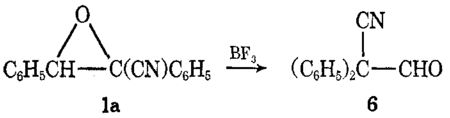
3

Boron Trifluoride Etherate Catalyzed Rearrangements of 2,3-Diaryl-2,3-epoxypropionitriles.—The boron trifluoride etherate catalyzed rearrangements of **1a–c** were chosen for study since it was felt that these might give a good opportunity to observe cyano group migration and greatly reduce the formation of α-fluorocyanohydrins, a major result when (1-cyanoethylidene)cyclohexane oxide is treated with excess boron trifluoride etherate.[10] The catalyzed rearrangement of **1a** and **1c** were first attempted in ether solvent but little or no rearrangement was observed over a short period of time. However, using benzene as solvent, complete rearrangement was observed almost immediately and the ratio of products was found to be quite independent of the concentration of catalyst used.

The boron trifluoride etherate catalyzed rearrangement of **1c** in benzene solution resulted in the formation of a single liquid product in 98% yield. The nmr spectrum (CCl_4, internal TMS[11]) of this liquid exhibited absorptions at τ 0.48 (s, 1), 2.68 (t, 5), 2.87 (s, 4), and 7.67 (s, 3), while the infrared spectrum showed characteristic absorptions at 4.45 (CN) and 5.75 μ (C=O). Chromatography of this liquid product on neutral alumina gave a 92% recovery of phenyl-*p*-tolylacetonitrile (**4**). The presence of the aldehyde function in the product, originally indicated from the nmr and infrared spectra, was established by a positive Tollens test, the product of this reaction followed by acidification being **4**, and preparation of the 2,4-dinitrophenylhydrazone derivative. These facts establish the structure of the product from the catalyzed rearrangement of **1c** to be α-cyanophenyl-*p*-tolylacetaldehyde (**5**), the easy decarbonylation during chromatography being due to a retrograde Claisen condensation which also occurred when **5** was treated with bases or distilled. Aldehyde **5** could be obtained in a fairly pure state if the rearrangement solution is only washed briefly with a dilute, aqueous solution of sodium carbonate for the work-up.



When a benzene solution of α-cyano epoxide **1a** was similarly treated with boron trifluoride etherate, the nmr spectrum of the product indicated incomplete rearrangement. The nmr spectrum of the crude product (99% recovery) showed that along with **1a** only α-cyanodiphenylacetaldehyde (**6**) was present; integration of the aldehydic proton *vs.* that of the total aromatic protons indicated that 37% **6** had been formed. The presence of **6** was confirmed by the presence of the carbonyl absorption at 5.77 μ in the infrared spectrum.



With only a single mode of aryl migration established in the catalyzed rearrangements of **1a** and **1c**, we suspected that this same single process would be observed on similar treatment of **1b**. That this was not the case was immediately evident from the nmr spectrum of the rearrangement mixture which is recovered in 98% yield. Washing the rearrangement mixture with water until barely acidic, drying, and evaporation of the solvent gave the product residue whose nmr spectrum (CCl_4, internal TMS) exhibited absorptions at τ 0.53 (s, 0.47, CHO), 2.70–2.95 (m, 9, aromatic), 4.88 (s, 0.53, methine), and 7.71 (d, 3, methyl). Addition of deuterium oxide to this sample resulted in no exchange of the protons. The infrared spectrum showed two nitrile absorptions at 4.50 (w) and 4.55 μ (m), and a broadened carbonyl stretching frequency centered at 5.85 μ (s).

If the benzene solution from the rearrangement of **1b** was washed with a saturated aqueous solution of sodium bicarbonate in the work-up procedure the nmr spectral absorption at τ 4.88, above, was lost. Addition of deuterium oxide resulted in no noticeable proton exchange even though the infrared spectra of the rearrangement product so obtained showed a strong hydroxyl absorption at 3.14 μ. The lack of observing the hydroxyl proton in the nmr spectrum could simply be due to its exchange rate in the sample.

These facts suggested that the rearrangement mixture from **1b** was composed of aldehyde **5** (47%) and a cyano ketone **7** (53%) which is readily and, apparently, completely converted to its enol by base treatment.

Our approach to the proof of structure of this cyano ketone product was to consider that it might be the product of either cyano or hydrogen migration from **1b**

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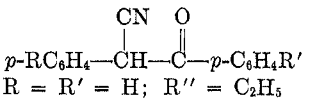
[9] I. P. Stepanov, O. A. Ikonopistseva, and T. I. Temnikova, *J. Org. Chem., USSR*, **2**, 2216 (1966).

[10] G. Stork, W. S. Worrall, and J. J. Pappas, *J. Amer. Chem. Soc.*, **82**, 4315 (1960).

[11] Tetramethylsilane.

which would yield α-cyano-α-(*p*-tolyl)acetophenone (**8b**) or α-cyano-*p*-methyl-α-phenylacetophenone (**8c**), respectively. These two α-cyano ketones, along with α-cyano-α-phenylacetophenone (**8a**), were prepared by the condensation of the appropriate alkyl arylcarboxylate and arylacetonitrile in ether with sodium hydride. The spectral data for **8b** and **8c** did not agree with that of the unknown cyano ketone **7**. The only remaining rearrangement to consider from **1b** would be phenyl migration leading to the formation of phenyl-*p*-tolypyruvonitrile (**7a**).

$p\text{-RC}_6\text{H}_4\text{CH}_2\text{CN} + p\text{-R}'\text{C}_6\text{H}_4\text{CO}_2\text{R}'' \longrightarrow$

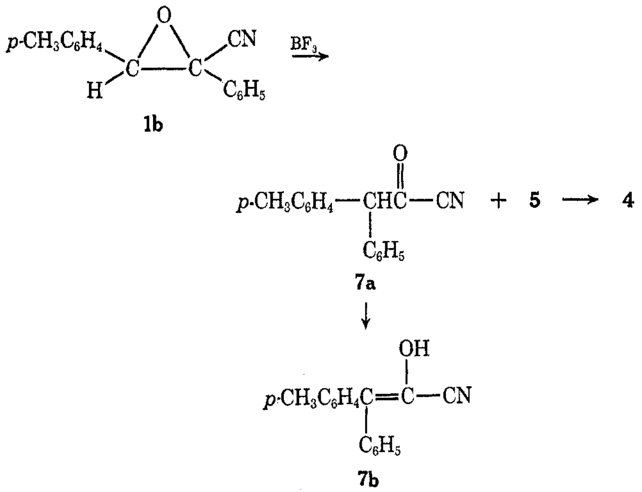


$p\text{-RC}_6\text{H}_4\text{—}\overset{\text{CN}}{\overset{|}{\text{C}}}\text{H—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—}p\text{-C}_6\text{H}_4\text{R}'$

8a, R = R′ = H; R″ = C_2H_5
b, R = CH_3; R′ = H; R″ = C_2H_5
c, R = H; R′ = CH_3; R″ = CH_3

The separation of **5** and **7** by column chromatography on silica gel failed and on neutral alumina gave only nitrile **4**, the "decarbonylation" product from **5**, which could be hydrolyzed in 70% sulfuric acid to phenyl-*p*-tolylacetamide. Treatment of the mixture of **5** and **7** with a slight excess of 2,4-dinitrophenylhydrazine (**9**) gave only recovered **9** and the 2,4-dinitrophenylhydrazone of **5**; this derivative of **5** could be isolated in 41% yield (87% yield based on available **5**).

After several fruitless attempts, **7** was finally separated from **5** and its decomposition product **4** by extraction of an ether solution of **5** and **7** with a dilute, aqueous potassium carbonate solution. Upon rapid separation of layers, acidification, and ether extraction of the acidic layer, **7** was obtained as a crystalline solid. Compounds **4** and **5** were obtained from the original ether layer which were completely converted to **4** when chromatographed on neutral alumina.



1b

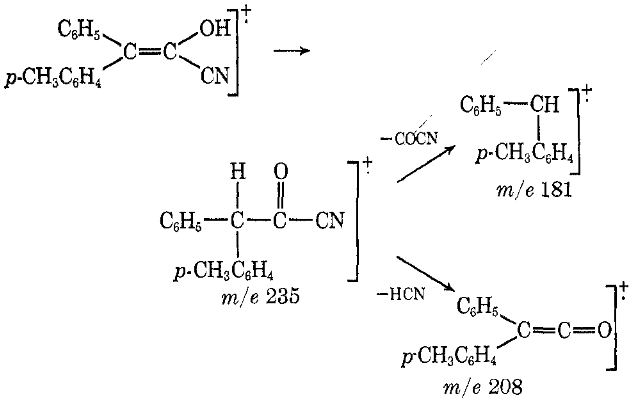
7a

7b

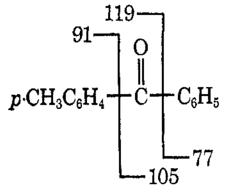
The infrared spectrum of **7** showed hydroxyl absorption at 3.09 μ and nitrile absorption at 4.50 μ with no evidence of a carbonyl stretch; a similar but more resolved infrared spectrum was obtained as a 15% solution of **7** in chloroform. The nmr spectrum (CDCl_3, internal TMS) of **7** exhibited a broad absorption at τ 4.05, assigned to the hydroxyl group of **7b**, which disappeared on addition of deuterium oxide. Other than the absorptions for the aromatic protons, two peaks were observed at τ 7.67 and 7.69 for the methyl protons. Our interpretation of these spectra is that we are dealing with the *cis* and *trans* isomers of **7b** and *not* with a measurable equilibrium mixture of **7a** and **7b**.

The ultraviolet spectrum of **7b** was similar to the spectra observed for α-cyano ketones **8a–c** but exhibited a greater molar absorptivity. This can be rationalized since Russell[12] has shown that the keto–enol tautomerism of **8a** occurs even in nonpolar solvents.

The 70-eV mass spectrum of **7b** was quite interesting. The fragmentations which are most informative and require our structural assignment of **7b** involve the losses of HCN (*m/e* 27) and COCN (*m/e* 54) from the parent ion radical ($\text{M}\cdot^+$, *m/e* 235); both processes show the required metastables. It seems reasonable to assume the ketonization occurs in $\text{M}\cdot^+$ which is analogous to the same reaction used to describe the most important fragmentations of phenol.[13]



Other peaks observed at 196, 165, 119 (base peak), and *m/e* 106 could not be explained by the fragmentation of **7**, **8b**, or **8c**, or other isomeric compounds. The presence of three of these peaks was rationalized by oxidation of **7b** occurring in the mass spectrometer at 70 eV to give 4-methylbenzophenone. These peaks were found to decrease in intensity in successive spectra and completely disappeared when observed at 11 eV. The origin of the ion at *m/e* 165 is uncertain.



Further evidence for structure **7b** was obtained when it was hydrolyzed with 25% sulfuric acid or 5% aqueous sodium hydroxide at 100° to phenyl-*p*-tolylacetic acid, which may be the direct result of hydrolysis of enol **7b** itself or proceed by way of an equilibrium, **7a** ⇄ **7b**, and **7a** undergoing hydrolysis.

The methyl ether of enol **7b** was also prepared by reaction with diazomethane. The infrared and nmr spectra, and the elemental analysis were in agreement with the structure of the product as α-methoxy-β-phenyl-β-(*p*-tolyl)acrylonitrile (**10**).

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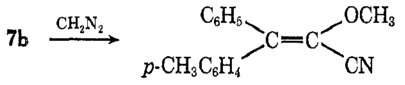
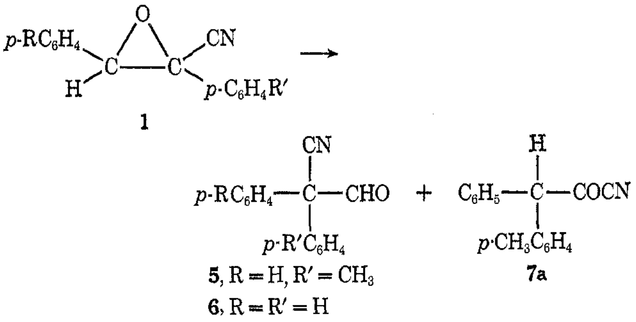
[12] P. B. Russell, *J. Amer. Chem. Soc.*, **74**, 2654 (1952).

[13] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 115.



10

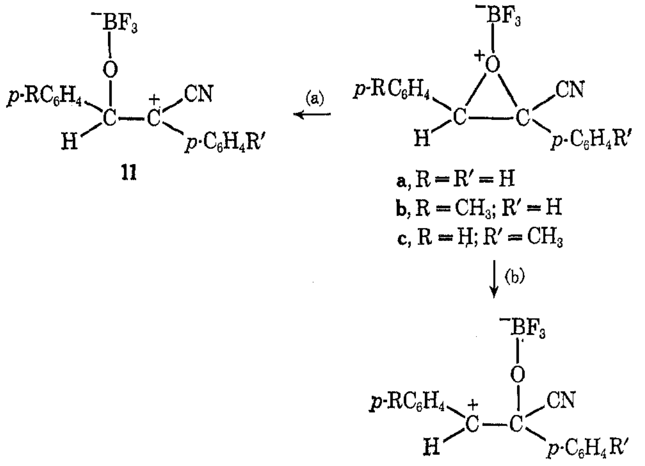
To summarize the rearrangement results, **1a** and **1c** rearrange in the presence of boron trifluoride etherate in benzene solution exclusively by phenyl migration to yield the corresponding α-cyanodiarylacetaldehyde, **6** and **5**, respectively, while **1b** produces **5** (47%) and **7a** (53%) by *p*-tolyl and phenyl migration, respectively. It should be noted that no evidence for cyano group migration was found.



If these catalyzed rearrangements occurred by a concerted mechanism, the stereochemistry of the transition state would be very nearly the same for **1a–c**. If we assume little or no charge buildup, then rearrangement of the best migrating group should be the major control on product formation, and similar distributions of products should be observed from the three α-cyano epoxides. With **1b**, since *p*-tolyl is a better migrating group than phenyl, we would expect that the resulting product, **5**, would predominate; the opposite situation is observed. Stereochemistry cannot be a factor since all are *trans*.[14] Also, arguments opposed to such concerted epoxide–carbonyl rearrangements have been presented.[4]

If, however, a stepwise rearrangement occurs involving epoxide ring opening followed by aryl migration, the effect of substituent groups in the aryl group should be influential in controlling the course of the rearrangements. This influence would appear to be greatest if the heterolytic epoxide ring opening is rate determining followed by a fast aryl migration step, the latter process being facilitated by concurrent generation of the carbonyl group.

If we assume that the unaccounted for 2% of starting material from the rearrangements of **1a** and **1c** went by way of intermediate **12**, then the replacement of hydrogen by methyl (R) in **12** would require a lowering of the transition-state energy in forming **12b** relative to **12a** or **12c** by $\Delta\Delta F^{\ddagger} \approx 2.3$ kcal/mol. This is equal to a rate factor of about 50 for the *p*-CH_3 *vs.* hydrogen substituent effect.[15] This does not seem too unreasonable since the same substituent effect in the aqueous acetone solvolysis of benzyl tosylates gives a rate factor of 30.[16] It should be surprising that the influence of substituents would be greater in the present case since the electron demand on the substituent is greatly increased in benzene as solvent as compared with aqueous acetone used in the benzyl tosylate solvolyses.



12

An interesting corollary arises if the stepwise mechanism and the discussion above are correct. This is that the cyano group in **11** is stabilizing to the carbonium ion center. If the cyano group destabilized the attached carbonium ion, we would expect to find ring opening (b) occurring in **1a–c** and a substituent effect as R′ of **11** is changed from hydrogen (**1a**) to methyl (**1c**). This is not observed; however, the results can be rationalized by cyano group stabilization of **11** swamping out the substituent, R′, effect.

Experimental Section[17]

***trans*-α-Phenyl-β-(*p*-tolyl)acrylonitrile (2b).**—The method used here was that described for the synthesis of **2a**.[5c] The crude product from 39.7 g (0.33 mol) of *p*-tolualdehyde and 38.6 g (0.33 mol) of phenylacetonitrile was repeatedly recrystallized from ethanol to give 37.2 g (52%) of **2b**, mp 58.5–59.0° (lit.[5a] mp 61°). The infrared spectrum (KBr) exhibited nitrile absorption at 4.53 μ while the nmr spectrum (CCl_4, internal TMS) showed absorptions at τ 2.10–2.90 (m, 10, aromatic and vinyl) and 7.65 (s, 3, methyl).

***trans*-β-Phenyl-α-(*p*-tolyl)acrylonitrile (2c).**—Using the same procedure as for the preparation of **2b**, 47.7 g (0.36 mol) of *p*-tolylacetonitrile and 41.7 g (0.39 mol) of benzaldehyde gave, after recrystallization from ethanol, 69.6 g (87%) of **2c**, mp 77.5–78.0° (lit.[5b] mp 74°). The infrared spectrum (KBr) exhibited nitrile absorption at 4.52 μ and the nmr spectrum (CCl_4, internal TMS) showed absorptions at τ 2.10–3.00 (m, 10, aromatic and vinyl) and 7.69 (s, 3, methyl).

***trans*-2,3-Diphenyl-2,3-epoxypropionitrile (1a).**—The procedure for the preparation of **1a** has been described.[8] Crude **1a** (8.7 g) was recrystallized from methanol to give 5.0 g (59%) of **1a**, mp 70.0–70.5° (lit.[8] mp 70.0–70.5°). The nmr spectrum (CCl_4, internal TMS) exhibited absorptions at τ 2.67 (s, 10, aromatic) and 5.98 (s, 1, epoxide ring).

***trans*-2-Phenyl-3-(*p*-tolyl)-2,3-epoxypropionitrile (1b).**—As per the procedure used to prepare **1a**, 41.6 g (0.19 mol) of **2b** gave, after recrystallization from methanol, 37.0 g (84%) of α-cyano epoxide **1b**. Further recrystallizations from a small volume of ether gave product with a melting point of 81.0–81.5°. The nmr spectrum (CCl_4, internal TMS) exhibited absorptions centered at τ 2.65 and 2.82 (m's, 9, aromatic), 6.05 (s, 1, epoxide ring), and 7.65 (s, 3, methyl).

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[14] H. O. House and D. J. Reif, *J. Amer. Chem. Soc.*, **77**, 6525 (1955).

[15] If 1% of the rearrangement of **1a** and **1c** go by way of **12** the rate factor would be about 100, $\Delta\Delta F^{\ddagger} \approx 2.7$ kcal/mol.

[16] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

[17] All melting points were taken on a Kofler hot stage and are corrected; boiling points are uncorrected. Infrared, nmr, and ultraviolet spectra were recorded using P-E Model 137, Varian A-60, and Cary Model 11 spectrophotometers, respectively. Mass spectra were determined with an MS-9 mass spectrometer. Solution molecular weights were obtained with a Mechrolab osmometer, Model 301A, and microanalyses were performed by Galbraith Laboratories, Inc.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.65; H, 5.57. Found: C, 81.67; H, 5.44.

***trans*-3-Phenyl-2-(*p*-tolyl)-2,3-epoxypropionitrile (1c).**—As per the procedure used to prepare **1a**, 24.1 g (0.11 mol) of **2c** gave, after recrystallization from methanol, 19.7 g (76%) of **1c**. Further recrystallizations from a small volume of ether gave product with a melting point of 77.8–78.2°. The nmr spectrum (CCl_4, internal TMS) exhibited absorptions at τ 2.60–2.90 (m, 9, aromatic), 6.02 (s, 1, epoxide ring), and 7.68 (s, 3, methyl).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.65; H, 5.57. Found: C, 81.77; H, 5.64.

Boron Trifluoride Etherate Catalyzed Rearrangement of 1a.—Boron trifluoride etherate (0.28 ml, 2.0 mmol) was added to a solution of 1.00 g (4.25 mmol) of α-cyano epoxide **1a** in 13 ml of dry benzene. After standing for 10 min at room temperature, this reaction mixture was washed with water until the aqueous washings were barely acidic and dried ($CaCl_2$), and the solvent was removed under reduced pressure to give 0.99 g of crude product.

The infrared spectrum of this product showed absorptions at 4.45 (CN) and 5.77 μ (C=O) while the nmr spectrum (CCl_4, internal TMS) exhibited absorptions at τ 0.45 (s, 0.37, aldehyde), 2.55–2.88 (m, 10, aromatic), and 5.95 (s, 0.63, epoxide ring). It was concluded that this product was a mixture of 63% starting material (**1a**) and 37% diphenyl-α-cyanoacetaldehyde (**6**). The combination of the spectra of **1a** and **6** account for every peak in the nmr and infrared spectra of this rearrangement mixture.

Boron Trifluoride Etherate Catalyzed Rearrangement of 1b.—To a stirred solution of 2.09 g (8.5 mmol) of α-cyano epoxide **1b** in 25 ml of dry benzene was added 0.55 ml (4.0 mmol) of freshly distilled boron trifluoride etherate. After 10 min, the solution was washed with water until barely acidic, dried ($CaCl_2$), and filtered. Evaporation of the solvent gave 2.04 g of rearrangement product. The infrared and nmr spectra of this product are given in the discussion.

If a sample of the epoxide was treated with boron trifluoride etherate in benzene (as above) but the benzene solution was evaporated under reduced pressure, a green residue was obtained which exhibited the same nmr and infrared spectra as observed above. However, if the benzene solution was treated with a saturated solution of sodium bicarbonate in the work-up procedure, the nmr spectrum remained identical except for the peak at τ 4.88 which disappeared. Addition of deuterium oxide resulted in no obvious change in the spectrum. The infrared spectrum of this sample now exhibited a strong hydroxyl absorption at 3.14 μ.

A 1.09-g sample of the original rearrangement product from **1b** was chromatographed on neutral, activity II–III alumina. Evaporation of the solvent from the various fractions gave only one fraction (petroleum ether–benzene) which solidified on standing. The crystalline solid, 0.40 g, was sublimed (60°, 0.05 mm), recrystallized from hexane, and resublimed to a final melting point of 61–62°. Molecular weight determination ($CHCl_3$) gave a value of 207 ± 2. The infrared spectrum (KBr) of this material exhibited nitrile absorption at 4.48 μ and the nmr spectrum (CCl_4, internal TMS) had absorptions at τ 2.75 (s, 5, aromatic), 2.90 (s, 4, aromatic), 5.05 (s, 1, methine), and 7.70 (s, 3, methyl). This data was in agreement with the structure phenyl-*p*-tolyacetonitrile (**4**) (lit.[18] mp 61–62°) for this product.

Utilizing the method of Shine[19] for the preparation of 2,4-dinitrophenylhydrazones; 0.50 g (2.13 mmol) of rearrangement product from **1b** was added to 13 ml of a 0.168 *M* solution (2.18 mmol) of 2,4-dinitrophenylhydrazine in diglyme followed by 3 drops of concentrated hydrochloric acid. Evaporation of the solvent under reduced pressure left a bright yellow-red residue. Fractional recrystallization from ethanol–ethyl acetate gave a difficult to purify residue and excess 2,4-dinitrophenylhydrazine. Only one 2,4-dinitrophenylhydrazone was indicated as being present.

Repeating the above procedure using 7 ml (1.17 mmol) of 2,4-dinitrophenylhydrazine reagent; 0.36 g (41% yield) of the 2,4-dinitrophenylhydrazone was obtained after recrystallization from ethanol–ethyl acetate. Repeated recrystallization from ethanol–ethyl acetate gave an analytical sample with mp 178–178.5°.

Anal. Calcd for $C_{22}H_{17}N_5O_4$: C, 63.61; H, 4.13; N, 16.86. Found: C, 63.86; H, 4.02; N, 16.93.

The infrared and nmr spectra indicated the product to be α-cyanophenyl-*p*-tolylacetaldehyde (**5**) 2,4-dinitrophenylhydrazone. The nmr spectrum ($CDCl_3$, internal TMS) exhibited peaks at τ −1.15 (broad s, 1, NH), 0.19 (d, 1, aromatic), 1.6–1.8 (q, 1, aromatic), 1.82 (s, 1, aromatic), 2.10 (s, 1, methine), 2.57 (s, 5, aromatic), 2.73 (s, 4, aromatic), and 7.63 (s, 3, methyl). The infrared spectrum exhibited absorptions at 3.09 (NH), 4.46 (C≡N), and 6.20 μ (C=N).

A 2.0-g sample of the original rearrangement mixture in 50 ml of ether was rapidly extracted with three portions of 5% aqueous potassium carbonate. The chilled basic solution was immediately acidified and extracted three times with ether. The ether extracts were combined, washed with water, and dried ($CaCl_2$). Evaporation of the ether left an oil (1.0 g) which solidified on addition of carbon tetrachloride. Recrystallization from cyclohexane gave 0.64 g of product, mp 111–112° (sealed tube). A sample was taken and purified further by slow sublimation at 70° (0.05 mm), followed by two recrystallizations from cyclohexane, mp 114–115° (sealed tube). An nmr spectrum of the sample indicated no change in purity. The product was resublimed and submitted for analysis.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57. Found: C, 81.27; H, 5.64.

The product is assigned the structure of α-hydroxy-β-phenyl-β-(*p*-tolyl)acrylonitrile (**7b**) from this and its spectral data. The infrared spectra (KBr and $CHCl_3$ solution) of **7b** have been presented in the discussion while the nmr spectrum ($CDCl_3$, internal TMS) exhibited absorptions centered at τ 4.05 [broad, 1, hydroxyl (removed with D_2O)], 2.70 and 2.85 (m, 9, aromatic), and 7.68 (d, 3, methyl). The ultraviolet spectrum (ethanol) of this compound exhibited absorption maxima at 290 (log ϵ, 4.23) and 235 nm (log ϵ 4.08). The mass spectrum has been discussed.

Boron Trifluoride Etherate Catalyzed Rearrangement of 1c.—To a stirred solution of 2.03 g (8.5 mmol) of **1c** in 25 ml of dry benzene was added 0.55 ml (4.0 mmol) of freshly distilled boron trifluoride etherate. After 10 min, the solution was washed with water, until barely acidic, dried ($CaCl_2$), and filtered. An oil (1.99 g) was obtained after evaporation of excess benzene. The nmr spectrum (CCl_4, internal TMS) of this oil indicated complete rearrangement; absorptions at τ 0.48 (s, 1, aldehyde), 2.68 (t, 5, aromatic), 2.87 (s, 4, aromatic), and 7.67 (s, 3, methyl) were observed in the nmr spectrum. The infrared spectrum exhibited absorptions at 4.45 (CN) and 5.75 μ (CO).

The oil (0.20 g, 0.85 mmol) was chromatographed on neutral alumina, activity II–III. Evaporation of the solvents gave only one fraction (0.16 g) which solidified upon standing. The solid was sublimed at 60° (0.05 mm), to give the product (92%) with a melting point of 60–61°. The infrared and nmr spectra were identical with those previously obtained for phenyl-*p*-tolylacetonitrile (**4**).

A 0.50-g sample of rearrangement product from **1c** was added to 15 ml of a 0.168 *M* solution of 2,4-dinitrophenylhydrazine in diglyme followed by 3 drops of concentrated hydrochloric acid. The solution was cooled and a residue formed on addition of water. Recrystallization from ethanol–ethyl acetate gave 0.48 g (55%) of the 2,4-dinitrophenylhydrazone, mp 178.0–178.5°. The infrared and nmr spectra were identical with those of α-cyanophenyl-*p*-tolylacetaldehyde (**5**) 2,4-dinitrophenylhydrazone.

Purification of **5** was difficult owing to the ease of decarbonylation in the presence of base. Attempted bisulfite addition and distillation also resulted in quantitative yields of phenyl-*p*-tolylacetonitrile. If the crude aldehyde dissolved in benzene was washed once with a saturated solution of sodium bicarbonate followed by water, dried, and solvent evaporated, the purest **5** was obtained. The infrared spectrum exhibited absorptions at 4.45 (CN) and 5.75 μ (C=O). The nmr spectrum (CCl_4, internal TMS) exhibited absorptions at τ 0.45 (s, 1, aldehyde), 2.72 (t, 5, aromatic), 2.68 (s, 4, aromatic), and 7.67 (s, 3, methyl).

Treatment of 0.75 g (3.2 mmol) of **5** with Tollens reagent[20] produced a silver precipitate which was filtered and washed with hot water and methanol, and the combined filtrates were acidified. The solution was cooled and filtered, and the crystals obtained were sublimed at 60°, (0.05 mm) giving 0.43 g (65%) of nitrile **4**, mp 60–61°.

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Phenyl-*p*-tolylacetamide.—Phenyl-*p*-tolylacetonitrile (0.40 g, 1.93 mmol) was hydrolyzed in 10 ml of 75% sulfuric acid at 100° for 11 hr. The cooled solution was poured over ice and extracted with ether. The ether layers were combined, extracted three times with a 5% solution of potassium carbonate, and washed with water. The etheral solution was dried and excess solvent was removed leaving a crystalline product (0.14 g). The infrared and nmr spectra indicated the product to be phenyl-*p*-tolylacetamide, mp 155.7–156° (lit.[21] 151°). The infrared spectrum exhibited characteristic absorptions at 6.05 (C=O) and 3.20 μ (NH_2). The nmr spectrum ($CDCl_3$, internal TMS) exhibited absorptions at τ 2.75 (s, 5, aromatic), 2.88 (s, 4, aromatic), 3.70–4.50 (broad s, 2, NH_2), 5.13 (s, 1, methine), and 7.70 (s, 3, methyl).

Hydrolysis of α-Hydroxy-β-phenyl-β-(*p*-tolyl)acrylonitrile (7b). 1. **With Aqueous Sulfuric Acid.**—α-Hydroxy-β-phenyl-β-(*p*-tolyl)acrylonitrile (0.20 g, 0.89 mmol) was hydrolyzed in 10 ml of 25% aqueous sulfuric acid at 100° for 6 hr. The solution was cooled and extracted with ether. The combined ether extracts were extracted with 5% aqueous potassium carbonate followed by water. Evaporation of the ether layer left a residue (2 mg) which was not further investigated. After acidification of the carbonate extracts with 10% hydrochloric acid and extraction with ether, the ether layer was washed with water, dried ($CaCl_2$), and evaporated to yield 0.14 g of an oil which soon solidified. Recrystallization from cyclohexane gave 90 mg (45%) of phenyl-*p*-tolylacetic acid, mp 114.5–115° (lit.[22] mp 115–116°). The infrared and nmr spectra obtained were identical with those of an authentic sample.

2. **With 5% Aqueous Sodium Hydroxide.**—α-Hydroxy-β-phenyl-β-(*p*-tolyl)acrylonitrile (0.20 g, 0.89 mmol) was hydrolyzed with 10 ml of 5% aqueous sodium hydroxide at 100° for 6 hr. After the cooled solution was extracted with ether, the basic solution was acidified with 10% sulfuric acid and extracted again with ether. The ether extracts of the acidified solution were combined, washed, and dried, and the excess solvent was evaporated. The solid obtained (0.17 g) was recrystallized from cyclohexane to yield 0.16 g (80% yield) of phenyl-*p*-tolylacetic acid, mp 114–115°.

α-Methoxy-β-phenyl-β-(*p*-tolyl)acrylonitrile (10).—An excess of diazomethane was added to 0.30 g (1.28 mmol) of α-hydroxy-β-phenyl-β-(*p*-tolyl)acrylonitrile in ether. After 3 hr, the excess diazomethane and ether were removed under vacuum to obtain an oil whose nmr spectrum indicated a good yield of the methyl vinyl ether. The oil was taken up in ether and extracted with a dilute solution of sodium bicarbonate to rid the solution of any enol that might be present. The solid obtained upon evaporation of ether was sublimed three times (60°, 0.05 mm) and recrystallized twice from pentane interchangably until the product appeared pure from the nmr spectrum. An analytical sample of **10** was obtained with mp 79.5–80.5°.

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.91; H, 6.07. Found: C, 82.01; H, 6.08.

The infrared spectrum exhibited a nitrile absorption at 4.58 μ. The nmr spectrum (CCl_4, internal TMS) exhibited absorptions at τ 2.73 (s, 5, aromatic), 2.94 (m, 4, aromatic), 6.26 (s, 3, methoxyl), and 7.70 (s, 3, methyl).

α-Cyano-α-phenylacetophenone (8a).—To a well-stirred solution of 6.1 g (0.10 mol) of a 40% sodium hydride dispersion in 50 ml of dry ether, 5.84 g (0.05 mol) of phenylacetonitrile was added dropwise. The etheral solution was heated under reflux for 0.5 hr, cooled, and ethyl benzoate (7.50 g, 0.05 mol) was added dropwise. This mixture was stirred overnight and then hydrolyzed by the slow addition of water and extracted with ether. The aqueous layer was cooled, acidified (10% H_2SO_4), and extracted with ether. The combined ether extracts were washed and dried ($CaCl_2$), and the ether was removed under reduced pressure. Compound **8a** (7.9 g) was recrystallized from ether–cyclohexane to give 7.0 g (64%) of product, mp 91.5–92.0° (lit.[23] mp 91–92°).

The infrared spectrum exhibited absorptions at 4.47 (CN), and 5.95 μ (CO). The nmr spectrum ($CDCl_3$, internal TMS) exhibited absorptions at τ 1.95–2.18 and 2.40–2.85 (complex m, 9, aromatic) and 4.33 (s, 1, methine). Addition of deuterium oxide resulted in no exchange with deuterium. The ultraviolet spectrum[12] exhibited absorption maxima at 291 (log ϵ 4.12) and 249 nm (log ϵ, 3.97) in ethanol.

α-Cyano-α-(*p*-tolyl)acetophenone (8b).—The procedure described for the synthesis of **8a** was employed here. Recrystallization of the crude product from ether–cyclohexane gave 9.5 g (81%) of **8b**, mp 94.0–94.5°.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57. Found: C, 82.02; H, 5.66.

The infrared spectrum exhibited absorptions at 4.48 (CN) and 5.95 μ (CO). The nmr spectrum ($CDCl_3$, internal TMS) exhibited absorptions at τ 1.95–2.17 and 2.42–2.97 (complex m, 9, aromatic), 4.37 (s, 1, methine), and 7.73 (s, 3, methyl). Addition of dueterium oxide resulted in no exchange with deuterium. The ultraviolet spectrum in ethanol exhibited an absorption maximum at 293 nm (log ϵ 4.14).

α-Cyano-*p*-methyl-α-phenylacetophenone (8c).—The procedure used in the preparation of **8a** was employed. From 5.84 g (0.05 mol) of phenylacetonitrile and 7.50 g (0.50 mol) of methyl *p*-toluate 7.7 g (66%) of **8c** was obtained after recrystallization from ether–cyclohexane, mp 104–104.5°.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57. Found: C, 81.78; H, 5.71.

The infrared spectrum exhibited absorptions at 4.45 (CN) and 5.97 μ (C=O). The nmr spectrum ($CDCl_3$, internal TMS) exhibited absorptions at τ 2.05–2.30 and 2.50–2.90 (complex m, 9, aromatic), 4.37 (s, 1, methine), and 7.65 (s, 3, methyl). Addition of deuterium oxide resulted in no exchange with deuterium. The ultraviolet spectrum in ethanol exhibited an absorption maximum at 290 nm (log ϵ 4.12).

Near Thermal Rearrangement of 1b.—α-Cyano epoxide **1b** (2.0 g, 8.6 mmol) was heated at 200° under full vacuum and passed successively through a 200-mm column containing Pyrex helices heated to 350° by a coil furnace. The rearrangement was followed by nmr spectroscopy. The crystalline product was recrystallized from methanol to remove some of the epoxide (0.43 g). The residue obtained was chromatographed on neutral alumina, activity II–III. Elution with cyclohexane–carbon tetrachloride gave 0.61 g of recovered epoxide, 0.52 g of a mixture of epoxide and isomerized product, and 0.14 g of thermally isomerized product. Three successive sublimations gave 0.12 g of pure isomerized epoxide, mp 85.5–86°.

Times through column	% rearranged
1	11
3	27
4	40

The infrared and nmr spectra indicated the product to be *cis*-2-phenyl-3-(*p*-tolyl)-2,3-epoxypropionitrile. The infrared spectrum exhibited absorption at 4.45 μ (CN); other bands present at 8.48 and 11.13 μ were attributed to the symmetric and asymmetric stretch of the epoxide ring.[24] The nmr spectrum (CCl_4, internal TMS) exhibited peaks at τ 2.70 (s, 5, aromatic), 3.00 (s, 4, aromatic), 5.32 (s, 1, epoxide ring), and 7.77 (s, 3, methyl).

Neat Thermal Rearrangement of 1c.—The procedure for the thermal rearrangement of this compound was the same as described above for **1b**. The per cent of rearranged product, as determined by nmr spectroscopy, is given below. It was concluded that *trans* to *cis* isomerization must be occurring also for this compound.

Times through column	% rearranged
1	11
2	20
3	28
4	40

Registry No.—**1a**, 15115-82-9; **1b**, 25125-18-2; **1c**, 25125-28-4; **2b**, 25125-29-5; **2c**, 25125-30-8; **3b**, 25125-31-9; **5**, 25125-32-0; 2,4-dinitrophenylhydrazone of **5**, 25125-33-1; **7b**, 25125-34-2; **8a**, 5415-07-6; **8b**, 25124-91-8; **8c**, 25124-92-9; **10**, 25124-93-0; phenyl *p*-tolylacetamide, 25124-94-1.

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Condensation of Cyclic Olefins with Paraformaldehyde and Hydrogen Chloride

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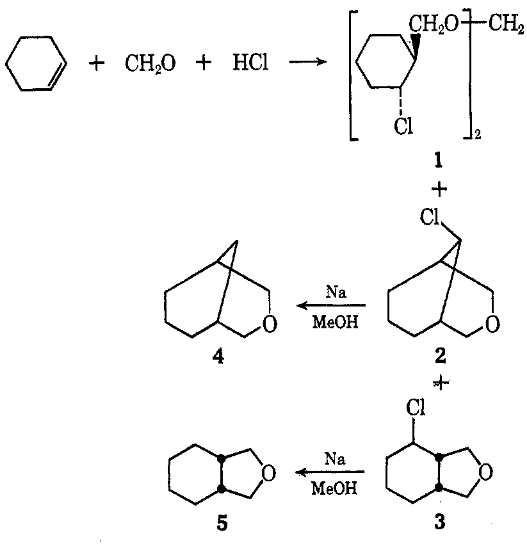
Condensation of cyclohexene with paraformaldehyde and hydrogen chloride at −60 to −70° gave a good yield of a mixture of two bicyclic chlorinated ethers along with a small amount of the formal of *trans*-2-chlorocyclohexanemethanol (**1**). The structure of the principal component (80% of the mixture) was established by chemical degradation, synthesis, and nmr as *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane (**2**), and the minor component was identified as *trans*-6-chloro-*cis*-3-oxabicyclo[4.3.0]nonane (**3**). Under similar conditions, cyclopentene gave 2-chlorocyclopentanemethanol (**7**) (60% yield) and a mixture of two isomeric bicyclic chlorinated ethers (32%) in a ratio of 2:1. These were separated and identified as 6-chloro-*cis*-3-oxabicyclo[3.3.0]-octane (**8**) and 8-chloro-3-oxabicyclo[3.2.1]octane (**9**), respectively. Calculated nmr spectra were obtained which were useful in establishing the stereochemistry and nature of ring fusion in both the 3-oxabicyclononanes and 3-oxabicyclooctanes.

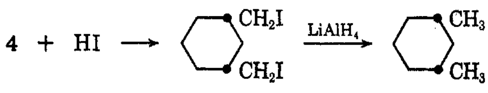
A number of investigators have studied the sulfuric acid catalyzed reaction of cyclohexene and formaldehyde in acetic acid solution.[1–3] The reaction leads to a complex mixture of products, but the major constituents are derivatives of *trans*-2-hydroxymethylcyclohexanol and none of the *cis* isomer is found. Blomquist[1] identified *trans*-9-hydroxy-*cis*-3-oxabicyclo[3.3.1]nonane as a minor by-product and Dolby[3] later isolated and identified small quantities of *trans*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane from a similar reaction. In a related study of the reaction of cyclohexene, paraformaldehyde, and hydrochloric acid, Volynskii[4] identified the formal of *trans*-2-chlorocyclohexanemethanol (**1**) as the major product and found 5% each of *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane (**2**) and *trans*-6-chloro-*cis*-3-oxabicyclo[4.3.0]nonane (**3**).[5] The stereochemistry of **2** and **3** was elucidated by conversion to the known hydroxy compounds.

In previous articles[6–8] we described a novel modification of the Prins reaction in which various olefin types were treated with paraformaldehyde and hydrogen halides at low temperatures. Extension of this modified Prins reaction to include the condensation of cyclohexene and cyclopentene with paraformaldehyde is considered in this report. As a number of bicyclic compounds became available during the course of this work, an opportunity was afforded to consider some aspects of theoretical calculations of the nmr spectra of these bicyclic systems.

Introduction of hydrogen chloride into a paraformaldehyde–cyclohexene mixture (1.5:1 mol ratio) in methylene chloride at −60 to −70° gave, in addition to a substantial quantity of cyclohexyl chloride and a small amount of **1**, 65–75% yields of a mixture of two bicyclic chlorinated ethers. The structure of the principal component (80% of the mixture) was established by elemental analysis, chemical degradation, and its nmr spectrum as *trans*-9-chloro-*cis*-3-oxabicyclo-[3.3.1]nonane (**2**) and the minor component was assigned the structure of *trans*-6-chloro-*cis*-3-oxabicyclo-[4.3.0]nonane (**3**) (Scheme I). The structures of the basic ring systems were established by removal of the chlorine from the mixture of bicyclics with sodium and methanol to give *cis*-3-oxabicyclo[3.3.1]nonane (**4**) and *cis*-3-oxabicyclo[4.3.0]nonane (**5**) in the same 4:1 ratio. These were separated by preparative glpc; elemental analyses, mass spectra, and nmr spectra were in complete agreement with the assigned structures. Chemical confirmation of **4** as *cis*-3-oxabicyclo[3.3.1]nonane

SCHEME I





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[5] In naming **2** as *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane, Volynskii[4] differs from earlier investigators by designating the ring fusion as *cis*. We are not aware of any derivatives of *trans*-3-oxabicyclo[3.3.1]nonane; hence it might appear that this is unnecessary. Inspection of molecular models of 3-oxabicyclo[3.3.1]nonane suggests that a *trans* fusion is possible, though strained, and to avoid possible ambiguity we will use the nomenclature of Volynskii.

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