amino-derivatives, followed by Hofmann degradation.

2. Ozonization of 3-keto-4,20-pregnadiene constitutes a better route than any hitherto suggested to 3-keto-4-*etio*-cholenic acid. Likewise ozonization of 3(α),12(α)-diacetoxy-20-pregnene gave 3(α),-12(α)-diacetoxy-*etio*-cholanic acid in good yield.

3. Hydroxylation of 3-keto-4,20-pregnadiene gave the isomeric 20,21-diols which have been separated and characterized.

4. This degradation of *bisnor*-acids facilitates the preparation of compounds containing the ketol structure of the cortical hormones.

CHICAGO, ILLINOIS RECEIVED SEPTEMBER 15, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE]

Studies in the Quinoline Series. IX. The Mononitrophenyllepidylcarbinols and Related Compounds

BY R. STUART TIPSON AND ANNE FARLEY WALTON

In a recent communication,[1] methods were described for the preparation of the three mononitrophenylquinaldylcarbinols and certain of their derivatives. We now describe related work on the lepidyl isomers.

In an attempt to prepare *p*-nitrophenyllepidylcarbinol by Bulach's[2] method (used for the preparation, in good yield, of the corresponding quinaldyl compounds[1]) the yield was only 7% of the theoretical; this is in agreement with Eibner's work[3] showing that a methyl group at position 4 reacts less readily with aldehydes than one at position 2. However, on lengthening the reaction time to eight hours, and changing the method of isolating the product, the yields of the lepidylcarbinols were: *o*- and *p*-, 24%; *m*-, 19%. A lower yield of *m*-derivative had also been noted[1] in the quinaldyl series. The *o*- and *p*-derivatives were isolated directly; because of the greater solubility of the *m*-derivative, it was found more convenient to extract it as the hydrochloride and to reconvert the latter to the base.

When *two* moles of lepidine were used to one of aldehyde, the yield of *m*-carbinol (after eight hours at 120°) was increased to 24%, but for the *o*- and *p*- isomers there was no great improvement in yield of isolable product (presumably because these compounds were, to a somewhat greater extent, retained in solution in the excess lepidine, and the dissolved part could not be readily separated from it). Various attempts were made to increase the yield of *m*-derivative still further. It was found that heating the reaction mixture at 120° for twenty-four hours, or at 145° for eight hours, always gave a mixture of the carbinol and the corresponding *styryl* compound. Moreover, after cooling to room temperature, the reaction mixture was invariably found to be acid to litmus and it was concluded that this acid, presumably formed from the aldehyde during the reaction, had facilitated conversion of some of the carbinol to the styryl derivative. (The ability of acid to catalyze this dehydration has already been proved[1] for the corresponding quinaldyl carbinols.) It was therefore decided to add to the reaction mixture some substance which would neutralize acid as fast as it was formed. After examining the effect of a number of materials, anhydrous sodium carbonate was finally selected, and the reaction mixture was heated at 145° for twenty-four hours. At the end of this time, the reaction mixture was still alkaline to litmus, and *no* styryl derivative had formed, but the yield obtained (33%), though higher, was scarcely increased enough to warrant using this method.

Just as for the three quinaldyl isomers, we find the three nitrophenyllepidylcarbinols exhibit two melting points, depending on whether heated rapidly or slowly. On cooling until crystallized and remelting, the melting point is found to be lower in each case, presumably owing to partial conversion to the corresponding styryl derivative on heating. The carbinols were transformed to their monohydrochlorides which were isolated as colorless, crystalline substances showing no tendency to become dehydrated to the styryl derivatives during five months at room temperature, as evidenced by the recovery of pure carbinol on reconversion to the base. The acetyl derivatives of the three carbinol compounds were also prepared. Attempts to reduce each nitro carbinol to the corresponding amino derivative gave inconclusive results suggestive of formation of some β-hydroxylamino derivative[4]; we were unable to purify the products satisfactorily by fractional recrystallization.

It has been shown previously[5] that the reaction of *p*-dimethylaminobenzaldehyde with quinaldine gives rise to the corresponding styryl derivative *plus* *p*-dimethylaminobenzylidene diquinaldine (β-*p*-dimethylaminophenyl-α,γ-di-2-quinolylpropane) and that a preponderance of either product is obtainable by appropriate choice of the conditions. Similarly, on attempting to prepare the pure *styryl* derivatives by condensation of the appropriate nitrobenzaldehyde with lepidine in

(1) Walton, Tipson and Cretcher, THIS JOURNAL, **67**, 1501 (1945).
(2) Bulach, *Ber.*, **20**, 2046 (1887).
(3) Eibner, *Ber.*, **37**, 3605 (1904); Fischer, *et al.*, *J. prakt. Chem.*, **100**, 91 (1920).
(4) Fieser and Hershberg, THIS JOURNAL, **62**, 1640 (1940).
(5) Tipson, *ibid.*, **67**, 507 (1945).

TABLE I

MELTING POINTS AND ANALYSES OF THE MONONITROPHENYLLEPIDYLCARBINOLS AND THE 4-(NITROSTYRYL)-QUINOLINES

Vol. (cc.) of absolute ethanol (E) plus chloroform (C) for recryst. of 10 g. -phenyllepidylcarbinol	M. p., °C. Initial Fast	Initial Slow	Second Cooled and reheated	Formula	Analyses, % Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
o-Nitro 150 (E) + 120 (C)	191–192	182–184	180	$C_{17}H_{14}N_2O_3$	69.36	4.8	9.53	69.66	5.2	9.46
m-Nitro 160 (E)	166–167	162–163	157	$C_{17}H_{14}N_2O_3$	69.36	4.8	9.53	69.45	5.1	9.34
p-Nitro 150 (E) + 120 (C)	187–188	182–184	180	$C_{17}H_{14}N_2O_3$	69.36	4.8	9.53	69.18	5.0	9.79
-styryl)-quinoline										
4-*o*-Nitro 150 (E) + 50 (C)			172–173[a]	$C_{17}H_{12}N_2O_2$	73.88	4.4	10.15	73.77	4.5	10.43
4-*m*-Nitro			133–134[b]	$C_{17}H_{12}N_2O_2$	73.88	4.4	10.15	73.83	4.3	10.14
4-*p*-Nitro			227–229[c]	$C_{17}H_{12}N_2O_2$	73.88	4.4	10.15	73.70	4.5	9.95

[a] Loew (*Ber.*, **36**, 1666 (1903)) gave m. p. 162°. [b] Heymann and Koenigs (*Ber.*, **21**, 2167, 1424 (1888)) gave m. p. 131–132° and 135–136°; Kaslow and Stayner (THIS JOURNAL, **67**, 1716 (1945)) gave 130.5–131.5°. [c] Loew, ref. *a*, gave 221°.

the presence of an inorganic acid, it was found that the *dilepidine* derivatives are formed together with the nitrostyryl compounds. Indeed, the *m*- and *p*-nitrobenzylidene dilepidines could be isolated in good yield (77% and 63%, respectively, of the theoretical amount) by heating one mole of the appropriate aldehyde with two moles of lepidine in the presence of concentrated sulfuric acid for three hours at 165° (bath temperature). On the other hand, on treating lepidine with the *o*-aldehyde under the same conditions, a violent reaction ensued, resulting in extensive decomposition. At a reaction temperature of 100°, a mixture of the *o*-nitrostyryl-quinoline and its corresponding *carbinol* derivative was formed.

The three 4-(nitrostyryl) derivatives have now been isolated in pure form and are found to have melting points higher than those previously recorded in the literature. The *o*-nitrostyryl derivative was readily prepared pure since it was the *sole* product resulting either on boiling a solution of the pure carbinol compound in acetic anhydride,[2,6] or on boiling a solution of the *o*-aldehyde and lepidine in acetic anhydride.

The 4-(*m*-nitrostyryl)-quinoline could not be obtained as the *sole* product in any of the reactions attempted. On performing the reactions involving acetic anhydride (successfully used to prepare the pure *o*-styryl compound), the *m*-nitrostyryl derivative formed was contaminated with a higher melting, more insoluble compound (either the carbinol or dilepidine derivative, depending on the conditions). When propionic anhydride (b. p. 165–168°) was used instead of acetic anhydride, a mixture of the styryl and carbinol derivatives resulted. Again, on heating equimolecular proportions of aldehyde and lepidine in the presence of hydrochloric or sulfuric acids, a mixture of the styryl and dilepidine compounds was obtained. It was difficult to separate pure *m*-nitrostyryl compound from these more insoluble derivatives, but we succeeded in isolating it by fractional recrystallization of its mixture with the dilepidine compound.

On boiling pure *p*-nitrophenyllepidylcarbinol with acetic anhydride, the product consisted essentially of the styryl derivative plus a trace of *p*-nitrobenzaldehyde, which was detected by sublimation. This scission of *p*-nitrobenzaldehyde from the nitrophenyllepidylcarbinol molecule was presumably accompanied by formation of the corresponding amount of the dilepidine derivative. When lepidine was heated with *p*-nitrobenzaldehyde in the presence of hydrochloric acid, the styryl derivative was formed together with the dilepidine compound (which could not be removed by repeated crystallization), but the pure *p*-styryl compound was separable therefrom by conversion to the hydrochloride; the hydrochloride of the dilepidine derivative is fairly soluble in boiling water, whereas that of the *p*-nitrostyryl derivative is difficultly soluble.

(6) Wartanian, *Ber.*, **23**, 3644 (1890).

Experimental

***o*- and *p*-Nitrophenyllepidylcarbinols.**—The nitrobenzaldehyde (10.6 g., completely free from acid[1]) was treated with distilled lepidine (10 g.) at 120° (temperature of reaction mixture) during eight hours, and then allowed to stand overnight at room temperature. Chloroform (50 cc.) was now added to the partly crystalline mixture, the suspension cooled in ice during several hours, and filtered. The crystals were washed with two 10-cc. portions of chloroform and dried in the vacuum desiccator over phosphorus pentoxide.

A small second crop was obtained by extracting the chloroform filtrate with three 50-cc. portions of 5 *N* hydrochloric acid. The *aqueous* layer was separated from the chloroform layer (A), made alkaline to litmus with 8 *N* sodium hydroxide solution, and the lepidine plus product extracted with chloroform. The chloroform extract was washed, dried over anhydrous sodium sulfate, and evaporated to dryness. Heptane (50 cc.) was added to the resulting dark oil, and, on scratching and chilling, a second crop of crystals appeared. (The *chloroform* layer (A) was freed from acid by shaking with dilute sodium hydroxide solution, washed, dried, filtered and evaporated to dryness, giving unchanged aldehyde which could be used directly for another preparation.)

The crude product was recrystallized from a boiling mixture of ethanol and chloroform (see Table I); the hot solution was filtered and the filtrate cooled and kept overnight in the refrigerator. The *o*- and *p*-nitrophenyllepidylcarbinols were obtained as pale yellow crystals, fairly soluble in hot methanol, ethanol, chloroform, and acetone, and sparingly soluble in ether, benzene, and heptane. They were more soluble in methanol than in any of the other solvents mentioned. The *o*-compound was slightly more soluble than the *p*- in all these solvents.

m-**Nitrophenyllepidylcarbinol.**—*m*-Nitrobenzaldehyde (10.6 g., free from acid) was heated, as in the previous section, but with *two* molar proportions of distilled lepidine (20 g.), and then kept overnight at room temperature. The resulting oil was washed into a flask with 50 cc. of chloroform and 5 *N* hydrochloric acid (50 cc.) was added, whereupon the fairly insoluble, colorless carbinol hydrochloride slowly separated out in the aqueous layer. The mixture was kept in an ice-bath for two hours, and the solid was then filtered off and washed successively with 5 *N* hydrochloric acid (25 cc.) and chloroform. The hydrochloride was now suspended in about 50 cc. of water, and 8 *N* sodium hydroxide solution was added until, after vigorous shaking, the suspension remained alkaline to litmus. The precipitated base was dissolved by extracting with chloroform, and the chloroform solution washed with water, dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The yield of crude product was 24% of the theoretical. It was recrystallized from boiling ethanol (see Table I) and was obtained as colorless crystals. It was more soluble than the corresponding *o*- or *p*-compounds in all the solvents tested.

The yield was increased to 33% of the theoretical amount by heating 2 moles of lepidine plus 1 mole of the aldehyde and 0.5 mole of anhydrous sodium carbonate, with continuous stirring, during twenty-four hours at 145°.

Nitrophenyllepidylcarbinol Monohydrochlorides.—The base (2 g.) was dissolved in the minimum volume of cold chloroform and the calculated amount of concentrated hydrochloric acid (0.25 g.), dissolved in 10 cc. of absolute ethanol, was added rapidly to the solution, with stirring. A colorless precipitate of hydrochloride appeared slowly; after keeping the mixture overnight at room temperature, this was filtered off, washed successively with 10 cc. of ethanol and 10 cc. of chloroform, and dried.

All three hydrochlorides were obtained as colorless crystals which were stable at room temperature but started to decompose at about 200°. They were slightly soluble in water and sparingly soluble in absolute ethanol, the salt of the *m*-compound being more soluble than the hydrochlorides of either the *o*- or *p*-derivatives.

Anal. Calcd. for $C_{17}H_{14}N_2O_3 \cdot HCl$: N, 8.48. Found: (*o*-), N, 8.53; (*m*), N, 8.63; (*p*-), N, 8.51.

Samples of each were stored at room temperature for five months and then reconverted to the free base; there was no change in m. p. or analysis.

Acetylation of the Nitrophenyllepidylcarbinols.—The carbinols were acetylated as previously described[1] for the acetylation of *m*-nitrophenylquinaldylcarbinol; yield, quantitative.

o-**Nitrophenyllepidylcarbinyl Acetate.**—The crude compound was recrystallized from 10 volumes of hot absolute ethanol, the resulting crystals were dissolved in 3 volumes of chloroform, hexane (10 volumes) was added to faint opalescence, and the solution kept overnight in the refrigerator; colorless crystals; m. p. 103–105°.

Anal. Calcd. for $C_{19}H_{16}N_2O_4$: C, 67.83; H, 4.8; N, 8.34. Found: C, 68.19; H, 5.0; N, 8.16.

m-**Nitrophenyllepidylcarbinyl Acetate.**—The crude compound was first recrystallized from 9 volumes of methanol by adding 6.5 volumes of water. The resulting crystals were dried, extracted with 20 volumes of cold, dry ether, and the pure, colorless, acety derivative filtered off and dried; m. p. 95–97°.

Anal. Calcd. for $C_{19}H_{1}{}_{2}O_4$: C, 67.83; H, 4.8; N, 8.34. Found: C, 67.81 H, 4.8; N, 8.40.

p-**Nitrophenyllepidylcarbinyl Acetate.**—The crude compound was recrystallized from 7 volumes of boiling absolute ethanol; pale yellow crystals, m. p. 120–121.5°.

Anal. Calcd. for $C_{19}H_{16}N_2O_4$: C, 67.83; H, 4.8; N, 8.34. Found: C, 67.87; H, 5.0; N, 8.22.

m-**Nitrobenzylidene Dilepidine.**—A mixture of lepidine (10 g.), *m*-nitrobenzaldehyde (5.3 g.) and concentrated sulfuric acid (1.4 g.) was heated for three hours at 165° (glycerol bath) in a two-necked flask (thermometer). It was then cooled to room temperature and dilute sodium hydroxide solution added to the reaction mixture. After standing overnight at room temperature, the lumps of solid were readily broken up, the solid was transferred to a large beaker with water, 8 *N* sodium hydroxide was added until the solution was alkaline to litmus, and the mixture allowed to stand for about seven hours. The solid was then filtered off, washed with water until the washings were free from sulfate (barium hydroxide test), and dried; weight (cocoa-colored solid), 14.2 g.

The crude product was treated with 10 volumes of boiling absolute ethanol during one hour, the suspension cooled in ice, and the light-brown solid filtered off and dried. The weight of crude dilepidine compound was 11.2 g. (77%); m. p., 226–232° (shrinks at 220°).

The alcoholic mother liquor was evaporated to dryness (2.9 g.) and found to consist essentially of the styryl derivative.

Recrystallization of the crude dilepidine compound from boiling chloroform and absolute ethanol was unsatisfactory. One gram of material (partially purified thus) was treated with 75 cc. of water plus 2 cc. of concentrated hydrochloric acid. A trace of undissolved solid was filtered off and 8 *N* sodium hydroxide (about 3 cc.) was added to the filtrate until the solution was alkaline to litmus. The pure, colorless dilepidine compound which separated was filtered off and dried (0.8 g.); shrinks at 220°, followed by partial melting, and melts to brown liquid at 227–232°. This melt would not resolidify on cooling to room temperature.

Anal. Calcd. for $C_{27}H_{21}N_3O_2$: C, 77.29; H, 5.1; N, 10.03. Found: C, 77.24; H, 4.7; N, 9.89.

p-**Nitrobenzylidene Dilepidine.**—The procedure for preparing the *p*-dilepidine compound was initially similar to the one used for the corresponding *m*-compound but, after filtering it from the first alkaline solution, the cocoa-colored solid was suspended in water and enough 5 *N* hydrochloric acid was added to bring the solution to *p*H 1–3. The undissolved material was filtered off, suspended in dilute sodium hydroxide solution, the orange-colored product filtered off, washed with water and dried (13.3 g.).

The crude product was treated with a boiling mixture of absolute ethanol (10 volumes) and chloroform (15 volumes) during one hour, cooled to room temperature, and the undissolved solid was filtered off and dried; 6.1 g. of pink crystals. A second crop (3.2 g.) was obtained by allowing the mother liquor of this first crop to stand in the refrigerator for several days; total yield of crude product, 63%.

The mother liquor of the second crop was evaporated to dryness (4.1 g.) and found to be mainly composed of the styryl derivative.

The crude dilepidine compound (2 g.) was treated with 150 cc. of boiling 1% hydrochloric acid, the hot suspension filtered, and dilute sodium hydroxide added to the filtrate, giving colorless, free base; shrinks at 220°, followed by partial melting, and melts to a dark brown liquid at 237–240°.

Anal. Calcd. for $C_{27}H_{21}N_3O_2$: C, 77.29; H, 5.1; N, 10.03. Found: C, 77.25; H, 5.4; N, 10.15.

4-(*o*-**Nitrostyryl**)-**quinoline.**—A solution of pure *o*-nitrophenyllepidylcarbinol (2 g.) in 8 cc. of acetic anhydride was boiled under reflux for two hours, and the solution cooled and poured into 250 cc. of ice plus water, with stirring. The product was filtered off, washed with water until the washings were neutral to litmus, and dried; yield of crude product, 80% of the theoretical (increased to quantitative yield by working up the aqueous mother liquor). It was recrystallized from 15 volumes of boiling absolute ethanol plus 5 volumes of chloroform, giving bright yellow crystals having a silvery sheen.

4-(*o*-**Nitrostyryl**)-**6-methoxyquinoline** was prepared as for the 4-styryl derivative[7]; unchanged starting materials were removed by distillation[7] at 0.05 mm. The still residue was crystallized from absolute ethanol (m. p., 122–124°) and recrystallized from pyridine (10 volumes) plus water (10 volumes), giving bright yellow crystals, m. p., 128–129°.

(7) Campbell, Tipson, *et al.*, *J. Org. Chem.*, **11**, 803 (1946).

Anal. Calcd. for $C_{18}H_{14}N_2O_3$: C, 70.56; H, 4.6; N, 9.15. Found: C, 70.48; H, 4.5; N, 9.44.

4-(*m*-Nitrostyryl)-quinoline.—After repeated recrystallization, the styryl compound was finally obtained in pure form from a mixture with the corresponding dilepidine derivative.

Lepidine (5 g.), *m*-nitrobenzaldehyde (5.3 g.), and 3 cc. of concentrated hydrochloric acid were heated in a two-necked flask at 120° (inside temperature) during three hours. After cooling to room temperature, chloroform (50 cc.) was added and the mixture kept in an ice-bath for two hours. The solid was then filtered off, washed with 50 cc. of chloroform, the yellow-brown crystals suspended in water, and made alkaline to litmus with 8 *N* sodium hydroxide solution. The yellow solid was dissolved in chloroform, the solution washed with water, dried over anhydrous sodium sulfate, filtered, and the filtrate evaporated to dryness, giving 6.2 g. of yellow solid.

The crude product was dissolved in 15 volumes of boiling absolute ethanol plus 8 volumes of chloroform, filtered, and the filtrate kept in the refrigerator overnight. A small crop of cream-colored crystals which separated was filtered off and dried (0.7 g.); m. p. 220–230°. Microchemical analysis indicated that it was slightly impure dilepidine derivative. The mother liquor was kept in the refrigerator for a week, giving a second crop of cream-colored solid (0.5 g.); m. p. 217–231°.

The mother liquor of the second crop was evaporated to dryness (4.9 g.); m. p. 130–134°. It was recrystallized from 8 volumes of boiling absolute ethanol. The pure *m*-styryl compound separated on cooling, and was filtered off and dried (3.7 g.).

4-(*p*-Nitrostyryl)-quinoline.—When prepared as described for the *m*-styryl compound, in the presence of hydrochloric acid, the *p*-styryl derivative could not be separated from its impurity (probably the dilepidine compound) by repeated recrystallization. The most satisfactory method for obtaining the pure *p*-styryl compound when the impurity was the dilepidine derivative (*not* the carbinol compound) was by treatment with hydrochloric acid, as follows:

Impure *p*-styryl derivative (4 g.) was treated with 240 cc. of chloroform and a trace (0.1 g.) of insoluble material (which seemed to consist mainly of the more insoluble dilepidine derivative) filtered off. To the filtrate was added 100 cc. of 5% hydrochloric acid and the mixture swirled. The hydrochlorides which separated were filtered off, suspended in 150 cc. of 1% hydrochloric acid, the suspension boiled for a few minutes, filtered while hot, and the yellow solid washed with about 50 cc. of hot 1% hydrochloric acid. The solid hydrochloride was then suspended in dilute sodium hydroxide solution, the base extracted with chloroform, the chloroform solution washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness (2.5 g.). This material was now recrystallized by dissolving in 15 volumes of boiling absolute ethanol plus 25 volumes of chloroform. The solution was kept in the refrigerator overnight, and the crystals filtered off and dried (2.2 g.).

Summary

The three mononitrophenyllepidylcarbinols and their acetates and monohydrochlorides have been prepared and some of their properties are described. The corresponding styryl derivatives were isolated in pure form.

A method has been developed for the preparation of the *m*- and *p*-nitrobenzylidene dilepidines in good yield, and some of their properties are recorded.

PITTSBURGH 13, PA. RECEIVED OCTOBER 3, 1947

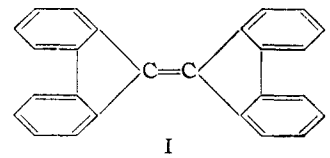
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Addition of Grignard Reagents to the Olefin, Bidiphenyleneethylene

BY REYNOLD C. FUSON AND HERSCHEL D. PORTER[1]

Attempts to add Grignard reagents to olefins, involving a large number of hydrocarbons and a wide range of experimental conditions, have yielded only negative results.[2,3,4] Apparently successful attempts reported in some instances,[5,6] were subsequently found to have been misleading.[7]

The demonstration by Pinck and Hilbert[8] that bidiphenylethylene (I) as well as its tetrabromo derivative was capable of reacting additively with various carbonyl reagents suggested that this highly conjugated olefin might also combine with Grignard reagents. This idea was favored by the discovery of Ziegler and Schäfer[9] that phenyllithium condensed with bidiphenyleneethylene to give 1-phenyl-1,2-bidiphenyleneethane (II, R = C_6H_5).



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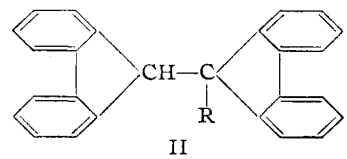

II

In the present work it has been found that certain Grignard reagents will react with bidiphenyleneethylene to produce the corresponding substituted ethanes (II). It appeared that the best chance of success was to employ *t*-butyl or benzyl Grignard reagents, shown by Kharasch and Weinhouse[10] to be the most reactive.

When *t*-butylmagnesium chloride was allowed to react with bidiphenyleneethylene, 1-*t*-butylbidiphenyleneethane (II, R = C_4H_9) was produced in good yield. Similarly, benzylmagnesium chlo-

(1) Rohm and Hass Research Assistant, 1946–1947.
(2) Gilman and Crawford, THIS JOURNAL, **45**, 554 (1923).
(3) Kinney and Larsen, *ibid.*, **57**, 1054 (1935).
(4) Gilman and Peterson, *ibid.*, **48**, 423 (1926).
(5) Rupe and Bürgin, *Ber.*, **43**, 172 (1910).
(6) Rupe, *Ann.*, **402**, 149 (1913).
(7) Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928).
(8) Pinck and Hilbert, THIS JOURNAL, **57**, 2398 (1935); **68**, 2014 (1946).
(9) Ziegler and Schäfer, *Ann.*, **511**, 101 (1934).
(10) Kharasch and Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).