

rule,"²⁰ and is typified by the experimental fact that *cis*-1,4-dimethylcyclohexane (axial-equatorial) has a higher density than *trans*-1,4-dimethylcyclohexane (equatorial-equatorial),²¹ for example. The internal pressure of a solvent, therefore, would be expected to shift the equilibrium between the axial and equatorial conformations of substituted cyclohexanes toward the axial conformation. This is exactly what is observed in the great majority of cases where conformational free energies have been determined in both the gas phase and in solution.⁷

It is thus to be expected that the more polar the solvent, the higher the internal pressure, and therefore the larger the shift in equilibrium towards the axial isomer. This is certainly consistent with the value of 0.93 ± 0.03 kcal/mol determined for the unsubstituted carboethoxycyclohexane in acetonitrile. Unfortunately the data for this compound in the less polar acetone do not reveal this effect.

In conclusion, it can be said that there is definite evidence for an increase in the conformational energy of the carboethoxy group when hydrogen bonding to the solvent is possible. While an explanation of the effect of polar solvents is more complicated, there is no doubt that this effect is quite significant. Perhaps the most important point to be made is that the conformational energy of a group is not a constant but is quite dependent on solvent, as is evidenced by the variation of about 0.5 kcal/mol observed in this limited study.

Experimental Section

Spectra.—All nmr spectra for this work were run on a Varian A-60 spectrometer using two Hewlett-Packard wide-range oscillators, Model 200 CDR, for the side-band calibration. The frequency of the oscillation was determined using a Hewlett-Packard electronic counter, Model 523 CR. This frequency was counted as the reciprocal to gain more accuracy, and the reading taken was the average of three ten-period averages displayed. The spectra were all run at a sweep time of 250 sec with a sweep width of 50 Hz, filter bandwidth of 4 Hz, and a radiofrequency field of 0.01 mG. In order to minimize machine error (nonlinear sweep, magnetic field shift, etc.), at least four spectra were run, each at different offset settings, and then each peak position was measured twice. In order to minimize other sources of error, several precautions were taken. All samples for a particular determination were made up to equal mole per cent concentration. This concentration was picked so as to make as dilute a solution as possible and still get a useful nmr signal. In one solvent (chloroform), determinations were made at two concentrations and the results indicated that the measurements were insensitive to concentration in the range used.

Preparation of Samples.—All samples were made up to a standard mole per cent concentration. The concentrations follow: carbon tetrachloride, 0.8 mmol/g; chloroform, 0.8 and 0.5 mmol/g; acetonitrile, acetone, isoctane, and acetic acid, 10 mmol/g. All samples had a standard amount of TMS measured by volume (20 μ l).

The samples were then vacuum degassed using the standard method of freeze-vacuum-thaw cycles, freezing with liquid nitrogen.

Preparation of Compounds.—All compounds were synthesized as reported.^{8d} The separation of the *cis* and *trans* isomers was by gas chromatography using a 6 ft \times $\frac{3}{8}$ in. glass column packed with 22% E-20,000 on Chromsorb W. The column temperature ranged from 105° for the 4-methyl derivative to 135° for the 4-*t*-butyl derivative. All compounds gave infrared spectra identical with those obtained before and the nmr spectra were all consistent with the structure assigned.

(20) N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Amer. Chem. Soc.*, **81**, 4074 (1959).

(21) C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958-1959.

Purification of Solvents.—All solvents were obtained as reagent grade and then (with the exception of acetic acid which was used as is) dried over sodium sulfate overnight. The solvent was then decanted and distilled through a Vigreux column under nitrogen. All refractive indices checked within experimental error with those reported.²¹

Calculation of Data.—Since the determinations were made using the methylene hydrogens of the ester, any of four peak positions could have been used. Owing to some second-order broadening, all four peak positions were not equally well defined. In all cases the lowest field peak seemed to be the most distinctive, and it was this peak that was used in the reported data. Use of any of the other three peaks gave essentially the same results. Using the chemical shifts of the *cis*- and *trans*-4-*t*-butylcarboethoxycyclohexanes as the standard, the unknown equilibrium constants were calculated using eq 1.

The eight values obtained for each compound in each solvent were then used to calculate eight free energy differences using eq 2. These eight values were then used to calculate the mean free energy and the standard deviations by the standard method.

$$-\Delta G^\circ = RT \ln K \quad (2)$$

Registry No.—I, 3289-28-9; *cis*-II, 25244-23-9; *cis*-III, 25244-24-0.

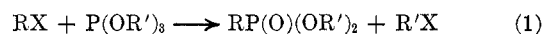
Dehalogenation of Vicinal Dibromoalkanes with Triethyl Phosphite¹

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AND VIRGINIA M. PETERS

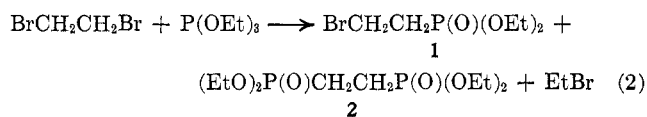
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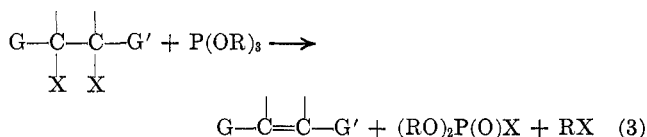
In the most common example of the Michaelis-Arbuzov reaction,² a phosphonate ester is formed from an alkyl halide and a trialkyl phosphite (eq 1). When



1,2-dibromoethane is the alkyl halide, the reaction is normal, *i.e.*, the major products are the phosphonate esters 1 and 2 (eq 2).³⁻⁶ However, for vicinal dihalides



with electron-withdrawing groups adjacent to both halogen atoms, dehalogenation is the principal reaction (eq 3). A number of electronegative substituents (G



(1) Supported by National Science Foundation Undergraduate Research Participation Grant No. GY-5830.

(2) R. G. Harvey and E. R. De Sombre, "Topics in Phosphorus Chemistry," Vol. I, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1964, p 57.

(3) G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **66**, 109 (1944); **70**, 1971 (1948).

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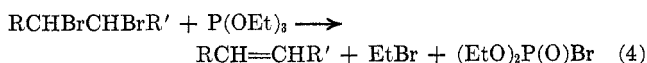
(5) A. N. Pudovik and M. G. Imaev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 916 (1952).

(6) A. Y. Garner, E. C. Chapin, and P. M. Scanlon, *J. Org. Chem.*, **24**, 532 (1959).

and G') have been shown to be effective: halogen,⁷⁻¹¹ carbonyl (including acyl, carboxyl, carbalkoxyl, and carbamyl),¹²⁻¹⁴ aryl,^{12,13,15} and perchloro-1,3-butadienylene.¹⁶ An interesting related reaction is the dechlorination of 1,4-bis(trichloromethyl)benzene, a vinyllog of hexachloroethane, by triethyl phosphite.¹⁷

There have been conflicting results as to the course of the reaction when only one electron-withdrawing substituent is present. 1-Alkoxy-1,2-dibromoethanes¹⁸⁻¹⁹ and the methyl esters²⁰⁻²² and nitriles²⁰ of 2,3-dichloro- and 2,3-dibromopropionic acid were found to give phosphonate esters as the major products. However, Abramov and Il'ina²⁰ reported that a small amount of methyl acrylate is also formed from methyl 2,3-dibromopropionate, and one of us²³ found that the acrylate is the main product of this reaction. Arbuzov and Lugovkin²⁴ obtained styrene from 1,2-dibromo-1-phenylethane.

These contradictory observations prompted the present investigation. The objective was to broaden and clarify knowledge as to the effects of substituents (and, particularly, single substituents) on the reaction. The experimental method was to heat an equimolar mixture of a vicinal dibromoalkane and triethyl phosphite to 180-185° over a period of 5-6 hr with concurrent distillation of the more volatile products and then to distill the residue at reduced pressure. We confirmed the formation of styrene from 1,2-dibromo-1-phenylethane²⁴ and of methyl acrylate from methyl 2,3-dibromopropionate.²³ Debromination was also found to be the main reaction of 2,3-dibromopropionitrile. The last two results are in disagreement with those reported in ref 20-22. Turning to previously untried dibromides, we found that 3,4-dibromo-2-butanone and 2,3-dibromobutyronitrile behave similarly. In these reactions, about 2 mol of ethyl bromide per mole of substituted alkene and a viscous residue with the properties of ethyl metaphosphate²⁵ were obtained, suggesting the sequence shown in eq 4 and 5.



Equation 4 is the usual representation of the dehalogenation reaction,^{2,9} and the diethyl phosphohalidate

(7) H. R. Davis (to M. W. Kellogg Co.), U. S. Patent 2,742,510 (1956).

(8) G. Kamai, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 923 (1952).

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(16) V. Mark, *Tetrahedron Lett.*, 333 (1961).

(17) V. W. Gash, *J. Org. Chem.*, **32**, 2007 (1967).

(18) V. S. Abramov and G. A. Karp, *Dokl. Akad. Nauk SSSR*, **91**, 1095 (1953); *Zh. Obshch. Khim.*, **24**, 1823 (1954).

(19) V. S. Abramov and A. P. Rekhman, *ibid.*, **26**, 163 (1956).

(20) V. S. Abramov and N. A. Il'ina, *ibid.*, **26**, 2014 (1956).

(21) G. Kamai and V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **91**, 837 (1953); *Tr. Kazan. Khim. Tekhnol. Inst.*, **21**, 141 (1956).

(22) V. S. Abramov and A. I. Bol'shakova, *Zh. Obshch. Khim.*, **27**, 441 (1957).

(23) J. P. Schroeder, unpublished results.

(24) B. A. Arbuzov and B. P. Lugovkin, *Zh. Obshch. Khim.*, **21**, 99 (1951).

(25) G. N. Kosolapoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950, p 352.

has, in fact, been isolated when the halogen is chlorine^{7,10,16,17} or fluorine.^{10,11} Under our experimental conditions, the diethyl phosphobromidate appears to pyrolyze (eq 5) in the manner described by Balarew²⁶ for the chloro compound.

3,4-Dibromobutyronitrile gave a 90% yield of ethyl bromide based on eq 4 and 5 but no alkene and a large amount of tar. We also repeated the reaction of 1,2-dibromopropane, which had been studied by Ford-Moore and Williams,⁴ and confirmed their finding that it is strikingly unreactive. Most of the dibromide was recovered and no propene was formed. Finally, we dehalogenated stilbene dibromide which, surprisingly, had not been investigated before in this reaction.

In some of the runs, diethyl ethylphosphonate was a by-product. This is readily accounted for by the Michaelis-Arbuzov reaction of ethyl bromide with triethyl phosphite (eq 1, R = R' = Et). In some instances small amounts of high-boiling liquids were obtained which were assumed to be normal Michaelis-Arbuzov products from the dibromide.

In Table I, the dibromides that were examined are listed in order of apparent reactivity toward debromina-

TABLE I
EFFECT OF SUBSTITUENTS ON THE DEBROMINATION OF
RCHBrCHBrR' WITH TRIETHYL PHOSPHITE

R	R'	Registry no.	C ₂ H ₅ Br, % yield ^a	RCH=CHR', % yield ^a	% conversion of dibromide
H	COCH ₃	25109-57-3	95	0	100
			88 ^b	49 ^b	95 ^b
H	CH ₂ CN	25109-74-4	90	0	100
H	CN	4554-16-9	80	83	c
CH ₃	CN	25109-76-6	75	85	100
H	COOCH ₃	1729-67-5	70	70	83
C ₆ H ₅	C ₆ H ₅	5789-30-0	50	58	58
H	C ₆ H ₅	93-52-7	35	29	42
H	CH ₃	78-75-1	8	0	14

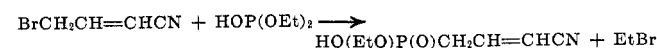
^a Based on eq 4 and 5. ^b Reaction run under milder conditions. ^c Not determined.

tion, using the ethyl bromide yield as the criterion. The first two compounds gave no alkene and a large amount of undistillable residue by the regular procedure. Under milder conditions, 3,4-dibromo-2-butanone produced 3-buten-2-one, indicating that the latter, a highly reactive vinyl monomer,²⁷ had polymerized completely in the earlier experiment. This explanation is not satisfactory for 3,4-dibromobutyronitrile, however, since the corresponding alkene polymerizes much less readily and none was isolated under milder conditions. It is also puzzling that this dibromide is apparently more reactive than 2,3-dibromopropionitrile in which the cyano group is nearer the reaction site. Almost certainly a different process is involved here²⁸

(26) D. Balarew, *Z. Anorg. Allg. Chem.*, **99**, 187, 190 (1917); **101**, 225 (1917).

(27) C. S. Marvel and C. L. Levesque, *J. Amer. Chem. Soc.*, **60**, 280 (1938); **61**, 3234 (1939).

(28) A possible alternative is



This also yields 2 mol of ethyl bromide/mol of dibromide and a high-boiling compound (a phosphonic acid) as the other product.

TABLE II
REACTION OF *vic*-DIBROMOALKANES, RCHBrCHBrR', WITH TRIETHYL PHOSPHITE

R	R'	Products, mol/mol of dibromide				
		Unreacted dibromide	EtBr	RCH=CHR'	Nonvolatile residue ^a	Other
H	COOCH ₃	0.17	1.4	0.70	0.99	b
H	CN	c	1.6	0.83 ^d	c	c
CH ₃	CN		1.5	0.85	1.24 ^e	
H	COCH ₃	0.05	1.75	0.49	1.15	f, g
H	C ₆ H ₅	0.58	0.69	0.29	0.77 ^h	i
C ₆ H ₅	C ₆ H ₅	0.42	1.0	0.58	c, j	
H	CH ₂ CN		1.8		1.48	k
H	CH ₃	1.0			0.18 ^e	l
		0.86	0.16		0.14	m, n

^a Assumed to be EtOPO₂ for calculation of yield. ^b Diethyl ethylphosphonate and an unidentified liquid, bp 63° (1.5 mm) in low yields. ^c Not determined. ^d Hydrolysis with 90% H₂SO₄ gave acrylamide, mp 81–83° (lit.³³ mp 84.5°). ^e High yield probably due to incomplete distillation. A higher pressure (30 mm) was used. ^f Diethyl ethylphosphonate, 0.14. ^g Reaction run at 30-mm pressure and volatile products collected in a cold trap. ^h Soluble in both CHCl₃ and ether, *d*₄²⁵, 1.421, *n*_D²⁰ 1.469. ⁱ Diethyl ethylphosphonate, 0.18, three unidentified high-boiling liquids in low yields. ^j Principally unreacted dibromide and stilbene. ^k Liquid (lachrymator) bp 49° (2 mm), *n*_D²⁰ 1.4542, *d*₄²⁵ 1.252, 2.1 g from 0.10 mol run. ^l Unreacted triethyl phosphite 0.70, liquid bp 92–94° (29 mm), 1.7 g from 0.10 mol run. ^m Unreacted triethyl phosphite, 0.54, diethyl ethylphosphonate, 0.03, three unidentified high-boiling liquids, 4.4 g from 0.10 mol run. ⁿ Reaction mixture refluxed (bath temperature 180°) for 5 hr.

and, therefore, it does not seem valid to compare this reaction with the others.

For the remaining dibromides, there is a good correlation between the yields of ethyl bromide and alkene by the stoichiometry of eq 4 and 5 except for 1,2-dibromopropane which gave no alkene. Again with this exception, a comparison of alkene yield with per cent dibromide conversion shows that debromination was the principal reaction.

In general, the reactivity order is consistent with the expected activating effects of the substituents (COCH₃, CN, COOCH₃ > 2C₆H₅ > C₆H₅ > CH₃), but in consideration of the marked deactivating effect of the electron-releasing methyl group in 1,2-dibromopropane, it is somewhat surprising that there is no significant difference in reactivity between 2,3-dibromopropionitrile and its 3-methyl homolog.

The most significant conclusion to be drawn from the results is that, in the reaction of equimolar amounts of a vicinal dibromoalkane and triethyl phosphite, a single electron-withdrawing substituent on one of the bromine-bearing carbon atoms is sufficient to make dehalogenation the principal reaction path, a situation which was by no means clear before.² In fact, the dehalogenation is a high-yield reaction when the substituent is strongly electron withdrawing. This is not to say that the products cannot be altered by varying the conditions. *E.g.*, it has been shown^{9,13} that the dihalide-trialkyl phosphite ratio makes a difference when two activating groups are present. Formation of phosphonate esters is encouraged by excess phosphite, dehalogenation by excess dihalide. The same effect would undoubtedly be observed with only one activating substituent. Also, halo groups other than bromo might behave differently, although this seems unlikely.

Experimental Section

Materials.—The chemicals were commercial products with the exception of four of the dibromo compounds which were prepared by bromination of the appropriate substituted alkenes. These are listed with their boiling points and the bromination conditions (solvent and temperature): 2,3-dibromopropionitrile, bp 99–100° (25 mm) [lit.²⁹ bp 106–107° (22 mm)], CCl₄, 0–5°; 2,3-

dibromobutyronitrile, bp 102–108° (17 mm) [lit.³⁰ bp 106–110° (18 mm)], CCl₄, 0–5°; 3,4-dibromobutyronitrile, bp 100–105° (3 mm) [lit.³¹ bp 125–127° (10 mm)], CCl₄, 0–5°; 3,4-dibromo-2-butanone, isolated as a residue product in quantitative yield, pentane, –15°.³²

Reaction of *vic*-Dibromides with Triethyl Phosphite.—The following procedure is typical. To 24.6 g (0.100 mol) of methyl 2,3-dibromopropionate in a 50-ml pear-shaped flask, 16.6 g (0.100 mol) of triethyl phosphite was added gradually with ice cooling and stirring. A few crystals of hydroquinone were placed in the reaction flask and in each of the receivers as a polymerization inhibitor. The flask was connected to a distillation apparatus (Vigreux column, condenser, ice-cooled receiver), and the mixture was heated to 185° over a period of 6 hr. Two fractions, bp 38–41° and 48–72°, were collected during this time. The residue was distilled at reduced pressure to yield two more fractions, bp 55–63° (1.5 mm) and 63° (1.5 mm).

The boiling points, densities, refractive indices, and ir spectra of fractions 1 and 2 indicated that they were mixtures of ethyl bromide and methyl acrylate. This was confirmed and the compositions determined by glpc (Carbowax 20M on Chromosorb-W column) using authentic samples of these compounds as standards. Fraction 3 was unreacted methyl 2,3-dibromopropionate (glpc and ir spectrum). Fraction 4 was shown by glpc to contain additional unreacted dibromide, diethylethylphosphonate, and a third component which was not identified.

The residue from the distillation (10.7 g) was a viscous liquid. From its properties and yield, it appeared to be crude ethyl metaphosphate. This is reported²⁵ to be an undistillable syrup, soluble in halogenated solvents, insoluble in ether, *d*₄²⁵, *ca.* 1.42, *n*_D²⁵ *ca.* 1.438. Our product was soluble in CHCl₃ but partly soluble in ether (ether-insoluble fraction, *d*₄²⁵, 1.45, *n*_D²⁰ 1.450), ether-soluble fraction, *d*₄²⁵, 1.33, *n*_D²⁰ 1.438.

Differences in the stabilities and physical properties of the products necessitated some variations in the method. Using the procedure described above, 3,4-dibromo-2-butanone gave a 95% yield of ethyl bromide but no other distillable material. However, by mixing the reactants at Dry Ice temperature and conducting the reaction at 30-mm pressure with flash distillation of the volatile products into a cold trap as formed, a 49% yield of 3-buten-2-one was obtained. 3,4-Dibromobutyronitrile also gave a high yield (90%) of ethyl bromide and little other distillable material by the standard procedure. Accordingly, the same modification was tried here but without success. Apparently, this dibromide is much less reactive than 3,4-dibromo-2-butanone, because the distillate was mainly unreacted triethyl phosphite.

For the stilbene dibromide reaction, the residue after distillation proved to be largely unreacted dibromide. This was purified by washing with water and then methanol. Stilbene was obtained from the methanol extract, but the aqueous washings

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(31) L. Leclercq and A. Bruylants, *ibid.*, **58**, 5 (1949).

(32) E. R. Buchman and H. Sargent, *J. Amer. Chem. Soc.*, **67**, 400 (1945).

(29) C. Moureu and R. L. Brown, *Bull. Soc. Chim. Fr.*, **27**, 901 (1920).

left only a small residue on evaporation, suggesting that most of the ethyl metaphosphate decomposed during the distillation.

All of the 1,2-dibromopropane was recovered using the standard procedure. Even when the reaction mixture was refluxed for 5 hr, 86% of the dibromide survived. In both runs, provision was made to collect evolved propene over water, but none was produced. The experimental data are summarized in Table II.

Registry No.—Triethyl phosphite, 122-52-1.

(33) E. L. Carpenter and H. S. Davis, *J. Appl. Chem.*, **7**, 671 (1957).

Formation of α,β -Diphenyl- γ -butyrolactone from Styrene Oxide by the Action of Organo Transition Metal Complexes

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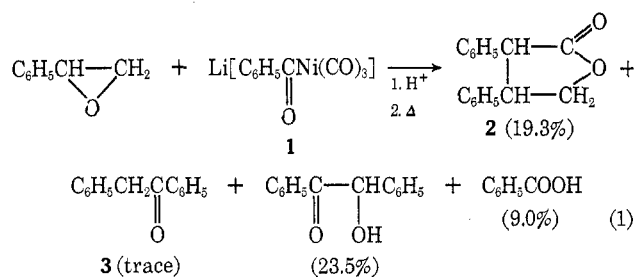
It has been known that epoxides are transformed to the corresponding ketones by the action of cobalt tetracarbonyl anion or dicobalt octacarbonyl.¹ In the presence of carbon monoxide, carbon monoxide insertion reactions occur to give β -hydroxy carboxylic acid esters in alcohol solution² and α,β -unsaturated acids in benzene solution.³ Furthermore, under the oxo conditions, α,β -unsaturated aldehydes are produced.⁴ Although the interesting reaction behaviors of σ -organo-metallic compounds toward olefins, acetylenes, ketones, or aldehydes have been revealed during these 10 years, the reactivity of alkyl or acyl transition metal complexes toward epoxides has not yet been defined. However, the facility with which π -methalynickel bromide reacts with styrene oxide to give 2-methyl-4-phenyl-5-hydroxypentene-1⁵ suggests that the analogous reactions of alkyl or acyl transition metal complexes might be important in organic synthesis.

Lithium acylmetal carbonylates, prepared by the reaction between organolithium compounds and metal carbonyls, are efficient nucleophilic acylating agents, and many useful organic reactions using these reagents, such as syntheses of aldehydes,⁶ acylolins,⁷ α -diketones,⁷ unsymmetrical ketones,⁷ and 1,4-dicarbonyl compounds⁸ have been reported. The reaction of lithium aroylnickel carbonylate with styrene oxide was carried out and it was found that the product is not the expected aroylphenylethyl alcohol but α,β -diphenyl- γ -butyrolactone, which seemed to be produced by dimerization and hydrogen abstraction of styrene oxide. In this paper, we report the formation of α,β -diphenyl-

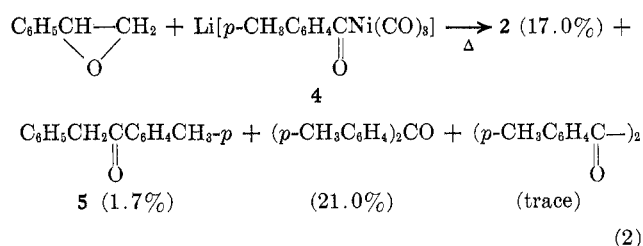
γ -butyrolactone from styrene oxide by the action of lithium aroylnickel carbonylate or dibenzyliron tetracarbonyl, which is a new type of transformation of olefin oxide and would promise a unique synthetic route to lactones from olefin oxides.

Results and Discussion

Styrene oxide undergoes reaction with lithium benzoylnickel carbonylate (1) to give *trans*- α,β -diphenyl- γ -butyrolactone (2, 19.3%), benzyl phenyl ketone (3, trace), benzoin (23.5%), and benzoic acid (9.0%). The latter two compounds are produced by the hydrolysis of 1,⁷ and the former two seem to be the products derived from the reaction between styrene oxide and 1.



The formation of 2 was not explained by the combination of benzoyl group in 1 with styrene oxide; so, in order to clarify whether the phenyl groups in 2 came from styrene oxide or 1, an analogous reaction was carried out using lithium *p*-toluoylnickel carbonylate (4) instead of 1.



After the reaction was complete, the ether was evaporated and the benzene-soluble part was distilled under reduced pressure. Then, 2 was obtained in a similar yield to that from reaction 1, and the formation of benzyl *p*-tolyl ketone 5 corresponded to the formation of 3. Di-*p*-tolyl ketone and *p,p'*-bitolyl are the products formed by thermal decomposition of 4.⁷ The fact that 2 was obtained in both reactions 1 and 2 in similar yields shows that the aroyl group in 1 or 4 is not incorporated into the structure of 2, and so 2 mol of styrene oxide is transformed to 1 mol of 2 with the aid of the aroylnickel carbonylate complex. As the reaction mixture before distillation (bath temp 200–250°) under reduced pressure does not show a peak due to the carbonyl group of the γ -lactone at 1780 cm⁻¹, heating is necessary for the formation of 2 in addition to the aroylnickel carbonylate complex. By column chromatographic separation of the residual oil after removal of the solvent, the crude material, which had a peak at 3600–3200 cm⁻¹ and no peaks in the carbonyl region (2100–1630 cm⁻¹), was obtained from the methanol eluate, and this material, which could not be purified by recrystallization, was transformed to 2 by heating above 200°. This suggests that an alcoholic compound is

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