and oil was eluted with 800 ml. of petroleum ether (b.p. 30–60°), 500 ml. 10% benzene in petroleum ether (b.p. 30–60°) and 500 ml. of 20% benzene in petroleum ether (b.p. 30–60°). These products remain to be identified. The next fraction was removed with benzene and was 0.28 g. (7%) of 1,2-diphenylpropanone-1, m.p. 43–47°. Recrystallization from methanol and water gave 0.25 g. of ketone, m.p. 48.5–49° (lit.,[6] m.p. 50–52°), a mixture melting point with an authentic sample was not depressed. The final fraction eluted with ether and methanol was 1.29 g. (30%) of unchanged *threo*-1,2-diphenyl-1-propanol.

When *threo*-1,2-diphenyl-1-propanol (3.0 g., 0.014 mole) was heated alone at 160–170° for 16 hr. and processed as above, the products were *cis*-methylstilbene (7%), *trans*-methylstilbene (1%), unknown solid and oil (34%), 1,2-diphenylpropanone-1 (4%), and *threo*-1,2-diphenyl-1-propanol (46%).

A series of dehydration experiments were performed at 175° for 9 hr. using pure *threo*- and pure *erythro*-1,2-diphenyl-1-propanol in the presence and absence of *m*-dinitrobenzene. The reaction was processed as above and the methylstilbenes were separated from the other products by chromatography. The olefin mixtures were analyzed by separation into pure components by column chromatography, by the ultraviolet spectroscopic procedure used by Kingsbury and Cram,[32] and by vapor phase chromatography.

The ultraviolet spectra were determined in 95% ethanol using a Beckman Model DU spectrophotometer and the mixture composition calculated from absorbancies at 260 mμ (λ_{max} for *cis*-methylstilbene) and 272 mμ (λ_{max} for *trans*-methylstilbene). The results of these studies are summarized in Table II.

Control Experiments. *m*-Dinitrobenzene plus *threo*- and *erythro*-1,2-Diphenyl-1-propanol.—A mixture of 1.00 g. (0.0047 mole) of alcohol, 0.19 g. (0.0094 mole) of *m*-dinitrobenzene and 4.90 g. (0.0376 mole) of *p*-cymene was heated at 175° for 9 hr. After the *p*-cymene was removed by distillation, chromatography on Alcoa F-20 activated alumina, showed the absence of methylstilbenes. The recovered alcohol was converted to the *p*-nitrobenzoates which was purified by chromatography on Alcoa F-20 activated alumina and recrystallization. When the *threo* alcohol was processed as described above, 1.00 g. (53%) of its *p*-nitrobenzoate, m.p. 141–143° (lit.,[6] m.p. 143–144°) was recovered; the *erythro* alcohol gave 1.10 g. (58%) of its *p*-nitrobenzoate, m.p. 102–106° (lit.,[6] m.p. 106–107°) and 0.08 g. of unchanged *erythro* alcohol, m.p. and mixture m.p. 47–48°, for a total recovery of 66%.

Isomerization of *cis*- and *trans*-Methylstilbenes in Dimethyl Sulfoxide.—Solutions of pure *cis*- and of pure *trans*-methylstilbene with and without *m*-dinitrobenzene were heated in dimethyl sulfoxide at 175° for 9 hr. or 45 hr. and processed according to method A. The methylstilbenes were separated from contaminants by chromatography on alumina and the mixture analyzed by the above spectroscopic method and by vapor phase chromatography. Table III lists the results of this study.

---

[32] C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1812 (1960).

Lithium Aluminum Hydride Reactions in Pyridine Solution. IV. Metalation of Di- and Triarylmethanes[1]

PETER T. LANSBURY AND ROOSEVELT THEDFORD[2]

Department of Chemistry, University of Buffalo, Buffalo 14, N. Y.

Received February 16, 1962

Although fluorene, triphenylmethane, and related arenes are not metalated by lithium aluminum hydride in ethyl ether, the use of pyridine as solvent allows the metalation to proceed to an appreciable extent, particularly with fluorene. Carbanions generated in this way have been used in alkylation and carboxylation reactions. Fluorene gives 9,9-dibenzylfluorene, in addition to 9-benzylfluorene, in highest yield when carbanion solutions are slowly benzylated and unchanged lithium aluminum hydride is still present. Triphenylmethane is more acidic than 4-benzyl- and 2-benzylbiphenyl toward butyllithium in ether as well as lithium aluminum hydride in pyridine.

Hydrocarbons of the cyclopentadiene series are unusually acidic, since removal of a proton from the methylene group leads to a resonance-stabilized anion possessing an aromatic sextet.[3] Fluorene has been extensively studied and has been shown to be more acidic than triphenylmethane, which, in turn, is more acidic than diphenylmethane, etc.[4] Aldol-type condensations involving fluorene have generally been carried out in hydroxylic solvents, utilizing hydroxide or alkoxide as base, and in ether using organometallic bases or alkali amides as metalating agents.

A more facile method for carrying out aldol condensations, and also alkylations and ionic autoxidations, utilizing 9-fluorenyl anion, has been developed by Sprinzak and co-workers.[5] These investigators have shown that fluorene is extremely acidic toward Triton B in pyridine at room temperature,[5b] thus allowing the isolation of 9-(α-hydroxyalkyl)fluorenes,[5a] whereas dibenzofulvenes are usually obtained, as a result of dehydration of the above alcohols, when the aldol condensations are carried out in hydroxylic solvents at higher temperatures. Hydrogen-tritium exchange studies[5b] confirmed that carbanion formation was extremely rapid in pyridine solution, both 9-hydrogens of fluorene being completely exchanged in an hour at room temperature. Triphenylmethane shows no tendency to

---

[1] Part III, P. T. Lansbury, and J. O. Peterson, *J. Am. Chem. Soc.*, **83**, 3537 (1961).

[2] Based on the M.A. thesis of R. Thedford, the University of Buffalo, June, 1962.

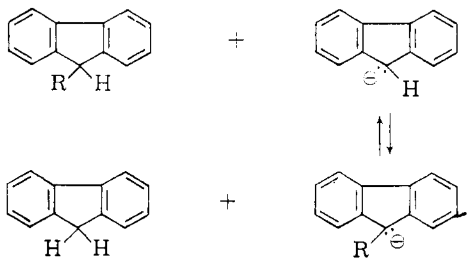
[3] J. E. Leffler, "The Reactive Intermediates in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 174.

[4] (a) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932). (b) A. A. Morton, *Chem. Rev.*, **35**, 1 (1944).

[5] (a) E. Ghera and Y. Sprinzak, *J. Am. Chem. Soc.*, **82**, 4945 (1961). (b) M. Avramoff and Y. Sprinzak, *ibid.*, **82**, 4953 (1961). (c) Y. Sprinzak, *ibid.*, **80**, 5449 (1958).

ionize under the above conditions[5b]; extremely strong bases are required, *e.g.*, sodamide in liquid ammonia or butyllithium in ether.

Another general method for preparing 9-substituted fluorenes involves the reaction of alkali metals with fluorene in ether solvents to give the alkali salt which is then allowed to react with various electrophiles. Scherf and Brown[6] have recently made a detailed study of the effect of various alkali metals and ether solvents on the metalation of fluorene and other arenes. Although such metalations and subsequent alkylations were sometimes rendered difficult due to heterogeneity of the system, several interesting points were found. Alkylation of 9-fluorenylpotassium with a variety of alkyl halides always led to a mixture of 9-alkylfluorene, 9,9-dialkylfluorene, and unchanged fluorene, the latter two in roughly equal amounts, suggesting that the monoalkylfluorenes are more acidic than the parent hydrocarbon. Thus, the monoalkyl derivatives apparently can undergo further metalation as follows:



The unexpected acid-strengthening effect of a 9-alkyl group was further substantiated by NMR studies.[6] Moreover, 9,9-fluorenyldipotassium could not be prepared[6] and therefore was not a precursor for dialkylated fluorenes.

In our earlier studies on the reactions of lithium aluminum hydride in pyridine[7] we noted that this combination readily metalated not only fluorene but also other arylalkanes such as triphenylmethane, 4-benzylbiphenyl, 1-benzylnaphthalene, and even diphenylmethane. This behavior may be contrasted with the nonacidity of such compounds to aluminohydride when ethyl ether is solvent.[7] Pyridine possesses a greater dielectric constant than ether, thus providing a more polar medium for generating the carbanion. Moreover, it has been suggested that pyridine enhances the basicity of aluminohydride ion by coordination of incipient alane as hydride is released.[7] Sprinzak[5c] observed that Triton B in pyridine does not metalate triphenylmethane, not unexpectedly considering the weaker basicity of hydroxide ion. We have investigated the extent of metalation of several arenes by means of lithium aluminum hydride, using mainly benzyl chloride and carbon dioxide as electrophiles for capturing the carbanions. The reactions occur readily in a homogeneous medium and provide convenient methods for preparing alkylated arenes and carboxylic acids. More detailed data on the individual compounds studied follow.

The metalations of fluorene (I) in pyridine by lithium aluminum hydride were studied most intensively. Two experimental procedures were used in "trapping" the carbanion by alkylation with benzyl chloride, and they gave significantly different results. In one procedure (A) benzyl chloride was *slowly* added to a stirred solution of the carbanion, in a nitrogen atmosphere. This gradual addition of the halide *sometimes* resulted in the formation of *both* 9-benzylfluorene (II) and 9,9-dibenzylfluorene (III) approximately in equal amounts. The second procedure (B), in which benzyl chloride was rapidly added, gave mainly II under a variety of conditions. The same result could be obtained if carbanion solutions were rapidly injected into excess benzyl chloride in pyridine. However, small amounts of III were obtainable when large quantities of lithium aluminum hydride were used (see Table II). The results of a number of fluorene metalations are summarized in Table I.

TABLE I

METALATION OF FLUORENE BY LITHIUM ALUMINUM HYDRIDE IN PYRIDINE

Run No.	Mole Ratio, I/LiAlH$_4$	Time, Hr.	Benzylation Procedure	% I	% II	% III
1[a]	1:1	2	A	39	30	31
2[a]	1:1	1	A	48	26	26
3[a]	1:1	18	B	52	48	..
4	1:2	5	A	19	34	47
5	1:1	5	B	29	71	..

[a] Duplicate runs gave similar product distributions within ±3%.

The unimportance of acid-base equilibration of 9-fluorenyl ion and 9-benzylfluorene[6] in determining product distribution is shown by the observation that only when some unchanged lithium aluminum hydride is still present does dibenzylation occur. This requirement was demonstrated as follows: Equimolar amounts of hydride and fluorene were allowed to interact for *ca.* eighteen hours and the solution then was divided into two aliquots, one benzylated according to procedure A and one according to B. No 9,9-dibenzylfluorene was observed in either case; in fact, the product composition was essentially identical from the two samples (*ca.* 40% 9-benzylfluorene and 60% fluorene). In considering these results, it is important to note that any lithium aluminum hydride not consumed by metalation of fluorene during the overnight period has been largely converted to lithium *N*-dihydropyridylaluminum hydride,[8] which does not metalate I, as shown in an independent experiment.

---

(6) G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 697 (1960); **39**, 799, 856, 1388 (1961).

(7) P. T. Lansbury, *J. Am. Chem. Soc.*, **83**, 429 (1961).

(6) P. T. Lansbury and J. O. Peterson, *ibid.*, **83**, 3537 (1961).

On the other hand, in those experiments where 9,9-dibenzylfluorene was formed, the reaction times were short enough to prevent complete consumption of the hydride, thus allowing further metalation of 9-benzylfluorene, mainly by the original hydride rather than by 9-fluorenyl ion, when procedure A was employed. When procedure B was used in a fluorene metalation where no excess hydride was present, no detectable amount of III was formed, even when short reaction times were employed, as shown in Table II, which reports the results of a large scale run from which aliquots were periodically removed and benzylated (procedure B), then immediately decomposed with methanol. Also listed are results from a fluorene metalation by *excess* lithium aluminum hydride. In this case, the ratio of hydride to I was 2:1 and even though alkylation was rapidly followed by methanolysis, a substantial amount of 9,9-dibenzylfluorene (III) was now obtainable in the early phase of the run when a large excess of lithium aluminum hydride was still present, although the yields of III were much greater when benzylation was carried out slowly (Table I, run No. 4). The increased recovery of I, after long reaction times, is commented on below.

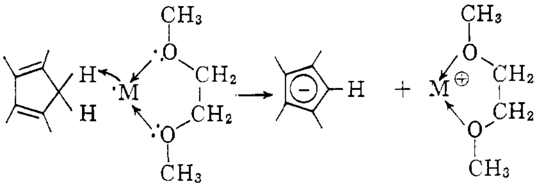
Table II

Metalation of Fluorene (I) by $LiAlH_4$ Followed by Rapid Benzylation (Procedure B)

Reaction Time, Hr.	% I	% II	% III
a. Equimolar Quantities of I and $LiAlH_4$ Used			
0.5	83	17	..
1.0	81	19	..
2.0	77	23	..
4.0	75	25	..
7.0	66	34	..
24.0	60	40	..
b. Two Moles of $LiAlH_4$ per Mole of I			
0.5	56	36	8
1.0	47	44	9
2.0	39	45	16
4.0	37	46	17
7.0	47	50	3
24.0	67	32	1

From the data collected above, it can be seen that, although 9-phenyl-9-fluorenyl ion may be less basic than 9-fluorenyl ion,[6] acid-base equilibration of I and II is much slower than alkylation of the carbanions by benzyl chloride, which proceeds quite rapidly in homogeneous solution. Furthermore, lithium aluminum hydride is clearly more basic than either of the anions mentioned above, since it could metalate II at a rate competitive with the alkylation reaction, as shown in Table II. Scherf and Brown's experiments[6] involved slow heterogeneous alkylation, especially in hydrocarbon solvents, thus allowing greater opportunity for further metalation of II by fluorenyl ion than in our case. They also noted that disubstitution was more prevalent when 9-fluorenylpotassium rather than sodium was used, in accord with the more ionic carbon-metal bond in the former species.[4b] The more covalent organolithium (or aluminum) compounds involved in the present study would be expected to equilibrate even more slowly, other things being equal, and, in fact, this phenomenon, was significant only when alkylation was performed slowly (Table I).

In addition to the metalations carried out in pyridine solution, a brief examination was made of tetrahydrofuran and dimethoxyethane as solvents, using the same reactant ratios and conditions as above. Scherf and Brown[6] interpreted the superiority of the latter as solvent for the metalation by alkali metals as due to the possible bidentate chelation of the diether with the incipient metal ion.



When lithium aluminum hydride was the metalating base, a higher yield of II was obtained with tetrahydrofuran (13%), rather than dimethoxyethane (6%), although neither rivaled pyridine. One possible explanation is that alane (AlH_3) is too large to accommodate both basic oxygens of one dimethoxyethane in its coordination sphere, as is pictured above when an alkali metal ion is involved. Finally, fluorene was treated with lithium *N*-dihydropyridylaluminum hydride,[8] which has been shown to be a more selective reducing agent than the parent hydride. No coloration due to carbanion was evident nor did treatment with benzyl chloride give rise to any alkylation product.

Triphenylmethane was subjected to metalation by lithium aluminum hydride in pyridine, using hydrocarbon: hydride ratios of 1:0.5 to 1:3 and reaction times ranging from one hour to a day, prior to benzylation. The maximum yield of 1,1,1,2-tetraphenylethane was 18%. Thus, as expected, triphenylmethane is not as acidic toward lithium aluminum hydride in pyridine as is fluorene. Carbonation of the triphenylmethide solution on Dry Ice afforded a 19% yield of triphenylacetic acid.[7] Similar yields (22% of triphenylacetic acid and 24% 1,1,1,2-tetraphenylethane) were attainable when the source of carbanion was benzpinacolone.[9]

Diphenylmethane gave a 1.4% yield of 1,1,2-triphenylethane when metalated for one day prior to benzylation.

Although 4-benzylbiphenyl (IV) readily gave deep purple-colored solutions when treated with lithium aluminum hydride in pyridine,[10] repeated attempts to effect benzylation and carbonation of

---

(9) Several of these experiments were performed by Dr. N. Simmons.

(10) P. T. Lansbury, J. R. Rogozinski, and F. L. Coblentz, *J. Org. Chem.*, **26**, 2277 (1961).

this carbanion met with little success. Similarly, no isolatable quantity of benzylated material was obtained in a metalation experiment on 2-benzylbiphenyl (V). Although these biphenyls would give carbanions isomeric with triphenylmethide, certain factors apparently cause appreciable differences in stability of the ion or its ease of formation. Resonance stabilization involving the biphenyl units of IV and V, which is not involved in triphenylmethane, may stabilize the acid and raise the activation energy for proton removal. Alternatively, there is considerable evidence that resonance contributions in the second ring of a diphenyl derivative are poorly transmitted to the first ring.[11] Keeping this latter fact in mind, one might expect IV and V to be only a bit more acidic than diphenylmethane, which reacted only slightly with aluminohydride. Not only is the extent of metalation of IV unknown, but there is also the possibility that the reaction medium, after suitable aging, contains a proton donor which can reverse the metalation appreciably without causing a perceptible loss of coloration (*vide infra*). It therefore seemed necessary to have an independent comparison of the acidity of all three arenes under conditions where any reprotonation of the anions would be less likely. The reaction chosen was metalation by *n*-butyllithium,[12] followed by carbonation and isolation of the derived carboxylic acids. Under identical conditions triphenylmethane gave 71% triphenylacetic acid, 4-benzylbiphenyl gave 41% phenyl-*p*-xenylacetic acid, and 2-benzylbiphenyl afforded 25% phenyl-*o*-xenylacetic acid. Since the above yields of carboxylic acids are of comparable magnitude, it seemed that a competing reprotonation reaction was responsible for the inability to trap the 4-benzylbiphenyl carbanion in pyridine solution containing excess lithium aluminum hydride. One potential proton donor, after the solution had been kept for several hours, might be an aluminohydride ion in which up to three hydrogens have been replaced by dihydropyridyl moieties.[8] These electron-withdrawing amino groups could conceivably activate the remaining hydrogen toward proton abstraction by the strongly basic carbanion.[13] It is known that hydride transfer toward electrophilic carbonyl groups (Lewis acid) from lithium tri-*t*-butoxyaluminohydride is quite sluggish,[14] so it is not too unlikely that a similar negatively substituted aluminohydride species might be a *proton* donor toward a carbanion (strong Lewis base). This possibility is under further investigation.

Experimental[15]

Preparation of Compounds.—Fluorene, triphenylmethane, 4-benzylbiphenyl, and 2-benzylbiphenyl were obtained from commercial sources and recrystallized before use. 1-Benzylnaphthalene was prepared according to the procedure of Tsukervanik.[16] 9-Benzyl- and 9,9-dibenzylfluorene were isolated from preparative scale benzylations of fluorenyl anion solutions, followed by separation of the products by combined fractional recrystallizations and elution chromatography. The melting points and infrared spectra of these compounds were in accord with those reported by Scherf and Brown.[6]

General Procedure for Metalation of Fluorene and Triphenylmethane, and Reactions of Carbanions.—Most of the metalations in pyridine solution were carried out on millimole quantities of arene, in 50-ml. round-bottom flasks equipped with a gas inlet tube, an air condenser connected to a mercury bubbler, and a side arm covered with a rubber septum through which solutions could be injected by a hypodermic syringe. Reactions were carried out under purified nitrogen which had been passed through a pyridine solution containing lithium aluminum hydride and triphenyl methide ion (from the cleavage of benzpinacolone). The latter solution is a convenient method for removing traces of oxygen and moisture from nitrogen, being usable as long as the characteristic red color of the anion is still present. By means of the rubber septum, it was possible to add a reagent to the carbanion solution or to remove aliquots of the solution for addition *to* excess reagent (procedures A and B in discussion). Several typical procedures follow.

A. To a solution of 10 ml. of pyridine containing 0.166 g. (1 mmole) of fluorene, in the apparatus described above, was added 0.038 g. (1 mmole) of lithium aluminum hydride through the condenser opening, while a flow of purified nitrogen was maintained through the gas inlet tube. The condenser was immediately replaced and the reaction mixture stirred intermittently during 18 hr. while a nitrogen purge was continued. The orange-colored solution was then treated with excess benzyl chloride (rapid addition *via* a syringe), followed by methanol to decompose unchanged hydride. At this stage, the reaction mixture was exposed to the atmosphere and worked up by pouring into a mixture of 5% hydrochloric acid and ether. The organic phase was washed with saturated sodium chloride solution, 5% sodium bicarbonate, sodium chloride solution again, and then dried over sodium sulfate. Evaporation of the ether solution to reduced volume, followed by gas chromatographic analysis[15] revealed that the product mixture contained 52% fluorene and 48% 9-benzylfluorene.

B. For following the progress of metalation with time, a larger scale run was begun, from which aliquots could periodically be removed and alkylated. A solution of 1.66 g. (10 mmoles) of fluorene in 40 ml. of pyridine was treated with 0.76 g. (20 mmoles) of lithium aluminum hydride, observing the precautions mentioned above. Aliquots of 5 ml. were removed at selected times by a hypodermic syringe and the

---

(11) H. C. Brown and T. Inukai, *J. Am. Chem. Soc.*, **83**, 4825 (1961); E. Berliner and E. A. Blommers, *ibid.*, **73**, 2479 (1951).

(12) H. Gilman and R. L. Bebb, *ibid.*, **61**, 109 (1939).

(13) Evidence favoring such an hypothesis is found in the bleaching action of solutions of the complex[8] on freshly prepared colored carbanion solutions from 4-benzylbiphenyl (purple) and 1-benzylnaphthalene (green). This decoloration occurs instantaneously, whereas the blood red color of the more stable triphenylmethide ion disappears quite slowly. Slow "internal" protonation of fluorenyl ion also has been noted (Table III). Also, when the carbanion solution from the reductive cleavage of benzpinacolone[9] was treated with benzyl chloride, deuterium oxide, and carbon dioxide, triphenylmethane was isolated in high yield each time, in addition to the expected products. In view of the observed complete bleaching of the carbanion solution when the above nonprotonic reagents had been added, some of the carbanion had apparently been protonated *before* hydrolysis of the mixture.

(14) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958).

(15) Melting points were determined on a "Mel-temp" capillary melting point apparatus and are uncorrected. All gas phase chromatography work was done on an F & M Model 300 linear programmed temperature chromatograph equipped with a two-foot silicone rubber-on-chromosorb column. By examining mixtures of known composition it was found unnecessary to use correction factors and mole ratios were calculatable from the peak areas.

(16) I. P. Tsukervanik and G. S. Semeshko, *Zh. Obshch. Khim.*, **27**, 1143 (1957).

carbanion solution rapidly added to a freshly prepared solution of benzyl chloride in pyridine, the addition being performed under the surface of the solution, in order to prevent exposure to the atmosphere. The individual reaction mixtures were worked up as above and analyzed by gas chromatography. The results are presented in Table II in the discussion.

C. Carbonation of pyridine solutions of fluorenyl anion was carried out by squirting the solution from a syringe directly onto a Dry Ice–ether slurry (very exothermic!). A solution of 0.01 mole each of fluorene and lithium aluminum hydride in 20 ml. of pyridine was kept overnight, then carbonated, and worked up in the usual manner yielding 0.34 g. (16%) of 9-fluorenecarboxylic acid, m.p. 218–222°, which was recrystallized from acetic acid, m.p. 230–231° (reported[17] 230–232°).

The metalations of triphenylmethane, followed by subsequent benzylation and carbonation of the carbanions, were carried out exactly as in parts A and C above, the maximum yield of 1,1,1,2-tetraphenylethane being about 18% and the amount of triphenylacetic acid reaching *ca.* 20%. Attempted metalations of 4-benzylbiphenyl and 1-benzylnaphthalene yielded colored solutions (purple and green, respectively) but alkylation products could not be obtained. Diphenylmethane gave a 1.4% yield of 1,1,2-triphenylethane when the bright orange carbanion solution was benzylated.

Generation of Triphenylmethide Ion from Reductive Cleavage of Benzpinacolone.—A solution of 1.59 g. (4.5 mmoles) of benzpinacolone and 0.30 g. lithium aluminum hydride (8 mmoles) in 20 ml. of pyridine was kept in a sealed Erlenmeyer flask for 1 hr. at room temperature, then treated with 2 ml. of benzyl chloride, whereupon the red color was completely bleached out. The reaction mixture was then hydrolyzed and the crude product chromatographed over alumina. Elution with 1:3 benzene–petroleum ether afforded 0.59 g. (53%) of triphenylmethane, m.p. 89–92° (after recrystallization from methanol), followed by 0.36 g. (24%) of 1,1,1,2-tetraphenylethane, m.p. 142.5–144° (from ethanol). Further elution with benzene-ethanol yielded 0.13 g. (8%) of benzpinacolyl alcohol.

Effect of Lithium *N*-Dihydropyridylaluminum Hydride on Carbanions.—When solutions of the reagent, prepared by aging pyridine solutions of lithium aluminum hydride,[8] were treated with freshly prepared pyridine solutions of the above carbanions which did not react appreciably with electrophiles, *instant* bleaching of the color was evident. The additions were performed in the nitrogen-flushed system by the hypodermic technique, being careful to inject the carbanion solutions below the surface of the other solution.

Metalation of Triphenylmethane, 4-Benzylbiphenyl, and 2-Benzylbiphenyl with *n*-Butyllithium.—Quantities (10 to 20 mmoles) of each of the three arenes were dissolved in 20–40 ml. of anhydrous ether and treated separately with a fivefold excess of *n*-butyllithium in ether. Each flask was flushed with nitrogen, tightly stoppered, and kept at room temperature for 18 hr. The colored solutions were carbonated by pouring onto Dry Ice–ether slurries, keeping exposure to the atmosphere as little as possible. Hydrolysis and work-up of each reaction mixture in the usual manner gave the following results, the data referring to crude acid before recrystallization: triphenylacetic acid, m.p. 240–265° (reported[18]: m.p. 265°), 71% yield; phenyl-*p*-xenylacetic acid, m.p. 132–136° (reported[19]: m.p. 141–142°), 41% yield; phenyl-*o*-xenylacetic acid, m.p. 161–169° (reported[20]: m.p. 171–173°), 25% yield.

Acknowledgment.—We gratefully acknowledge the generous support of this research by the National Science Foundation.

---

(17) R. B. Burtner and J. W. Cusic, *J. Am. Chem. Soc.*, **65**, 262 (1943).

(18) H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

(19) F. F. Blicke and N. Grier, *J. Am. Chem. Soc.*, **65**, 1725 (1943).

(20) C. F. Koelsch, *ibid.*, **56**, 450 (1934).

Reduction of Glycidic Esters with Lithium Aluminum Hydride[1]

H. M. Walborsky and C. Colombini

Chemistry Department, Florida State University, Tallahassee, Florida

Received February 16, 1962

A series of 2- and 3-substituted glycidic esters has been reduced with lithium aluminum hydride to yield mixtures of 1,2- and 1,3-glycols. The percentages of 1,2-glycol in the mixtures were determined by the periodic acid titration method. The effect of substituents on the ratio of 1,2- to 1,3-glycols produced is discussed.

There is an extensive literature on the reduction with lithium aluminum hydride of various functional groups in polyfunctional molecules.[2] However, the use of this reducing agent for the reduction of glycidic esters has received very little attention. It has been reported that ethyl 3,3-pentamethyleneglycidate and ethyl 3-trifluoromethylglycidate upon reduction with lithium aluminum hydride yield, respectively, 1-hydroxyethyl-1-cyclohexanol[3] and 4,4,4-trifluorobutan-1,3-diol.[4] In both cases a 1,3-glycol was produced although the substituents in the 3-position of the oxirane ring differed widely in both their steric and electronic effects. In order to gain some insight into the effects of various substituents on the course of the reduction of glycidic esters a series of 2- and 3-substituted glycidic esters was prepared and reduced with lithium aluminum hydride.

---

(1) This investigation was supported by a research grant (C-1461) from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) For a comprehensive review of the literature through 1953 see N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Ind., New York, N. Y., 1956.

(3) J. D. Billimoria and N. F. Maclagan, *J. Chem. Soc.*, 3067 (1951); M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. soc. chim. France*, 5, **19**, 1042 (1952).

(4) H. M. Walborsky and M. E. Baum, *J. Am. Chem. Soc.*, **80**, 187 (1958).