made for any combined water of crystallization in calculations of yield. Results are reported in Fig. 3.

Acknowledgment.—We are indebted to Samuel W. Blackman for the microanalyses which are reported here.

Summary

The formation of *p*-oxazino[2,3-*d*]pyrimidine derivatives from 6-hydroxy-5-α-chloroacylamidopyrimidines by treatment with aqueous barium hydroxide solution is described. This ring closure has been found to be dependent on the nature of the substituent in the 2-position of the pyrimidine ring.

TUCKAHOE 7, NEW YORK RECEIVED JULY 21, 1948

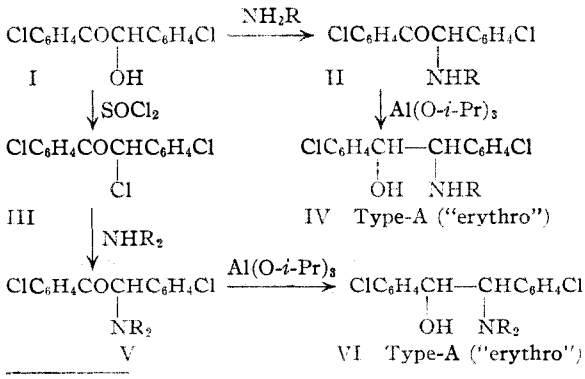
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Substituted-Amino Ketones and Alcohols Related to 4,4′-Dichlorobenzoin[1]

BY ROBERT E. LUTZ AND ROBERT S. MURPHEY[2]

In the light of evidence for the necrotizing action against mammalian tumors of several substituted-amino ketones and alcohols derived from benzoin,[3] it seemed worth while to investigate analogous compounds carrying in one or both phenyl nuclei substituents which might have the effect of enhancing the pharmacological activity. The present paper is the first of a series dealing with this phase of the problem. The 4,4′-dichloro series was chosen for study because of the well-known influence of halogen in increasing other types of pharmacological activity such as antimalarial and insecticidal.

The starting material, 4,4′-dichlorobenzoin (I),[4] has to date been obtainable only in poor yields by the benzoin condensation with *p*-chlorobenzaldehyde. By modification of the procedure developed by Willgerodt and Ucke[5] for the preparation of 4,4′-diiodobenzoin, the dichloro analog has been obtained consistently in yields of 80–88%. It is noteworthy that this product is exceptionally easily oxidized to 4,4′-dichlorobenzil upon manipulation involving contact with air.



The secondary amino ketones (II, see table) were made by the action of primary amines on 4,4′-dichlorobenzoin (the Voigt reaction[3,6]). In most runs phosphorus pentoxide was used as a catalyst; however, in one test using ethanolamine, an equally successful preparation resulted when the catalyst was omitted. All of the products were stable as the salts; however, in the form of the bases they underwent ready hydrolysis and oxidation to 4,4′-dichlorobenzil. Only one arylamino ketone, but none of the alkylamino ketones, was obtainable as a crystalline free base.

The amino ketones were reduced by means of aluminum isopropoxide to the amino alcohols (IV). Since only one of the two theoretically possible stereoisomers was isolated in each case, it is to be presumed that the configurations are of the same type (Type-A "erythro") and are analogous to those of the majority of the compounds prepared correspondingly in the parent benzoin series.[3] This presumption is supported by the synthesis of one of these (REL 691) through the *trans-p,p′*-dichlorostilbene oxide (see below).

4,4′-Dichlorodesyl chloride[4d] (III) was readily made by the action of thionyl chloride on 4,4′-dichlorobenzoin, but in poor yields (*ca.* 33%). It proved to be unstable and exceptionally easily converted into 4,4′-dichlorobenzil under various manipulations in contact with air.

Representative tertiary-amino ketones (V) were made by condensation of 4,4′-dichlorodesyl chloride (III) with the appropriate amine. These were reduced to the amino alcohols (VI) by means of aluminum isopropoxide. Since here also only one of the two possible diastereoisomers was obtained in each case, these compounds are presumed to be of the type-A ("erythro") configuration.

Two ethanolamino ketones were made. The monoethanolamino compound itself (II, R = CH_2CH_2OH) was made by the Voigt reaction from 4,4′-dichlorobenzoin and was readily re-

(1) Agents Causing Necrosis in Tumors, II. This work was carried out under a grant-in-aid from the National Institute of Health, recommended by the National Cancer Institute. The larger part of this work was included in a dissertation for the M.S. degree, University of Virginia, June, 1947.

(2) Holder of National Cancer Institute Junior Research Fellowship, 1947–1948.

(3) Lutz, Freek and Murphey, THIS JOURNAL, **70**, 2015 (1948).

(4) (a) Hantzsch and Glover, *Ber.*, **40**, 1519 (1907); (b) Kenner and Witham, *J. Chem. Soc.*, **97**, 1967 (1910); (c) Gomberg and Van Natta, THIS JOURNAL, **51**, 2241 (1929); (d) Karrer and Forster,

TABLE I

α-SECONDARY AND TERTIARY AMINO-4,4'-DICHLORODESOXYBENZOIN HYDROCHLORIDES (II AND V)

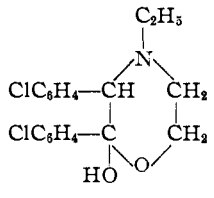
REL.[a] no.	NHR or NR_2	Method[b] of prepn.	Time of heating, hours	Yield, %	Crystallized from[c]	M. p., °C., cor.	Empirical formula	Analyses, % Carbon (or nitrogen) Calcd.	Found	Hydrogen (or chlorine) Calcd.	Found
619	NHC_4H_9	1a	4	42	But.-CH_3OH	249-250	$C_{18}H_{19}Cl_2NO\cdot HCl$	58.00	57.73	5.41	5.27
		1b	1.5	49	But.-CH_3OH	249-250					
626	NHC_8H_{17}	1b	2	42	But.-CH_3OH	226-227	$C_{22}H_{27}Cl_2NO\cdot HCl$	61.61	61.62	6.58	6.65
690	$NHCH_2CH_2OH$	1a,d	0.1	89	But.-CH_3OH	197-199	$C_{16}H_{15}Cl_2NO_2\cdot HCl$	53.28	52.95	4.47	4.28
		..	..	..	But.-CH_3OH	197-199					
	NHC_6H_5(base)	1a	2	69	CH_3OH	107-108	$C_{20}H_{15}Cl_2NO$	3.93	3.78	..	..
610	(Hydrochloride)	..	..	..	EtOH-H_2O	212-214	$C_{20}H_{16}Cl_2NO\cdot HCl$	...	...	9.03	9.10
683	$NHC_6H_4N(C_2H_5)_2$-*p*	1a, c	0.1	90	But.-CH_3OH	178-180	$C_{24}H_{24}Cl_2N_2O\cdot 2HCl$	5.60	5.31	..	..
		1b	2	84	But.-CH_3OH	178-180					
632	$N(C_2H_5)_2$	2	12	59	But.-CH_3OH	223-224	$C_{18}H_{19}Cl_2NO\cdot HCl$[e]	58.00	57.90	5.41	5.55
686	$N(C_2H_5)CH_2CH_2OH$	2	2	64	But.	185-186	$C_{28}H_{15}Cl_2NO_2\cdot HCl$[f]	55.61	55.53	5.19	5.20
628	Piperidyl[d]	2	18	65	EtOH-Acet.	247-248[g]	$C_{19}H_{19}Cl_2NO\cdot HCl$	59.31	59.19	5.24	4.99

2-SECONDARY AND TERTIARY AMINO-1,2-DI-(4-CHLOROPHENYL)-ETHANOLS (IV AND VI), BASES AND HYDROCHLORIDES

	NH_2[j]	4e,c	24	68	EtOH-H_2O	160-163	$C_{14}H_{13}Cl_2NO$	59.59	59.70	4.64	4.70
721	(Hydrochloride)	..	..	..	But.-CH_3OH	234-235	$C_{14}H_{13}Cl_2NO\cdot HCl$	52.77	52.51	4.43	4.57
	NHC_4H_9	3	5	90	EtOH-H_2O	129-130	$C_{18}H_{21}Cl_2NO$	4.14	3.99	..	..
625	(Hydrochloride)	..	..	..	But.-CH_3OH	254-256	$C_{18}H_{21}Cl_2NO\cdot HCl$	57.69	57.71	5.92	6.08
627	NHC_8H_{17}	3	4	76	EtOH	106-107	$C_{22}H_{29}Cl_2NO$	67.00	66.69	7.41	7.43
	(Hydrochloride)	..	..	..	Acet.-ligr.	182-183	$C_{22}H_{29}Cl_2NO\cdot HCl$	3.25	3.24	..	..
	$NHCH_2CH_2OH$	3	3	77	EtOH-H_2O	104-105	$C_{16}H_{17}Cl_2NO_2$	4.29	4.24	..	..
		4a,c	20	91		104-105[i]					
691	(Hydrochloride)	3	..	..	But.-CH_3OH	248-249	$C_{16}H_{17}Cl_2NO_2\cdot HCl$	52.98	53.06	5.00	5.21
		4a,c				245-248[i]					
	NHC_6H_5	..	..	..	...	Oil[h]	$C_{20}H_{17}Cl_2NO$	3.91	3.96	..	..
611	(Hydrochloride)	3	1	80	Acet.-Et_2O	198-199	$C_{20}H_{17}Cl_2NO\cdot HCl$	60.85	61.04	4.60	4.30
	$NHC_6H_4N(C_2H_5)_2$-*p*	..	..	..	EtOH	139-141	$C_{24}H_{26}Cl_2N_2O$	67.13	66.91	6.10	5.94
692	(Dihydrochloride)	3	3	92	But.-CH_3OH	205-207	$C_{24}H_{26}Cl_2N_2O\cdot 2HCl$	5.58	5.57	..	..
	$N(C_2H_5)_2$	..	..	..	EtOH	90- 91	$C_{18}H_{21}Cl_2NO$	63.91	63.80	6.26	6.18
682	(Hydrochloride)	3	8	15	But.-CH_3OH	226-227	$C_{18}H_{21}Cl_2NO\cdot HCl$	57.69	57.91	5.92	5.76
	Piperidyl[d]	3	6	37	EtOH	115-115.5	$C_{19}H_{21}Cl_2NO$	65.14	65.42	6.04	6.33
638	(Hydrochloride)[d]	..	..	..	EtOH	254-256	$C_{19}H_{21}Cl_2NO\cdot HCl$	59.00	59.01	5.74	5.74
	$N(C_2H_5)CH_2CH_2OH$	4b,d	10	70	EtOH-H_2O	101-102	$C_{18}H_{21}Cl_2NO_2$	61.52	61.30	5.97	6.26
722	(Hydrochloride)	..	..	..	...[k]	189.5-191	$C_{18}H_{21}Cl_2NO_2\cdot HCl$	55.32	55.38	5.68	5.47

[a] Code number from this Laboratory. [b] See descriptions in the experimental part. [c] But. = butanone, EtOH = 95% ethanol, acet. = acetone, ligr. = ligroin, Et_2O = ethyl ether. [d] Prepared by James A. Freek. [e] Calcd. for N, 3.76; found, 3.58. [f] Calcd. for N, 3.60; found, 3.63. [g] The base melts at 80–81° *in vacuo*. It was not analyzed. [h] The base was liberated from the pure salt by means of alkali and was isolated by extraction with ether and evaporation of the solvent. It was not distilled. [i] This product gave no mixture melting point depression with the first sample. [j] Unsuccessful attempts were made to prepare this compound through reduction of 4,4'-dichlorobenzil monoxime by stannous chloride and by sodium–alcohol reductions, and to prepare the stereoisomer by condensation of *p*-chlorobenzaldehyde with glycine [*cf.* Erlenmeyer, *Ann.*, **307**, 97 (1899)]. [k] Crystallized from acetone–methanol–isoöctane mixture.

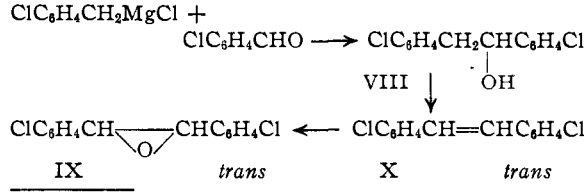
duced by aluminum isopropoxide to the di-alcohol (IV, R = CH_2CH_2OH). The ethylethanolamino analog (V, NR_2 = $N(C_2H_5)CH_2CH_2OH$), however, evidently has the cyclic structure (VII) since it is not reduced to a significant extent by aluminum isopropoxide under the conditions usually effective.[7]



VII

The corresponding tertiary-amino dialcohol (VI, NR_2 = $N(C_2H_5)CH_2CH_2OH$), and also the ethanolamino analog (IV, R = CH_2CH_2OH) and the parent amino compound (VI, NR_2 = NH_2), were successfully made by condensation of *trans*-4,4'-dichlorostilbene oxide (IX) with ethylethanolamine, ethanolamine and ammonia, respectively. The type A ("erythro") configurations are assumed in view of this mode of synthesis.

The *trans*-oxide, used above, was made from *trans*-4,4'-dichlorostilbene (X, known[8]) which has been obtained in a new and improved way by the action of *p*-chlorobenzylmagnesium chloride on *p*-chlorobenzaldehyde and dehydration of the resulting carbinol (VIII). The *trans* configurations have been assigned on the basis of the mode of synthesis (*cf.* ref. 3).



(7) Lutz and Jordan, THIS JOURNAL, **71**, in press (1949).

(8) For preparations of this compound by other methods see (a) Meyer and Hoffmann, *Monatsh.*, **38**, 141 (1917); (b) Pascal and Normand, *Bull. soc. chim.*, **9**, 1029, 1059 (1886); **11**, 21 (1888); (c) Spath, *Monatsh.*, **35**, 463 (1914); (d) Forrest, Stephenson and Waters, *J. Chem. Soc.*, 333 (1946); (e) Meerwein, Büchner and van Emster, *J. prakt. Chem.*, **157**, 237 (1939).

The *p*-diethylaminoanilino ketone hydrochloride [IV, R = $NHC_6H_4N(C_2H_5)_2$-*p*] was made in order to test the influence of an extra basic group. In the form of the free base this compound was extremely unstable; the salt, although relatively much more stable, deteriorated to a red resinous mass on standing in the air. The compound was reduced by means of aluminum isopropoxide to the corresponding alcohol which in contrast proved to be stable in the form of the free base.

The results of pharmacological tests, especially those dealing with tumor necrosis, which are in progress at the National Cancer Institute, will be reported elsewhere.[9]

Experimental[10]

The Preparation of 4,4'-Dichlorobenzoin (I).[4]—Due apparently to the low melting point and high solubility in ethanol, this compound separated as an oil under the usual conditions of the benzoin condensation.[11] For the best results it was important to remove all unreacted *p*-chlorobenzaldehyde. It was advantageous to diminish the reaction time in order to minimize side reactions such as oxidation of the desired product to the corresponding benzil. The compound crystallized well only from petroleum ether.

A saturated aqueous solution of 5 g. of a pure grade of potassium cyanide was added slowly to a refluxing solution of 500 g. of freshly distilled *p*-chlorobenzaldehyde in 300 ml. of methanol. A strongly exothermic reaction ensued. The mixture was refluxed for twenty minutes, and the methanol was evaporated under reduced pressure. The residual red, pasty mass was taken up in benzene. The benzene solution was extracted repeatedly with 20% sodium bisulfite until the extract liberated no aldehyde when treated with alkali; the solution was then washed with water and evaporated under reduced pressure. The residue crystallized as fine, colorless needles from petroleum of boiling range 70–110°; yield 440 g. (88%). After several recrystallizations it melted at 87–88°.[4a,c,d] On standing in air the surface of the white benzoin becomes coated with the yellow benzil.

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2$: C, 59.80; H, 3.58. Found: C, 59.61; H, 3.34.

4,4'-Dichlorodesyl Chloride (III).—A solution of 140.5 g. (0.5 mole) of 4,4'-dichlorobenzoin in 50 g. of pyridine at 5° was treated dropwise under cooling with 75 g. (0.63 mole) of thionyl chloride. The resulting viscous yellow mixture was extracted repeatedly with cold water until the test for chloride ion was negative, and was then extracted with petroleum ether to remove unchanged 4,4'-dichlorobenzoin; the product was crystallized from 95% ethanol, yield 53.3 g. (36%), colorless needles of melting point 60–61°.

Anal. Calcd. for $C_{14}H_{10}Cl_3O$: C, 56.12; H, 3.03. Found: C, 55.29; H, 2.96.

4,4'-Dichlorobenzil monoxime was made from 4,4'-dichlorobenzil by the procedure for the 4,4'-dibromo analog,[12] yield 90%, crystallized from dilute ethanol, m.p. 143–144°.

Anal. Calcd. for $C_{14}H_9Cl_2NO_2$: N, 4.76. Found: N, 4.50.

1,2-Di-(4-chlorophenyl)-ethanol (VIII).—A solution of 119 g. (0.848 mole) of *p*-chlorobenzaldehyde in 800 ml. of ether was added slowly under stirring to 4-chlorobenzylmagnesium chloride in 700 ml. of ether [made from 154 g. (0.956 mole) of 4-chlorobenzyl chloride and 46 g. (1.89 mole) of magnesium]; the mixture was heated for one hour, hydrolyzed with dilute acetic acid, washed with sodium hydroxide and then with sodium bisulfite, and was concentrated. The residual oil crystallized and the crude product was used in the next experiment. A small sample was recrystallized from isoöctane, hexagonal plates, m.p. 74–75°.

Anal. Calcd. for $C_{14}H_{12}Cl_2O$: C, 62.94; H, 4.53. Found: C, 62.99; H, 4.96.

***trans*-4,4'-Dichlorostilbene (X).**[8]—The crude alcohol (VIII) (above) was heated with 1 ml. of 48% hydrobromic acid at 230° for twenty minutes (evolution of water had ceased), and the product was distilled at 215–230° under 10 mm., yield 161 g. After two crystallizations from toluene the yield was 120 g. (57% calculated from VIII), m.p. 175–176°. *Anal.* Calcd. for C, 67.49; H, 4.05. Found: C, 67.55; H, 3.79.

***trans*-4,4'-Dichlorostilbene Oxide (IX).**—A solution of 93.5 g. of X in 3 liters of xylene was added to a solution of 83 g. of perbenzoic acid in 1.1 liters of chloroform. The mixture was allowed to stand for twenty-four hours at room temperature and five hours at 60°. (The reaction was very slow; a number of other solvents were tried but without improvement.) Evaporation to a volume of about 1.5 liters under reduced pressure, washing with sodium hydroxide, drying over sodium sulfate and evaporation of the rest of the solvent, and crystallization of the residual oil from ethanol, gave colorless needles, 50 g. (50%), m.p. 114–115.5°. Treatment in acetone with permanganate to remove unchanged X gave a product melting at 123–124°.

Anal. Calcd. for $C_{14}H_{10}Cl_2O$: C, 63.42; H, 3.80. Found: C, 63.41; H, 4.10.

General Procedures. (1) **The Preparation of the Secondary Amino Ketones from 4,4'-Dichlorobenzoin.**—A mixture of 0.25 mole of the benzoin, 0.27 mole of the primary amine and 2 g. of phosphorus pentoxide was heated on a water-bath. (a) When no solvent was used the water formed in the reaction was not removed. (b) When benzene was used as solvent the water formed in the reaction was removed by distillation of the azeotrope; and heating was continued until further distillation failed to give evidence of further formation of water in the reaction. In this case the solvent was removed under diminished pressure before working up the product. (c) In several experiments the amine and catalyst were added to the molten benzoin, and no further heat was applied. (d) In one experiment the catalyst was omitted. The amine was added to the benzoin which had been melted and brought to 110°. Without the application of heat the temperature of the mixture dropped to 85°, and upon slight shaking to mix the materials, it rose sharply to 112°. The mixture was allowed to cool slowly to room temperature and was worked up in the usual way.

α-Anilino-4,4'-dichlorodesoxybenzoin was purified as the base, and the hydrochloride was obtained in the usual way.

In the preparation of the α-monobutylamino-4,4'-dichlorodesoxybenzoin the reaction product was taken up in ether, the unreacted amine was extracted by water, the ether solution was dried over sodium sulfate, and the amino ketone salt was precipitated by the addition of ethereal hydrogen chloride. The corresponding octylamino ketone was purified by removing the unreacted amine under diminished pressure and obtaining the hydrochloride as in the case of the butylamino compound.

(2) **Preparation of the Tertiary-Amino Ketones from 4,4'-Dichlorodesylchloride.**—The α-diethylamino-4,4'-dichlorodesoxybenzoin (V) was prepared by allowing a mixture of 0.4 mole of diethylamine and 0.2 mole of 4,4'-dichlorodesyl chloride (III) to stand at room temperature, with exclusion of air, for the period of time stated in the table. The reaction mixture was dissolved in ether, and the unreacted diethylamine was extracted from this solution by water. The ether solution was dried over

(9) Unpublished work of Shear, Downing, MacArdle, Hartwell, *et al.*, at the National Cancer Institute.

(10) All melting points are "corrected." The microanalyses were carried out by Mrs. Joyce Blume Caliga and by the Clark Microanalytical Laboratory.

(11) "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., p. 94.

(12) Biltz, *Ber.*, **43**, 1815 (1910).

sodium sulfate and the amino ketone hydrochloride was precipitated by the addition of ethereal hydrogen chloride, yield 59%.

It was observed that the amino ketones were sensitive compounds and in several experiments the yields were very poor. The diethylamino compound, for example, suffered decomposition with the formation of appreciable amounts of 4,4′-dichlorobenzil. Each successive crystallization of the hydrochloride of this amino ketone from the methanol–butanone mixture involved the formation of significant amounts of 4,4′-dichlorobenzil which was difficultly soluble in the solvent and crystallized out during the manipulation.

In one preliminary experiment V was obtained in only 26% yield upon heating a solution of 0.2 mole of III and 0.424 mole of diethylamine in benzene on the water-bath without the precaution of excluding air.

(3) **Preparation of the 1,2-Di-(4-chlorophenyl)-N-substituted-ethanolamines by Reduction of Amino Ketones.**—The amino ketones prepared as above were reduced to the corresponding alcohols (IV and VI) in the usual way by means of an excess of 1.5 *N* aluminum isopropoxide. The butylamino and octylamino alcohols were purified as the free bases, while all the other amino alcohols were purified as the hydrochlorides.

(4) **The Preparation from 4,4′-Dichlorostilbene Oxide.**—A mixture of X and a large excess of the amine was heated at (a) 130° and (b) 150°, respectively, taken up in (c) benzene or (d) ether, washed with water to remove excess amine, dried over sodium sulfate, and treated with ethereal hydrogen chloride to precipitate the salt. (e) The condensation using 28% concd. aqueous ammonium hydroxide in dioxane as solvent (sealed tube) was at 100°.

Summary

An improved preparation of 4,4′-dichloro-benzoin and 1,2-di-(4-chlorophenyl)-ethanol, and the syntheses of 4,4′-dichlorodesyl chloride, *trans*-4,4′-dichlorostilbene and 4,4′-dichlorostilbene oxide, are described.

From these compounds a series of secondary and tertiary-amino desoxybenzoins and the corresponding amino and substituted-amino alcohols, have been prepared.

Resistance to aluminum isopropoxide reduction of the ethylethanolamino ketone as contrasted with the facile reduction of the monoethanolamino analog, indicates a cyclic hemiacetal structure for the former.

CHARLOTTESVILLE, VIRGINIA
RECEIVED SEPTEMBER 7, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. IX. Metalation during Alfin Polymerization of Butadiene and the Formation of Gel[1]

BY AVERY A. MORTON, RICHARD P. WELCHER,[2] FRANCES COLLINS, SIEGFRIED E. PENNER AND ROBERT D. COOMBS

The previous paper[3] showed that metalation of rubber caused gel to form in proportion to the metalating activity, and the paper[4] before that showed that an Alfin[5] catalyst was a poorer metalating agent than the allylsodium component of the catalyst. It seemed likely, therefore, that the amount of gel formed during Alfin polymerization would have a direct connection with the lack of correct proportioning of alkoxide with alkenylsodium, or, in the absence of a specific combination, would have a connection with the quantity of catalyst in excess of that needed for polymerization. In either event the relation would be expressed by the rule that minimum gel would accompany maximum polymerizing activity. The idea of a specific combination has been confirmed with two moderately active catalysts and that of quantity with an extremely active catalyst that is less sensitive to proportioning.

The first catalyst (PB_1)[5] was made from sodium isopropoxide and 1-butenylsodium. Two series of reagents, A and B, were used. A was made by combining the two components after each had stood for some time. Figure 1 shows clearly that in four separate trials during a period of over two months the peak of activity (with reagent no. 4) was also the one with minimum gel. B was made by mixing immediately after preparing the two components separately. Figure 2 shows again the relationship but only after the catalyst had aged for some time (test no. 3). The aging process (in B) unquestionably would have been accelerated if the mixing had been done in the high-speed stirring apparatus. Figure 3 confirms this action of the B series with a mixture of butadiene and isoprene, the latter being added to slow down the action, erase part of the gel formation (isoprene[5] forms little or no gel when polymerized) and bring out the action more distinctly. The particular proportions for maximum activity with A and B have no significance since particle size of the two components was probably not the same. The method of combination was not ideal, but was chosen because it permitted proportioning from stock preparations of the two components. The total amount of each present, therefore, has less significance than the composition of the available surface.

The second catalyst was made from sodium phenylmethyl carboxide and allylsodium and a

(1) This work was part of the program of research carried out in recent years under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation.

(2) Present address: The American Cyanamid Company, Stamford, Connecticut.

(3) Morton and Ramsden, THIS JOURNAL, **70**, 3132 (1948).

(4) Morton and Holden, *ibid.*, **69**, 1675 (1947).

(5) Morton Magat and Letsinger, *ibid.*, **69**, 950 (1947).