TABLE III

THIOPHENOL-CATALYZED DECARBONYLATIONS OF 2,3,3-TRIPHENYLPROPIONALDEHYDE-2-C^{14}

Starting aldehyde (A)					
Sp. act., mc./mole	1.365[a]	1.365[a]	1.201[b]	1.201	1.201[b]
Concn., *M*	0.51	0.51	0.50	0.50	0.50
Temperature, °C.	155–165	176–184	155–158	155–158	174–178
t-Bu_2O_2, mole % of A	30	30	31	31	31
Thiophenol, mole % of A	14	14	11	11	11
VI, sp. act., mc./mole			1.163[b]	1.178[b]	1.18[a]
VII, sp. act., mc./mole			2.42[c]	2.43[c]	
Oxidant for degradation	$KMnO_4$	$KMnO_4$	CrO_3	CrO_3	CrO_3
Ph_2CO from VI, mc./mole	0.0949[b]	0.224[d]	0.143[d]	0.147[d]	0.189[d]
Phenyl migration in VI, %	6.9[e]	16.4[e]	11.9[f]	12.2[f]	15.7[f]
Ph_2CO from VII, mc./mole			0.141	0.147	
Phenyl migration in VII, %			11.7[f]	12.2[f]	

[a] ±0.010 to 0.015. [b] ±0.006 to 0.008. [c] ±0.05. [d] ±0.0007 to 0.0015. [e] Not to be compared with figures in columns 3 and 5, respectively, due to differences in the experimental conditions of the decarbonylation and degradation. [f] Including rearrangement caused by oxidative degradation.

rearrangement). That from the experiment conducted at 178–184° had a specific activity of 0.0159 mc./mole (2.46% rearrangement).

Decarbonylation of 2,3,3-Triphenylpropionaldehyde-2-C^{14}.—The previous labeled aldehyde was decarbonylated in *o*-dichlorobenzene solvent in the manner described for the unlabeled analog, each reaction mixture being divided into several equal portions for decarbonylations at different temperatures. The decarbonylation products were isolated as before, assayed, and then degraded by either permanganate or chromic oxide oxidation. The final benzophenone 2,4-dinitrophenylhydrazone from each experiment was assayed to determine the extent of phenyl migration during each decarbonylation. The results of these experiments are summarized in Table III.

Nitrogen Analogs of Ketenes. VI.[1] Dehydration of Amides

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A novel method for the preparation of nitrogen analogs of ketenes has been developed which involves direct linear dehydration of the corresponding amides.

Ketenimines were first prepared in 1921 by Staudinger in unspecified yield by the interaction of a phosphinimine and a ketene,[3] and more recently Backer has successfully prepared several ketenimines by the reaction of diazomethane with negatively substituted nitriles.[4] Over the past decade this laboratory has sought more general and convenient methods for the synthesis of these interesting compounds. Two methods were developed which involved (1) the dechlorination of α-chloroimino chlorides with sodium iodide in acetone,[5a] and (2) the dehydrochlorination of imino chlorides with a tertiary amine.[5b] This paper reports a third new and general method for the facile preparation of ketenimines by the direct linear dehydration of N-monosubstituted amides.

Although the linear dehydration of N-monosubstituted amides for the preparation of nitrogen analogs of ketenes is not known, dehydration of amides to form nitriles is well known.[6] Some of the common dehydrating agents are phosphorus pentoxide, phosphorus oxychloride, phosphorus pentachloride, thionyl chloride, polyphosphoric acid, and phthalic anhydride. Phosphorus pentoxide is preferred for the dehydration of unsaturated amides where the use of dehydrating agents such as phosphorus pentachloride may give halogen-containing products.

Scheibler and co-workers[7] used phosphorus pentoxide in combination with a tertiary amine to dehydrate an acid-sensitive amide. From diethoxy acetamide they obtained diethoxyacetonitrile in 30% yield with phosphorus pentoxide and quinoline. In the same reaction, McElvain and co-workers[8] employed N-hexylpiperidine and triethylamine as tertiary bases with phosphorus pentoxide and obtained yields of 45% and 80%, respectively, of diethoxyacetonitrile. In the case of N-substituted amides, cyclic dehydration is the basis of the Bischler–Napieralski reaction.[9] Thus, β-phenethylamides on cyclic dehydration lead to 3,4-dihydroisoquinolines and Itoh and Sugasawa[10] used phosphorus pentoxide mixed with dry sand and pyridine to obtain isoquinoline derivatives in excellent yields.

In the present work, exploration of the dehydration of N-monosubstituted amides was initiated using various tertiary amines in combination with a five- to

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[1] The previous paper of this series was by C. L. Stevens and M. E. Munk, *J. Am. Chem. Soc.*, **80**, 4069 (1958).

[2] Abstracted in part from the dissertation of Gopal H. Singhal in partial fulfillment of the requirement for the degree of Doctor of Philosophy, Wayne State University, 1962. This work was supported by Grant No. CY3772 from the National Institutes of Health.

[3] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 887 (1921).

[4] R. Dijkstra and H. J. Backer, *Rec. trav. chim.*, **73**, 575, 695 (1954).

[5] (a) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657 (1953); (b) **76**, 4398 (1954).

[6] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 596–598; see also R. E. Kent and S. M. McElvain, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 493.

[7] H. Scheibler, *et al.*, *Ber.*, **67**, 1513 (1934).

[8] S. M. McElvain and Robert L. Clarke, *J. Am. Chem. Soc.*, **69**, 2659 (1947).

[9] W. M. Whaley and T. R. Govindachari, *Org. Reactions*, **6**, 99 (1951).

[10] N. Itoh and S. Sugasawa, *Tetrahedron*, **1**, 45 (1957).

TABLE I

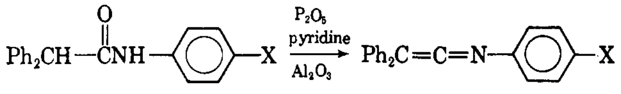
PROPERTIES OF KETENIMINES

Ketenimine	M.p. or b.p. (mm.), °C.	Yield, %	Recrystg. solvent	Analysis, %					
				Calcd.			Found		
				C	H	N	C	H	N
Diphenylketene-N-(*p*-tolyl)imine[a] (I)	82–84	87	Petr. ether						
Diphenylketene-N-(*p*-bromophenyl)imine (II)	78–80	69	Hexane	68.98	4.05	4.02	69.21	4.02	3.97
Diphenylketene-N-(*p*-anisyl)imine (III)	83–85	69	Petr. ether	84.24	5.69		84.30	5.81	
Diphenylketene-N-(*p*-methylthiophenyl)imine (IV)	82–83	75	Pentane	80.00	5.40	[b]	79.96	5.63	
Diphenylketene-N-(*o*-tolyl)imine (VII)	71–72	84	Petr. ether	89.00	6.05	4.94	89.01	5.95	4.84
Diphenylketene-N-(*o*-anisyl)imine (VIII)	90–92	67	Hexane	84.24	5.69	4.68	84.46	5.82	4.71
Diphenylketene-N-(*n*-butyl)imine[a] (IX)	150–153 (16)	50							
Diphenylketene-N-(*p*-methylsulfonylphenyl)imine (VI)	137–139	30	Ether	72.59	4.93	4.03	72.44	4.97	4.00
4,4′-Dithiobis[N-(diphenylvinylidine)aniline] (XII)	103–104	27	Benzene–pentane	79.98	4.67	[c]	80.00	4.85	
4,4′-Methylenebis[N-diphenylvinylidine)aniline] (XI)	122–123	84	Hexane	89.44	5.49		89.46	5.78	
Ethyl-*n*-butylketene-N-(*p*-tolyl)imine (X)	119 (0.3)	19		83.74	9.70		83.50	9.92	

[a] Ref. 5a. [b] Calcd.: S, 10.06. Found: S, 10.32. [c] Calcd.: S, 10.67. Found: S, 10.75.

tenfold excess of phosphorus pentoxide as the dehydrating agent. The reaction mixture, however, was difficult to stir and the reaction rate, as followed by infrared measurements[11] was very slow. The utilization of sand, Florisil, or alumina facilitated stirring and reduced markedly the time of reaction. In general, pyridine was found to be the most suitable base and served as the reaction medium as well. With the higher boiling 2,3,6-collidine, more polymeric byproducts resulted, whereas, with triethylamine, the reactions proceeded very slowly.

Diphenylketene *p*-substituted phenylimines, in which the *p*-substituent was CH_3, CH_3O, Br, or SCH_3, could be prepared by this method in 69–87% yield from the corresponding amides. Since the amides could be prepared in excellent yield from the acids, these ketemimines are now available in reasonable quantity by simple synthetic operations.



I, X = CH_3
II, X = Br
III, X = OCH_3
IV, X = SCH_3
V, X = NO_2
VI, X = SO_2CH_3

The scope of the dehydration does not include the preparation of the diphenylketene *p*-nitrophenylimine (V). Attempted preparation of the ketenimine (V) from the corresponding amide using the conditions successful for I–IV gave 80% of the starting material from the reaction mixture. Increasing the time of reaction until the amide had reacted gave only polymeric material. The *p*-nitrophenylketenimine (V) was made by dehalogenation of the α-chloroimino chloride[5a] and subjected to the condition of the attempted preparation. Under these conditions the ketenimine was shown to be unstable, only decomposition material being recovered.

The failure of the dehydration reaction with the strongly electronegative *p*-nitro-substituted amide suggested that the scope of the reaction might be limited and exclude a group such as a *p*-sulfone substituent. However, diphenylketene N-(*p*-methylsulfonyl)imine(VI) could be prepared by the linear dehydration of the corresponding amide, although the yield was lowered to 30%.

Two substituted phenylimines (VII and VIII) were prepared in good yield from the amides (see Table I). A straight-chain aliphatic substitution on the nitrogen of the amide did not limit the synthesis of the ketenimine.

Diphenylketene N-butylimine (IX) could be prepared in 50% yield. However, the corresponding *t*-butyl amide gave 69% nitrile and no ketenimine. An all aliphatic ketenimine could not be made by this method. *n*-Butylethylketene N-butylimine was not formed from the corresponding amide in pyridine with phosphorus pentoxide. When the liquid amide was distilled from phosphorus pentoxide, only the nitrile was isolated in 64% yield.

An example of an aliphatic ketene–aromatic imine was the synthesis of X. The yield was low at 19% but 35% of amide was recovered.

Two bisymmetrical ketenimines (XI and XII) were prepared by this method. The synthesis of the 4,4′-methylenebis[N-(diphenylvinylidine)aniline] (XI) was straightforward and XI was isolated in 84% yield. The disulfide ketenimine (XII) required Florisil as the inert ingredient and the yield was markedly lower (27%).

The sulfur-containing ketenimines (IV, VI, and XII) were made from *p*-aminothiophenol. When the thiophenol was treated with one mole of diphenylacetyl chloride, a mixture of products resulted although some of the desired N-(*p*-mercaptophenyl)diphenylacetamide was isolated. The *p*-aminothiophenol could be air oxidized in an alcoholic ammonium hydroxide solution at room temperature to *p*-aminophenyl disulfide in 89% yield.[12] Treatment of the latter with diphenylacetyl chloride formed 4,4-dithiobisdiphenylacetanilide (XXI) in 86% yield. The disulfide could be readily cleaved to the hydrosulfide with sodium borohydride and methylated with methyl iodide to form N-(*p*-methylthiophenyl)diphenylacetamide (XXII) in 92% yield. It also was found that the latter compound could be prepared in 80% yield directly from *p*-aminophenyl disulfide without isolation of the intermediate disulfide. The thioether, upon treatment with hydro-

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(11) The N-substituted amides absorb at 5.9 to 6.0 μ while the ketenimine products possess an intense absorption band at 4.9 to 5.0 μ.

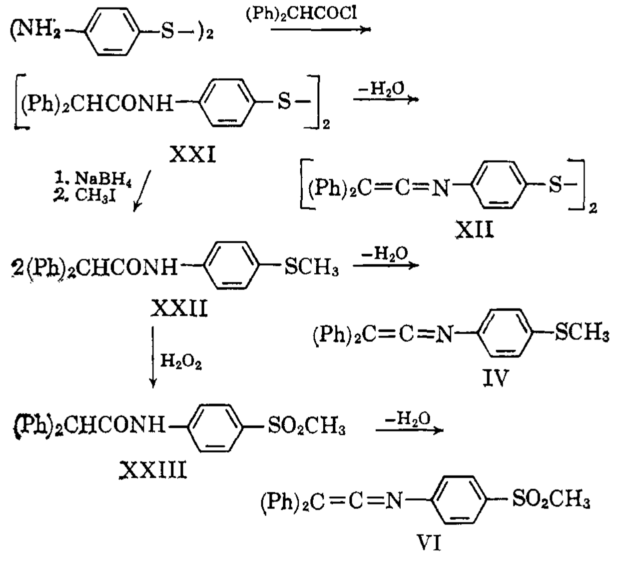
(12) E. C. Hornung, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 86, and reference thereto.

TABLE II

PROPERTIES OF STARTING AMIDES

Amide	M.p., °C.	Yield, %	Recrystg. solvent	Analysis, %					
				Calcd.			Found		
				C	H	N	C	H	N
N-(*p*-Tolyl)diphenylacetamide[a] (XIII)	179–180	90	Toluene						
N-(*o*-Tolyl)diphenylacetamide (XIV)	148	93	Ethanol–water	83.65	6.35	4.65	83.49	6.65	4.41
N-(*p*-Anisyl)diphenylacetamide (XV)	188–189	95	Ethyl acetate–petr. ether	79.45	6.03		79.19	5.88	
N-(*o*-Anisyl)diphenylacetamide (XVI)	150–151	85	Ethyl acetate–petr. ether	79.45	6.03	4.42	79.56	6.21	4.50
N-(*p*-Bromophenyl)diphenylacetamide (XVII)	203–205	85	Ethyl acetate–petr. ether	65.58	4.40		65.36	4.34	
N-(*n*-Butyl)diphenylacetamide[a] (XVIII)	93–94	70							
N-(*p*-Tolyl)-α-ethylcaproamide (XIX)	112–114	92	Ethyl acetate–hexane	77.26	9.94	6.00	77.41	9.87	6.20
4,4′-Methylenebisdiphenylacetanilide (XX)	265–267	76	Pyridine	83.93	5.84	4.78	84.08	5.79	4.85
4,4′-Dithiobisdiphenylacetanilide (XXI)	262–264	86	Pyridine–hexane	75.39	5.06	*b*	75.32	5.14	
N-(*p*-Methylthiophenyl)diphenylacetamide (XXII)	183–184	92	Ethyl acetate–hexane	*c*					
N-(*p*-Methylsulfonylphenyl)diphenylacetamide (XXIII)	212–214	83	Acetone–water	69.02	5.24	3.83	68.95	5.31	5.74

[a] Ref. 5a. [b] Calcd.: S, 10.06. Found: S, 9.99. [c] Calcd.: S, 9.62. Found: S, 9.43.



gen peroxide, gave the desired N-(*p*-methylsulfonylphenyl)diphenylacetamide (XXIII) in 83% yield.

Experimental

Preparation of N-Substituted Amides.—Amides were prepared from the acid chlorides and the corresponding primary amine. Yields are based on the acid used. Unless otherwise stated, the procedure employed is similar to that for N-(*p*-tolyl)diphenylacetamide (XIII) as reported by Stevens and French,[5a] and the properties of the amides are listed in Table II. The experimental procedures for the sulfur-containing amides are described separately.

4,4-Dithiobisdiphenylacetanilide (XXI).—Air was bubbled through a solution of 15.0 g. of *p*-aminothiophenol in 300 ml. of an equivolume mixture of ethanol, concentrated ammonia, and water for 24 hr. The resulting crystalline yellow precipitate of *p*-aminophenyl disulfide was filtered, washed with water, and dried to constant weight, 13.3 g. (89%), m.p. 76–78°.[12]

A portion (4.96 g.) of the disulfide was dissolved in 200 ml. of benzene containing 5.05 g. of triethylamine. To this solution was added, with stirring, a solution of 4.71 g. of diphenylacetylchloride in 120 ml. of benzene, the temperature being kept at 25° or below. The reaction mixture was heated to reflux for 2 hr.; 300 ml. of water was added with stirring, and the reaction mixture was allowed to stand overnight. The resulting white solid was filtered, washed with water and a little ether, and dried to give 11.1 g. (86%) of 4,4-dithiobisdiphenylacetanilide, m.p. 259–261°. Two recrystallizations from pyridine–hexane gave an analytical sample, m.p. 262–264°.

N-(*p*-Methylthiophenyl)diphenylacetamide (XXII). A. From XXI.—A suspension of 1.8 g. of sodium borohydride in 30 ml. of absolute alcohol was added with stirring and cooling to a solution of 3.18 g. of disulfide XXI in 30 ml. of pyridine. When the reaction had subsided, a solution of 5.0 g. of methyl iodide in 95% ethanol was added to the reaction mixture through a dropping funnel. The mixture was stirred for 45 min. and 200 ml. of water was added. The mixture was then allowed to stand for 30 min. and filtered. The precipitate was washed with water and a little petroleum ether and dried to give 3.05 g. (92%) of white solid, m.p. 180–182°. Two recrystallizations from ethyl acetate–hexane gave an analytical sample, m.p. 183–184°.

It was found that this compound could be prepared in 80% yield directly from *p*-aminophenyl disulfide without isolation of intermediates. In this case, pyridine was employed instead of triethylamine in the acylation step.

B. From *p*-Nitrothioanisole.—To 10.0 g. of *p*-nitrothioanisole (m.p. 70°) were added 30.0 g. of iron dust, 10 drops of concentrated hydrochloric acid, and 200 ml. of water. The mixture was stirred at 85–90° for 14 hr. The cooled mixture was made alkaline with sodium carbonate and filtered. The filtrate was extracted well with benzene to dissolve the oil, and the iron residue was extracted four times with hot benzene. The benzene was removed in major part by distillation and the last traces were removed *in vacuo*. The resulting *p*-aminothioanisole was obtained as an oil, 7.5 g. (91%). The oil and 6.0 g. of triethylamine were dissolved in 200 ml. of benzene to which was added 12.5 g. of diphenylacetylchloride in 170 ml. of benzene over a 10-min. period. The reaction mixture was refluxed and stirred for 4 hr. and filtered to remove triethylamine hydrochloride. The salt was washed with benzene and the benzene was removed by distillation and vacuum treatment. The residual crystalline mass of XXII was recrystallized from acetone–pentane to give 16.4 g. (92%) of a white crystalline solid, m.p. 181–183°, undepressed upon admixture with a sample from procedure A.

N-(*p*-Methylsulfonylphenyl)diphenylacetamide (XXIII).—To a solution of 1.1 g. of N-(*p*-methylthiophenyl)diphenylacetamide (XXII) in 15 ml. of glacial acetic acid was added 3 ml. of 40% hydrogen peroxide. The mixture was refluxed for 2 hr. The clear solution was cooled and poured with stirring into 300 ml. of cold water. The precipitate was filtered, washed well with water, and dried to give 1.0 g. (83%) of product, m.p. 206–209°.[14] One recrystallization from acetone–water raised the melting point to 212–214°.

Preparation of Kenenimines. Apparatus and Reagents.—The apparatus was flame-dried before use. The tertiary amines were distilled from phosphorus pentoxide and stored over potassium hydroxide or phosphorus pentoxide. Ether, petroleum ether (b.p. 30–60°), and benzene were dried over sodium, distilled, and stored over sodium. Alumina, Florisil, and sand were dried in an oven at 150° for 2 days. The particle size of these inert ingredients did not appear to be critical.

The preparation of diphenylketene-*p*-tolylimine (I) represents a general procedure for the preparation of ketenimines. Modifications, where used, are noted.

Diphenylketene-*p*-tolylimine (I).—To a stirred solution of 10.0 g. of N-(*p*-tolyl) diphenylacetamide (XIII) in 300 ml. of dry pyridine were added 25.0 g. of phosphorus pentoxide, 50.0 g. of alumina, and 200 ml. of pyridine. The mixture was refluxed for 7 hr., then allowed to cool, and filtered. The residue was leached with pyridine and the pyridine was evaporated under reduced pressure from the combined filtrates. The crystalline mass was dissolved in dry petroleum ether, filtered, concentrated, and allowed to crystallize. Bright yellow stout needles of ketenimine (I), 8.2 g. (87%), m.p. 82–84°,[5a] were obtained.

The replacement of alumina with Florisil or sand yielded approximately the same results. In the absence of these materials the reaction was very slow, although an 80% yield was obtained.

The *o*-methoxyketenimine (VIII) was prepared using Florisil instead of alumina. The *p*-bromoketenimine (II) was prepared in the stated yield with no inert ingredients added; using alumina in the dehydrating mixture lowered the yield to 26%.

In the preparation of the aromatic ketene aliphatic imine (IX), triethylamine was preferred to pyridine. In the preparation of the aliphatic ketene aromatic imine (X), 2,4,6-collidine was the preferred base. In the preparation of *p*-methylthiophenyl compound (IV), 10 equivalents of phosphorus pentoxide instead of the usual 5 equivalents were required to obtain 75% yield.

Hydrolysis of Ketenimines.—For proof of structure, all the ketenimines were hydrolyzed to the starting amides.[5b] For this purpose, 200 mg. of the ketenimine was dissolved in 10 ml. of acetone and 1 ml. of 4 *N* hydrochloric acid was added. The solution was allowed to stand until the characteristic yellow color of the ketenimine was discharged. The reaction mixture was made turbid by the addition of water, if necessary, and allowed to stand overnight. The resulting solid was filtered and recrystallized from the proper solvent. The yield of recrystallized amide in all cases was over 75%. Mixture melting points with the original amide were undepressed in all cases.

Asymmetric Reductions. XI. The Grignard Reagent from (+)-1-Chloro-2-phenylbutane[1]

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Reduction of a series of alkyl phenyl ketones by the optically active Grignard reagent from (+)-1-chloro-2-phenylbutane in ether at room temperature has produced the corresponding alkylphenylcarbinols with the following optical purities: methyl, 37%; ethyl, 52%; isobutyl, 53%; isopropyl, 82%; and *t*-butyl, 14%. These per cent asymmetric reductions parallel, but, with the exception of the *t*-butyl case, are much higher than those observed when the same ketones were reduced with the Grignard reagent from (+)-1-chloro-2-methylbutane. The use of tetrahydrofuran instead of ether solvent reduced the stereoselectivity from 82 to 75% at 35°. The effect of a 66° variation in temperature on this reaction in tetrahydrofuran was to increase the per cent asymmetric reduction from 69% at 66° to 78% at 0°; however, the difference in free energy of activation, $\Delta\Delta F^*$, did not vary over this range. The 82% asymmetric reduction of the isoproply phenyl ketone (which corresponds to the production of 91% *l*-, 9% *d*-carbinol ($\Delta\Delta F^* = 1.45$ kcal./mole) is the highest asymmetric synthesis reported for a reagent containing a single asymmetric center. The factors contributing to this high stereoselectivity and the surprisingly low value obtained in the phenyl *t*-butyl case are discussed.

With the specific purpose of finding variations which will lead to stereoselectivities approaching those of enzyme systems, we have continued our studies on the asymmetric Grignard reduction reaction. The highest asymmetric reductions which we observed with the Grignard reagent from (+)-chloro-2-methylbutane were 24% in the reduction of isopropyl ketone and 25% in the reduction of cyclohexyl phenyl ketone.[3,4]

Vavon and Angelo[5] reported a 72% asymmetric synthesis in the reduction of *t*-butyl phenyl ketone using the Grignard reagent from "pinene hydrochloride." The reducing agent in this case (isobornylmagnesium chloride) has three asymmetric centers and after the hydrogen is transferred the olefin formed (bornylene) still retains two of these three centers and is optically active. The reduction of 1-deuteriobenzaldehyde with isobornyloxymagnesium in a Meerwein–Ponndorf type reaction by Streitwieser and Wolfe[6] produced optically active 1-deuteriobenzyl alcohol which has been assumed to approach optical purity.[7] In this case the reducing agent has three asymmetric centers, only one of which is lost during the reduction.

The reduction of methyl *t*-butyl ketone by "diisopinocamphenylborane," prepared from diborane and α-pinene, carried out by Brown and Bigley,[8] has given methyl-*t*-butylcarbinol of 35% optical purity, and hydroboration of *cis*-2-butene followed by peroxide oxidation has given 2-butanol of better than 90% optical purity.[9] Again, this has been brought about with a reagent containing multiple asymmetric centers which are not destroyed in the reaction.

We believe that in a properly designed system containing only one asymmetric center the difference in the energies of activations between the *d*- and *l*-transition states may be sufficient to permit asymmetric reductions approaching 100%. In order to elucidate further the effect of structural variations in the Grignard reagent upon the degree of asymmetric reduction we have investigated the reduction of some alkyl phenyl

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[1] We acknowledge with gratitude support of these investigations by the U. S. Public Health Service (RG-5248) and the National Science Foundation (GF-955).

[2] National Science Foundation Post Doctoral Fellow, 1962.

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[5] G. Vavon and B. Angelo, *Compt. rend.*, **224**, 1435 (1947).

[6] A. Streitwieser, J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 340 (1959).

[7] In a preliminary investigation [H. S. Mosher, and V. Althouse, paper presented at the 140th National Meeting of the American Chemical Society Chicago, Ill., September, 1961] it was reported that reduction of 1-deuteriobenzaldehyde by actively fermenting yeast produced 1-deuteriobenzyl alcohol with a rotation 2.2 times that obtained from the isobornylmagnesium reduction. This case is still under investigation by the present authors and by Dr. Streitwieser (private communication.)

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[9] H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961).