ceptions: Twenty milligrams of etiohemin II was dissolved in 4 cc. of boiling isoamyl alcohol and 300 mg. of sodium was added. In the final chromatography, a mixture of 20 parts hexane, 10 parts ethylene dichloride, and 3 parts of absolute methanol was used; yield 31% of etiochlorin II, determined spectroscopically.

When 20 cc. of isoamyl alcohol was used in the reduction with 400 mg. of sodium, the yield dropped to 2%.

When the reaction was run as in the first procedure, but with the addition of 1.5 g. of dried Amberlite IRC-50 in its acid form, tetrachloro-*o*-benzoquinone oxidized the reduced product to bright red etioporphyrin II with only traces of etiochlorin.

Zinc–Pyridine–Acetic Acid Reduction.—Several milligrams of porphyrin or chlorin were dissolved in 3 or 4 cc. of pyridine (damp) and several milligrams of zinc dust were added. One drop of acetic acid was added and the reaction vessel flushed with nitrogen. Gentle warming produced an immediate color change and loss of the original spectral bands. Chlorin e_6 triester became bright red with no band absorption but only general absorption below 580 mμ. 2-Vinylchloroporphyrin e_6 triester became brown with general absorption below 519 mμ and then green with additional absorption at long wave lengths. Iron and zinc complexes of 2-vinyl chloroporphyrin triester were ununchanged but tin 2-vinylchloroporphyrin triester changed from its normal hue to reddish purple with two broad bands, a weak one at 609 mμ, and a strong one at 537 mμ.

These colored products were all oxidized back to their respective starting materials immediately upon the addition of oxygen or quinones. If the reaction mixtures stood for many minutes or were further warmed, all became colorless and finally would not oxidize to recognizable products.

Reduction of Tin 2-Vinylchloroporphyrin e_6 Trimethyl Ester. (a) To Chlorins.—The triester (500 mg.) was hydrolyzed in a mixture of 20 cc. of pyridine and 35 cc. of 15% aqueous potassium hydroxide which was blanketed with nitrogen and shaken for 36 hr. at room temperature. Tin was introduced to the free acid as outlined and the tin chelate treated with sodium–isoamyl alcohol as above, and drowned in ether containing about 10% ethylene dichloride. The ethereal solution was at first brown but as the acid was washed out with water, the ether layer became green. The solvents were vacuum stripped after esterification with diazomethane and the residue was chromatographed on 10% cellulose–Magnesol with a mixture of 20 parts hexane, 10 parts ethylene dichloride, and 3 parts absolute methanol. Two chlorin bands were visible, the first of which represented about 10–15 mg. of material whose spectrum in dioxane was qualitatively and quantitatively identical with that of tin mesochlorin e_6 trimethyl ester and the second of which was in smaller quantity (3–4 mg.). The spectrum of this second band in dioxane differed slightly from that of the major band.

(b) To Leuco-Porphyrins.—The tin chelate from 10 mg. of the vinylchloroporphyrin ester was dissolved in 10 g. of glacial acetic acid in a three-necked, 50-cc. flask fitted with nitrogen inlet, reflux condenser, and dry hydrogen chloride inlet. The mixture was heated to 80° and powdered iron was added while the contents of the vessel were blanketed with nitrogen. Hydrogen chloride was then bubbled through the mixture. After 20 min. at 120° the liquid was nearly colorless. It was cooled under nitrogen and drowned in 50 cc. of water. The water was extracted with ether containing a small amount of ethylene dichloride. After the ether was washed acid-free, it was pale yellow and showed no band spectrum. Tetrachloro-*o*-benzoquinone instantly oxidized the solution to maroon. Chromatography of the esterified product on Magnesol with a mixture of 20 parts ethylene dichloride and 4 parts acetone showed three bands. The first yellow band showed no spectrum; the red band following this showed the spectrum of metal-free 2-vinyl porphyrin. Near the top of the column was the purple tin complex.

(c) Control Reduction of Free Porphyrin in the Presence of Stannous Chloride.—The reaction was run exactly as above except that free porphyrin was used instead of the tin complex and 50 mg. of stannous chloride was added after the hydrogen chloride addition had begun. Chromatography of the products yielded a brown band as well as the red band of the porphyrin ester but no chelate band.

Additions of Phenyllithium to *cis*- and *trans*-Dibenzoylstyrenes[1,2]

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Phenyllithium adds 1,2 twice to the carbonyl groups of *trans*-dibenzoylstyrene, giving the *trans*-glycol. It adds similarly but stepwise to the *cis* isomer, giving first the γ-hydroxy ketone in its cyclic hemiketal form, and in the second stage the *cis*-glycol.

Because of the very considerable proportions of 1,4-addition of phenyllithium to *cis*- and *trans*-dibenzoylethylenes,[2c] to *cis*-chalcone[4] and to the *cis*- and *trans*-α-phenylchalcones,[5,6] it was predicted, incorrectly, it now transpires, that both *cis*- and *trans*-dibenzoylstyrenes I and III also would undergo 1,4-addition to a considerable extent.

The main crystalline product of the reaction between phenyllithium and *trans*-dibenzoylstyrene (I) was the *trans*-pentaphenyl glycol II (40%). This was the result of two successive 1,2-additions to the carbonyl groups. No one of the several easily isolable 1,4-addition products was isolated.

The structure of the *trans*-glycol II was shown by analysis, the very strong and normal type infrared hydroxyl absorptivity at 2.86 mμ, and the absence of carbonyl group absorptivity in the 6-μ region.

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[1] Work supported by a contract with the Office of Ordnance Research, U.S. Army, and a research grant from the National Science Foundation.

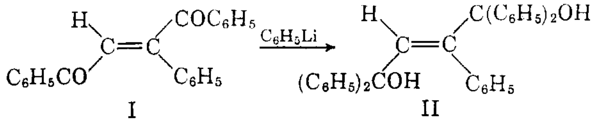
[2] (a) C. L. Dickerson, (b) W. J. Welstead, Jr., Ph.D. dissertations, University of Virginia, 1954, 1961; (c) R. E. Lutz and C. L. Dickerson, *J. Org. Chem.*, **27**, 2040 (1962).

[3] Present location, S. C. Johnson and Son, Inc., Racine, Wisconsin.

[4] R. E. Lutz and J. O. Weiss, *J. Am. Chem. Soc.*, **77**, 1814 (1955).

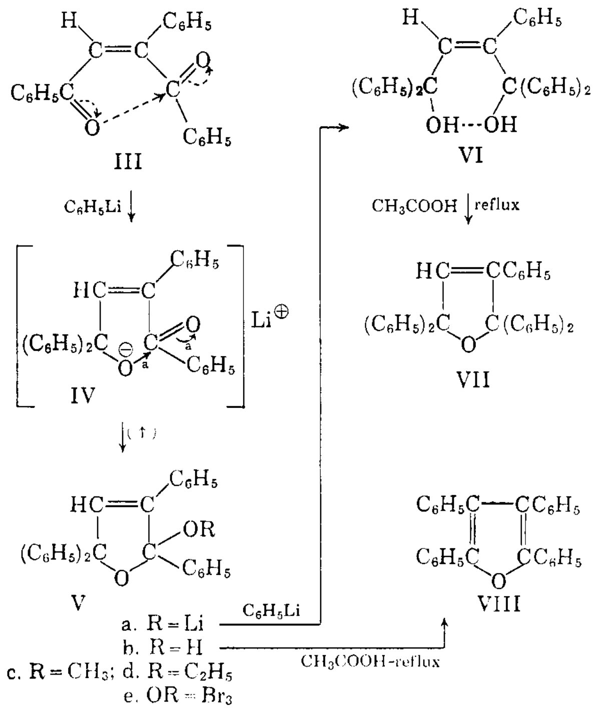
[5] R. E. Lutz and E. H. Rinker, Jr., *ibid.*, **77**, 366 (1955).

[6] (a) W. B. Black and R. E. Lutz, *ibid.*, **75**, 5990 (1953); (b) L. P. Kuhn, R. E. Lutz, and C. R. Bauer, *ibid.*, **72**, 5058 (1950).



I II

The compound lacked significant benzoyl group ultraviolet absorptivity at 240–250 mμ. Evidently the styryl group present, which would normally absorb at *ca.* 240 mμ, is conjugatively relatively ineffective because of non-planarity caused by the sandwiching of the phenyl group between the two very bulky *trans*-benzhydryl groups.



cis-Dibenzoylstyrene (III) reacted similarly but stepwise with phenyllithium, first giving the known[7] 2-hydroxy-2,3,5,5-tetraphenyldihydrofuran (Vb; 75%). Under more prolonged action of a large excess of reagent there was produced the *cis*-pentaphenyl unsaturated glycol VI which is the end result of two successive 1,2-additions to the two carbonyl groups. As with *trans*-dibenzoylstyrene, no 1,4-addition product was isolated.

The cyclic hemiketal structure of the first product Vb is supported by: (a) analysis; (b) acid-catalyzed alcoholysis to the interchangeable methyl and ethyl cyclic ketals, Vc and Vd; (c) the comparable ultraviolet absorptivities of the cyclic hemiketal Vb and the ketal Vd at 250 mμ; (d) the strong infrared hydroxylic absorptivity at 2.8 μ of the hemiketal Vb and lack of it for the cyclic methyl ketal Vc; and (e) the lack of benzoyl group absorptivity in the 6-μ region.

The structure of the second and end product, the *cis*-pentaphenyl glycol VI, is shown as follows: It gave the correct analysis. The broad strong hydroxylic infrared absorption band with its peak at *ca.* 3.1 μ indicated intramolecular hydrogen bonding between the *cis* hydroxyl groups which would be expected of the *cis* but not of the *trans* isomer. The slight shoulder on the ultraviolet absorption curve at 250 mμ, ε *ca.* 5700 indicated the presence of a sterically hindered styryl group but one less hindered than in the *trans* isomer II. Conversion was effected by refluxing glacial acetic acid into a dehydration product which gave the correct analysis for the pentaphenyldihydrofuran VII, showed no infrared absorptivity in the hydroxylic region, but showed strong ring-styryl ultraviolet absorptivity comparable with those of the cyclic hemiketal and ketal Vb and Vd.

The first product Vb obviously stems from cyclization of the *cis* hydroxy ketone lithium derivative IV, an alkoxide, which is the primary product of mono-1,2-addition of the reagent to the less sterically hindered of the two carbonyl groups of *cis*-dibenzoylstyrene (III). A ring–chain equilibrium or chelation of the anionic moiety evidently is engendered by the ring-stabilizing steric effects of the 2,3,5,5-phenyl groups, and doubtless is supported by some additional contribution toward stabilization of the cyclic form by the change from the alkoxide anion IV to the more stable cyclic or chelate anion IVa–Va of the relatively acidic hemiketal Vb. These effects are related to the base-induced cyclization of *cis*-dibenzoylstilbene to a cyclic hemiketal anion[8] and the reverse conversion of the weakly acidic hydroxylactone forms of the substituted β-aroylacrylic acids to the corresponding relatively stable acyclic carboxylic anions.[9] Predominance of the cyclic form Va in the ring–chain equilibrium would account for the appreciable resistance to, but not prohibition of, the second 1,2-addition of phenyllithium to the remaining more sterically hindered carbonyl group of the acyclic form IV.

It is pertinent to contrast the unknown and evidently non-isolable acyclic γ-hydroxy ketone (of IV) to the saturated analog,[2c] which was obtained

$$(C_6H_5)_2C(OH)CH(C_6H_5)CH_2COC_6H_5 \quad \text{IX}$$

by successive 1,2–1,4-additions of phenyllithium to dibenzoylethylene. The saturated hydroxy ketone exists only in the acyclic form IX, presumably because it lacks the double bond of *cis* configuration necessary to anchor the hydroxyl and keto groups in proximity to each other.

The cyclic compounds Vb, Vc, and Vd had been previously obtained by Salkind and Teterin[7] through rearrangement and alcoholysis during bromination of 2,2,5,5-tetraphenyldihydrofuran (X) and their structures had been shown by oxidative degradation. The further rearrangement to tetra-

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[7] J. Salkind and V. Teterin, *J. prakt. Chem.*, **133**, 195 (1932).

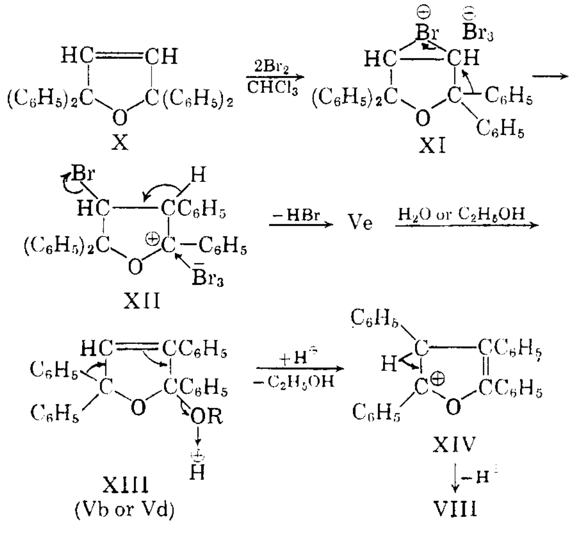
[8] R. E. Lutz and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 2763 (1962).

[9] R. E. Lutz, *et al.*, *J. Am. Chem. Soc.*, **75**, 5039 (1953).

[10] F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 673 (1890).

phenylfuran (VIII) had been carried out under acidic conditions.[7] The first of these rearrangements can be expressed in terms of 3,4-bromine addition, 3-ionization under bromonium and perbromide ion formation, 2- to 3-migration of a phenyl group and dehydrohalogenation to the cyclic perbromide (*e.g.* XI → XII → Ve), and then hydrolysis or ethanolysis to the cyclic hemiketal or ketal XIII (Vb or Vd). The further acid-catalyzed dehydrative rearrangement under 5-to-4 migration of a phenyl group with formation of the stable tetraphenylfuran (VIII), may be expressed in terms of protonation of the 2-hydroxyl or alkoxyl oxygen of XIII, ionization or development of positive polarization at the 4-carbon, migration to this point of one of the 5-phenyl groups, and ejection of the proton of XIV.

An interesting practical synthetic application stemming from the above relationships is the mono-1,2-addition of phenyllithium to the easily available *cis*-dibenzoylstyrene[10] followed by facile rearrangement of the resulting cyclic hemiketal Vb to tetraphenylfuran (VIII). A variety of aryl-substituted tetraphenylfurans and unsaturated diketones could thus be synthesized, starting from aryl-substituted dibenzoylstyrenes obtainable either through 1,4-addition of an aryl Grignard reagent to a diaroylethylene[2c] or through condensation of a diaryl α-diketone with an aryl methyl ketone,[10] and carrying out the mono-1,2-addition of a suitable aryllithium.



In the phenyllithium additions to *cis*- and *trans*-dibenzoylstyrenes it is significant that no 1,4-addition product was isolated in any one of its several possible forms, the *cis*- and *trans*-dibenzoyl stilbenes, the diastereoisomeric saturated diketones and the furan VIII. The seemingly complete suppression of 1,4-addition is in sharp contrast to the considerable extent of this mode of addition in the several related cases cited above.[2c,4,5] It can be explained in terms of: (a) the normal facility of 1,2-addition by phenyllithium; (b) the relatively low steric hindrance at the 4-carbonyl carbons of I and III, possibly with some activation of this carbonyl group in the *cis* isomer by carbonyl-group interaction (III); and (c) the relatively considerable steric hindrance at all of the β-carbon atoms of the parent compounds I and III and of the first-formed hydroxyketone lithium derivative IV and its *trans* counterpart.

Experimental[11]

***trans*-1,1,2,4,4-Pentaphenyl-2-butene-1,4-diol (II).**—To a solution of 0.2 mole of phenyllithium prepared in the usual way under nitrogen in 100 ml. of ether, 0.9 g. (0.003 mole) of *trans*-dibenzoylstyrene (I)[12] was added portionwise over 1 min. The resulting mixture was then hydrolyzed by pouring into ice water; the ether layer and extract were dried and evaporated. Crystallization of the residue from ethanol gave the *trans*-glycol II, m.p. 152–153°, 0.47 g. (40%).

Anal. Calcd. for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 86.87; H, 5.93.

Infrared absorption band: 286 μ (strong); none in the carbonyl region. Ultraviolet absorption (in 95% ethanol): shoulder at 255 mμ, ϵ *ca.* 2700.

Concentration of the mother liquors produced 0.043 g. (3.6%) of the cyclic hemiketal Vb which may have arisen from some *cis*-dibenzoylstyrene present as an impurity in the starting material or formed through *trans*-to-*cis* rearrangement to III during reaction or possibly through some stereoisomerization of the *trans*-mono-1,2-addition product (corresponding to IV) and cyclization to Va.

Preparation of 2,3,5,5-Tetraphenyl-2,5-dihydrofuranol-2 (Vb)[7].—One gram (0.0032 mole) of *cis*-dibenzoylstyrene (III) was added portionwise over 1 min. to a 100-ml. ether solution of 0.02 mole of phenyllithium. The mixture was hydrolyzed with work-up as above and crystallization of the product from ethanol; yield of Vb 0.93 g. (75%), m.p. 144–146°.[7] In some runs, involving long contact of the product with ethanol, the ethyl ether Vd[7] was isolated, instead of Vb, showing the facility of the etherification reaction.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 85.53; H, 5.69.

Ultraviolet absorption (in 95% ethanol): maximum, 252 mμ, ϵ 19,800; infrared band: 2.8 μ (strong); none for a carbonyl group.

Preparation of 2,3,5,5-Tetraphenyl-2-ethoxydihydrofuran (Vd)[7].—Conversion of the cyclic hemiketal Vb into the ethyl ether Vd was brought about in 75–85% yield by the action of ethereal bromine or iodine (4 hr.), evaporation, digestion with ethanol and crystallization.[7] A more logical preparation[13] is as follows: A solution of 7 g. of Vb in 75 ml. of absolute ethanol and 5 ml. of glacial acetic acid was warmed on the steam bath for a few minutes. The crude material which separated on cooling (6 g., m.p. 110–114°) was recrystallized from ethanol; 5.2 g. (70%); m.p. 116–118° (lit.,[7] 117°).

Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26; OC_2H_5, 10.77. Found: C, 85.92; H, 6.45; OC_2H_5, 10.44.

Ultraviolet absorption (in 95% ethanol): λ_{max} 252 mμ, ϵ 20,400.

Formation of 2,3,5,5-Tetraphenyl-2-methoxydihydrofuran (Vc).[7]—Refluxing, for 10 min., of a methanol solution of Vd containing a small amount of saturated methanolic hydrogen chloride, and fractional crystallization of the products,

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(11) Infrared: KBr pellet (Infracord).

(12) E. Oliveri-Mandalà, *Gazz. chim. ital.*, **45** (II), 138 (1915) [*Chem. Abstr.*, **10**, 1517 (1916)].

(13) This experiment was carried out by John I. Dale.

gave tetraphenylfuran (VIII, 47%) and the more soluble methyl ether Vc (34%), m.p. 129–131° (lit.,[7] 128°).

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98; OCH_3, 7.67. Found: C, 86.06; H, 6.10; OCH_3, 7.30.

No infrared absorption bands in the hydroxyl and carbonyl regions.

Treatment of the ethyl ether Vd with methanol to which saturated methanolic hydrogen chloride had been added (refluxing for 40 min.) gave VIII (59%) and Vc (32%).

Conversion of Vb into tetraphenylfuran (VIII) was effected in practically quantitative yield by refluxing glacial acetic acid (2 min.) (VIII was identified by mixture m.p. 174–176° and infrared absorption spectrum).

***cis*-1,1,2,4,4-Pentaphenyl-2-butene-1,4-diol** (VI).—Twenty grams (0.064 mole) of *cis*-dibenzoylstyrene (III) was added portionwise over 5 min. to a 200 ml. solution of 1.31 moles of phenyllithium (under nitrogen) with continued stirring for an additional 10 min. Hydrolysis with ammonium chloride solution and work-up with crystallization from methanol gave 10 g. (33%) of *cis*-glycol VI, m.p. 146–148°. It retained solvent of crystallization tenaciously, and it required drying under fusion for analysis.

Anal. Calcd. for $C_{34}H_{28}O_2$: C, 87.17; H, 5.97. Found: C, 87.06; H, 6.00.

Infrared absorption band (on sample dried by fusion): 3 μ, broad and strong; none for the carbonyl group. Ultraviolet absorption (in absolute ethanol): no maximum above 220 mμ; slight shoulder on the curve at 250 mμ, ϵ 5700. Crystallizations from solvent containing methanol gave material containing approximately 1 molecule of methanol. Samples carrying ethanol, methanol, or water of crystallization all showed strong broad absorption areas centering at *ca.* 3.1 μ. Crystallization from benzene–acetone mixture gave a product showing a strong carbonyl band at 5.9 μ (acetone of crystallization), and after drying under heating the sample showed complete absence of this carbonyl band.

The *cis*-glycol VI was also obtained by the action of phenyllithium exactly as above on the cyclic hemiketal Vb (total reaction time 18 min.); yield 15%, identified by melting point and infrared spectrum.

2,2,3,5,5-Pentaphenyldihydrofuran (VII).—A solution of 9.8 g. of the *cis*-glycol VI in 100 ml. of glacial acetic acid was refluxed for 3 min. Cooling precipitated the dihydrofuran VII, 5.9 g. (60%), recrystallized from methanol–benzene mixture; m.p. 199–200°.

Anal. Calcd. for $C_{34}H_{26}O$: C, 90.67; H, 5.77. Found: C, 90.28; H, 5.87. Infrared absorption: no hydroxyl or keto bands. Ultraviolet absorption (in absolute ethanol): λ_{max} 250 mμ, ϵ 14,500.

2,4,6-Trimethylbenzyl Hydroperoxide

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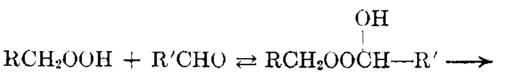
2,4,6-Trimethylbenzyl hydroperoxide has been synthesized and its thermal and acid-catalyzed decompositions examined. Acid-catalyzed decomposition products (mesitol and formaldehyde) complicate the thermal decomposition due to participation of formaldehyde in hydroxyperoxide formation. Mesityoxymethyl benzoate (III) is produced in good yield from decomposition of I with benzoic acid.

The decomposition of primary benzyl hydroperoxides has not been studied in detail, despite the importance of these compounds as intermediates in the autoxidation of the methylbenzenes. *p*-Methylbenzyl hydroperoxide has been shown to decompose to a limited extent *via* a hydroxyperoxide to give hydrogen as a product.[1] The involvement of the hydroxyperoxide and the yield of hydrogen are much less in this system than for the aliphatic primary hydroperoxides examined by Mosher,[2] a consequence of the lower reactivity of the aromatic aldehyde toward nucleophilic attack (equation 1). The importance of equation 1 in the overall decomposition can be further reduced if R′ is so substituted that attack on the aldehyde function is sterically hindered, such that the rate of formation of the hydroxyperoxide would be very much slower than the hydroperoxide decomposition. To test this viewpoint, 2,4,6-trimethylbenyl hydroperoxide (I), whose corresponding aldehyde is the highly hindered mesitaldehyde (R = R′ = 2,4,6-trimethylphenyl in equation 1) was synthesized and its decomposition examined.



$$RCH_2OOH + R'CHO \rightleftharpoons RCH_2OO\overset{OH}{\overset{|}{C}}H\text{—}R' \longrightarrow RCHO + R'COOH + H_2 \quad (1)$$

Results and Discussion

The synthesis of I was achieved *via* oxidation of the appropriate Grignard reagent with oxygen at low temperatures.[3] Although some peroxidic material was formed, the yield was poor (*ca.* 30%) and the product contaminated with 2,4,6-trimethylbenzyl alcohol and dimesitylethane, the latter presumably formed during preparation of the Grignard reagent.[4] Base extraction improved the purity of the hydroperoxide somewhat, but removal of the remaining impurities by recrystallization was a wasteful process. Excellent purification of the base extract could be obtained by chromatography on Cellulose powder,[5] from which could be recovered, after a single recrystallization, hydro-

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[1] W. J. Farrissey, Jr., *J. Am. Chem. Soc.*, **84**, 1002 (1962).

[2] H. S. Mosher and C. F. Wurster, *ibid.*, **77**, 5451 (1955); C. F. Wurster, L. J. Durham, and H. S. Mosher, *ibid.*, **80**, 327 (1958); L. J. Durham, C. F. Wurster, and H. S. Mosher, *ibid.*, **80**, 332 (1958).

[3] C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

[4] L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

[5] N. Milas and A. Golubovic, *J. Am. Chem. Soc.*, **81**, 3361 (1959)