Isolation of Glyoxal Bis-(2,4-dinitrophenylhydrazone).—The method of Grangaard, Gladding and Purves[24] was utilized on product II (200 mg.). This involves the formation of the bis-(dimethyl acetal) of glyoxal in methanol containing hydrogen chloride, steam distillation from a basic aqueous solution, hydrolysis with acid and precipitation as glyoxal bis-(2,4-dinitrophenylhydrazone); yield 7 mg., m.p. 315–320° dec. Product III (180 mg.) afforded 60 mg. of the derivative, m.p. 317–322° dec. Both samples had m.p. 318–325° dec. on admixture with authentic glyoxal bis-(2,4-dinitrophenylhydrazone) of m.p. 325–327° dec.[69]

Isolation of D-Glucitol Hexaacetate.—Product III (7.0 g.) was reduced with Raney nickel and hydrogen (2000 p.s.i.) in aqueous solution at 100° for 12 hr. After removal of the catalyst by filtration, the solution was made 0.6 *N* in sulfuric acid and heated at 100° for 24 hr. The acid was neutralized with barium hydroxide and the solution filtered. The residue obtained on evaporation of the filtrate was acetylated with acetic anhydride and fused zinc chloride at 50°. The reaction mixture was added to an ice and water mixture and the acid was neutralized with sodium bicarbonate. The aqueous solution was extracted with chloroform and the extracts were evaporated to a sirup; yield 5.8 g.

Chromatography of this sirup (1.9 g.) on Magnesol–Celite (column, 75 × 250 mm.) using 900 ml. of benzene/*t*-butyl alcohol 400/1 as the developer, afforded 0.2 g. of crystalline material (from the third zone from the top) after recrystallization from 75% ethanol, m.p. 98–99°, $[\alpha]^{21}D$ +10.7° (*c* 4, chloroform). The melting point was unchanged on admixture with authentic D-glucitol hexaacetate of m.p. 98.5–99.0° and $[\alpha]^{25}D$ +10° (*c* 4.6, chloroform).

ABERDEEN PROVING GROUND, MD.
COLUMBUS 10, OHIO

(69) H. H. Strain, THIS JOURNAL, **57**, 758 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING, KYÔTO UNIVERSITY]

Preparations of the Synthetic Estrogens. VII.[1] New Syntheses of 1,1,2-Tri-*p*-anisyl-2-chloroethylene

BY KEIITI SISIDO,[2] KÔITI OKANO, TAIITI ISIDA AND HITOSI NOZAKI

RECEIVED JULY 5, 1955

Treatment of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) with phosphorus pentachloride effected simultaneous chlorination and dehydrochlorination giving 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV). The required *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) was obtained by the condensation of *p*-anisylglyoxal or N,N-dimethylaminophenyl-α-*p*-anisoylnitrone (III) with anisole in the presence of concentrated sulfuric acid as a catalyst. *p*-Methoxy-α,α-di-*p*-anisylacetophenone (I) was reduced to corresponding carbinol V which was dehydrated to 1,1,2-tri-*p*-anisylethylene (VI). The tri-*p*-anisylethylene (VI) was also prepared by dehydration of 1,1,2-tri-*p*-anisylethanol (VII) which was obtained in good yield by means of a Grignard reaction between α-chloro-*p*-methoxyacetophenone and *p*-anisylmagnesium bromide.

In the previous paper[1] a new preparation of triarylbromoethylenes was described, in which the use of the Grignard reaction was avoided throughout the synthesis. An attempted adaptation of the method to the synthesis of triarylchloroethylenes resulted, however, in failure. Since some of such chloro derivatives are known to be not only active as estrogens but also effective in the treatment of prostatic cancer, investigation of new methods suitable for a large scale preparation has now been extended to these compounds. It was discovered that the treatment of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) with phosphorus pentachloride gave 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV) in a 43% yield.

The required intermediate, *p*-methoxy-α,α,-di-*p*-anisylacetophenone (I), was prepared by the condensation of *p*-anisylglyoxal with anisole in the presence of sulfuric acid. *p*-Anisylglyoxal[3] was obtained by the oxidation of *p*-methoxyacetophenone with selenium dioxide. The condensation product I, however, formed a yellow viscous oil, which could not be crystallized,[4] and gave very poor yields of 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV) upon treatment with phosphorus pentachloride. In an attempt to improve the yield, it was found that the condensed acetophenone derivative I could be obtained in a pure, crystalline form, when anisole reacted with *p*-anisylglyoxal prepared from N,N-dimethylaminophenyl-α-*p*-anisoylnitrone (III). The nitrone was obtained by the condensation of *p*-methoxyphenacylpyridinium bromide (II)[5] with *p*-nitrosodimethylaniline in the presence of 1 *N* sodium hydroxide solution according to the method of Kröhnke.[6] When this nitrone III was dissolved in an excess of anisole, hydrolyzed with 65% sulfuric acid to *p*-anisylglyoxal and treated with 98% sulfuric acid, *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) separated as crystals, m.p. 82–83°, in a 89% yield based on the nitrone III.[7]

$$p\text{-}CH_3O\text{—}C_6H_4COCHO + 2C_6H_5OCH_3 \xrightarrow{\text{concd. } H_2SO_4} p\text{-}CH_3O\text{—}C_6H_4COCH(C_6H_4\text{—}OCH_3\text{-}p)_2$$

I

(1) Previous paper: K. Sisido, K. Okano and H. Nozaki, THIS JOURNAL, **77**, 4604 (1955).

(2) Ben May Laboratory for Cancer Research, University of Chicago, until January, 1956.

(3) K. Sisido and H. Nozaki, THIS JOURNAL, **70**, 3326 (1948).

(4) E. C. Dodds, L. Goldberg, E. I. Grünfeld, W. Lawson, C. M. Saffer, Jr., and R. Robinson, *Proc. Roy. Soc. (London)*, **132B**, 83 (1944); *C. A.*, **38**, 3637[6] (1944), reported this compound as difficult to purify, b.p. 240° (0.1 mm.).

(5) E. Bamberger, *Ber.*, **20**, 3338 (1887).

(6) F. Kröhnke, *Angew. Chem.*, **65**, 605 (1953).

(7) For the condensation between phenylglyoxal and anisole see an abstract of a paper read before a meeting: K. Sisido and H. Nozaki, *Repts. Inst. Chem. Research, Kyôto Univ.*, **17**, 136 (1949); *C. A.*, **46**, 3032b (1952). α,α-Di-*p*-anisylacetophenone was reported in this abstract to form a yellow viscous oil, b.p. 267–273° (6 mm.), which could not be crystallized. Phenylglyoxal used was prepared by the oxidation of acetophenone with selenium dioxide according to the method of H. A. Riley and A. R. Gray ("Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509). In view of the experiences in the present synthesis of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) the condensation reaction was re-examined using phenylglyoxal hydrate prepared from N,N-dimethylaminophenyl-α-benzoylnitrone. The α,α-di-*p*-anisylacetophenone thus obtained formed colorless crystals, m.p. 91–92°, the details being described in the Experimental part. An attempted condensation of N,N-dimethylaminophenyl-α-benzoylnitrone with anisole in the same way as the *p*-anisoylnitrone (III) failed to afford the desired α,α-di-*p*-anisylacetophenone, giving a resinous product.

$$p\text{-}CH_3O\text{—}C_6H_4COCH_2Br + C_5H_5N \longrightarrow [p\text{-}CH_3O\text{—}C_6H_4COCH_2NC_5H_5]^+Br^-$$
II

$$II + ONC_6H_4\text{—}N(CH_3)_2\text{-}p \xrightarrow{NaOH} p\text{-}CH_3O\text{—}C_6H_4COCH{=}N(O)\text{—}C_6H_4\text{—}N(CH_3)_2\text{-}p$$
III

$$III + 2C_6H_5OCH_3 \xrightarrow[2,\ 98\%\ H_2SO_4]{1,\ 65\%\ H_2SO_4} I$$

$$I + PCl_5 \longrightarrow p\text{-}CH_3O\text{—}C_6H_4CCl{=}C(C_6H_4\text{—}OCH_3\text{-}p)_2$$
IV

When the crystalline *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) was treated with phosphorus pentachloride in toluene solution, simultaneous chlorination and dehydrochlorination of the acetophenone derivative occurred and 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV) was obtained in a yield mentioned above. Analogous chlorination and dehydrochlorination of benzyl methyl ketone to 1-chloro-1-benzylethylene and 2-chloro-1-phenyl-1-propylene have been reported by Zaki and Iskander.[8] More recently the reaction between *p*-methoxy-α,α-diphenylacetophenone and phosphorus pentachloride to afford 1,1-diphenyl-2-*p*-anisyl-2-chloroethylene was reported.[9] An attempted reaction of α,α-diphenylacetophenone with phosphorus pentachloride in toluene under the same conditions as the trimethoxy derivative, however, failed to afford the desired triphenylchloroethylene which was reported by Gardeur.[10] There was recovered a considerable quantity of starting material besides a small amount of tar. α,α-Di-*p*-anisylacetophenone[7] also did not react with phosphorus pentachloride under the same conditions.

On the other hand, tri-*p*-anisylethylene (VI) was prepared by dehydration of 1,2,2-tri-*p*-anisylethanol (V) which was obtained in 45% yield from the previously mentioned crystalline *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) by the reduction with sodium and ethyl alcohol.[11] The dehydration proceeded upon refluxing with *p*-toluenesulfonic acid in toluene, and the yield of tri-*p*-anisylethylene (VI) was 81%.

$$I \xrightarrow{Na + C_2H_5OH} p\text{-}CH_3O\text{—}C_6H_4CH(OH)CH(C_6H_4\text{—}OCH_3\text{-}p)_2$$
V

$$\xrightarrow{p\text{-}CH_3\text{—}C_6H_4SO_3H} p\text{-}CH_3O\text{—}C_6H_4CH{=}C(C_6H_4\text{—}OCH_3\text{-}p)_2$$
VI

In addition to these methods, tri-*p*-anisylethylene (VI) could be prepared by means of a new method utilizing the Grignard reaction of α-haloketone.[12] The Grignard reaction between α-chloro-*p*-methoxyacetophenone and *p*-anisylmagnesium bromide gave 1,1,2-tri-*p*-anisylethanol (VII) which was dehydrated with *p*-toluenesulfonic acid giving tri-*p*-anisylethylene (VI) in a 90% yield based on the starting chloroacetophenone derivative.

$$p\text{-}ClCH_2CO\text{—}C_6H_4OCH_3 + 2p\text{-}CH_3O\text{—}C_6H_4MgBr \longrightarrow p\text{-}CH_3O\text{—}C_6H_4CH_2C(OH)(C_6H_4\text{—}OCH_3\text{-}p)_2$$
VII

$$\xrightarrow{p\text{-}CH_3\text{—}C_6H_4SO_3H} VI$$

The chlorination of tri-*p*-anisylethylene (VI), thus obtained, with chlorine in carbon tetrachloride according to the method of Shelton, *et al.*,[13] gave 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV), which showed no depression when admixed with the product prepared by the reaction with phosphorus pentachloride.

Experimental[14]

p-Methoxy-α,α-di-*p*-anisylacetophenone (I).—(a) To a mixture of 42 g. (0.39 mole) of anisole, 90 ml. of glacial acetic acid and 78 g. (43 ml.) of concentrated sulfuric acid, a solution of 25.5 g. (0.15 mole) of *p*-anisylglyoxal prepared through oxidation of *p*-methoxyacetophenone with selenium dioxide[3] in 50 ml. of glacial acetic acid was added dropwise with stirring. The addition required about one hour, during which time the temperature of the mixture was maintained below 20°. The stirring was continued for an additional five hours at the same temperature, and the mixture was allowed to stand overnight. The product was poured into crushed ice, and the precipitated oil was extracted with benzene. The benzene solution was washed with water, dilute sodium hydroxide solution and water. After distilling off the solvent the residue was subjected to steam distillation in order to remove an excess of anisole. The residue was taken up in benzene and dried over anhydrous sodium sulfate. Distillation gave 47 g. (84%) of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) boiling at 299–301° (11 mm.)[4] which formed a yellow viscous oil and could not be crystallized.

(b) A solution of 8.5 g. (0.028 mole) of *p*-methoxyphenacylpyridinium bromide (II) in 14 ml. of water and a solution of 4.6 g. (0.031 mole) of *p*-nitrosodimethylaniline in 140 ml. of ethanol were mixed and cooled to −4°. To the mixture 28 ml. of 1 *N* sodium hydroxide solution was added rapidly with stirring and the color of the solution turned red. Red crystals, some of which separated after a while, were carefully precipitated by addition of water, then filtered and washed with water. A single recrystallization from benzene gave 6.1 g. (74%) of N,N-dimethylaminophenyl-α-*p*-anisoylnitrone (III) melting at 108–109°.

Anal. Calcd. for $C_{17}H_{18}O_3N_2$: N, 9.39. Found: N, 9.28.

To a mixture of 6.1 g. (0.020 mole) of N,N-dimethylaminophenyl-α-*p*-anisoylnitrone (III) and 21 g. (0.19 mole) of anisole, 32 ml. of 65% sulfuric acid was added dropwise under stirring and cooling with ice. After the addition was complete the stirring was continued for 0.5 hr. at room temperature, and 15 g. (8.2 ml.) of 98% sulfuric acid was added dropwise to this mixture. The reaction was continued for four hours, during which time white crystals separated. The solids were filtered with suction, thoroughly washed with water and dried. A single recrystallization from ligroin gave 6.6 g. (89%) of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) melting at 82–83°.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.49; H, 6.39.

1,1,2-Tri-*p*-anisyl-2-chloroethylene (IV).—To a solution of 4.0 g. (0.011 mole) of crystalline *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) prepared by method b in 50 ml. of dry toluene, 2.5 g. (0.012 mole) of phosphorus pentachloride[15] was added, and the mixture was refluxed on an oil-bath for

(8) A. Zaki and Y. Iskander, *J. Chem. Soc.*, 68 (1943).

(9) T. Nagano, THIS JOURNAL, **77**, 1691 (1955).

(10) A. Gardeur, *Bull. acad. roy. belg.*, [3] **34**, No. 7, 67 (1896); *Chem. Zentr.*, **68**, II, 660 (1897).

(11) For the reduction of α,α-di-*p*-anisylacetophenone with sodium and ethyl alcohol see ref. 7.

(12) For example see: R. L. Huang, *J. Org. Chem.*, **19**, 1363 (1954); *J. Chem. Soc.*, 2539 (1954).

(13) R. S. Shelton, M. G. Van Campen, Jr., D. F. Meisner, S. M. Parmerter, E. R. Andrews, R. E. Allen and K. K. Wyckoff, THIS JOURNAL, **75**, 5491 (1953).

(14) All temperatures are uncorrected.

(15) The compound freshly prepared by the method of "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 394, was used.

five hours. A vigorous evolution of hydrogen chloride took place in the initial stage of the reaction. The reaction mixture was cooled, the toluene and phosphorus oxychloride were removed under reduced pressure, ice was added, and the mixture was left overnight in an ice-chest. The semi-solid product was dissolved in benzene, and the benzene solution was washed with dilute sodium hydroxide solution and water. After drying over anhydrous sodium sulfate the solvent was removed. The residue (3.4 g.) crystallized when dissolved in a small amount of glacial acetic acid and was allowed to stand. Several recrystallizations from ligroin gave 1.8 g. (43%) of 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV), m.p. 113–114°, reported[13] m.p. 113–114°.

α,α-Di-*p*-anisylacetophenone.[7]—A mixture of 4.0 g. (0.037 mole) of anisole, 15 ml. of glacial acetic acid and 8 g. (4.4 ml.) of concentrated sulfuric acid was treated with a solution of 2.1 g. (0.014 mole) of phenylglyoxal monohydrate[16] in 20 ml. of glacial acetic acid under the same conditions as above and the product was worked up as usual. The residual semi-solid material was crystallized from glacial acetic acid, and 3.4 g. (74%) of α,α-di-*p*-anisylacetophenone, m.p. 91–92°, was obtained.

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.79; H, 6.29.

1,2,2-Tri-*p*-anisylethanol (V).—A solution of 5.3 g. (0.015 mole) of crystalline *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) in 80 ml. of absolute ethyl alcohol was heated to the reflux point, when 7 g. (0.30 mole) of sodium, cut in small pieces, was added, all at once, through the top of the condenser[17] (80 cm. long, internal diameter 2.8 cm.). A vigorous reaction occurred, but it subsided rapidly and the heating was continued to reflux until the pieces of sodium disappeared. The hot reaction mixture was poured into crushed ice and the precipitated solid was extracted with benzene. The extract was washed with water until neutral, dried with anhydrous sodium sulfate and evaporated. The residue crystallized on standing overnight and a single recrystallization from ethanol gave 2.4 g. (45%) of 1,2,2-tri-*p*-anisylethanol (V), m.p. 107–108°.

Anal. Calcd. for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.63; H, 6.57.

(16) This compound was prepared by hydrolysis of N,N-dimethylaminophenyl-α-benzoylnitrone which was prepared from phenacylpyridinium bromide, with 5 *N* sulfuric acid (*cf.* ref. 6).

(17) S. Bernstein and E. S. Wallis, THIS JOURNAL, **62**, 2871 (1940).

1,1,2-Tri-*p*-anisylethylene (VI).—A mixture of 1.7 g. (0.0047 mole) of 1,2,2-tri-*p*-anisylethanol (V) and 2 g. of *p*-toluenesulfonic acid in 80 ml. of dry toluene was heated to reflux for two hours. The reaction mixture was washed with water, dilute sodium hydroxide solution and water, and dried over anhydrous sodium sulfate. Removal of the solvent, followed by standing with ethanol, gave 1.3 g. (81%) of tri-*p*-anisylethylene (VI) which, after several recrystallizations from glacial acetic acid, melted at 97–98°. The recorded[13] m.p. is 100–101°.

1,1,2-Tri-*p*-anisylethylene (VI) by Grignard Reaction.—To a Grignard reagent, prepared from 37 g. (0.20 mole) of *p*-bromoanisole and 4.8 g. (0.20 mole) of magnesium in 85 ml. of dry ether, a solution of 9.5 g. (0.051 mole) of α-chloro-*p*-methoxyacetophenone in 100 ml. of benzene was added dropwise with ice-cooling and stirring. After boiling under reflux for two hours, a solution of 50 g. of ammonium chloride in 150 ml. of water was added and the precipitates were filtered off. The organic layer was separated and the aqueous layer and the precipitates were extracted with ether. The ether and benzene solutions were combined, washed with water and dried over anhydrous calcium chloride. After removing the solvent, the residue was treated with 2 g. of *p*-toluenesulfonic acid in 100 ml. of dry toluene and heated to reflux for two hours under exactly the same conditions as above. The residue was subjected to steam distillation in order to remove excess anisole. Two recrystallizations from glacial acetic acid gave 16 g. (90%) *p*-anisylethylene (VI), m.p. 97–98.5°,[13] which showed no depression when admixed with the product prepared from 1,2,2-tri-*p*-anisylethanol (V).

1,1,2-Tri-*p*-anisylethanol (VII) could be isolated, although with some difficulties, from the product of the above-mentioned Grignard reaction. The carbinol formed colorless prisms melting at 129° after several recrystallizations from ethyl alcohol. The recorded m.p.[13] is 130–131°.

NOTE ADDED IN PROOF.—Sumrell and Goheen[18] have reported that they could not obtain *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) in crystalline form and were unable to prepare 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV) or 1,1,2-tri-*p*-anisylethanol (V), from I with phosphorus pentachloride or sodium-ethanol, respectively. As yet the reason for this discrepancy has not been determined.

(18) G. Sumrell and G. E. Goheen, *ibid.*, **77**, 3805 (1955).

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE PHARMACEUTICAL INSTITUTE, MEDICAL FACULTY, UNIVERSITY OF KYUSHU]

Cholesterol and Related Compounds. IV. Synthesis of 11-Ketocholestan-3β-ol

BY KYOSUKE TSUDA AND RYOICHI HAYATSU[1]

RECEIVED MARCH 8, 1955

Chromic acid oxidation of 7-keto-$\Delta^{5,8(9)}$-cholestadien-3β-ol benzoate (III) yielded 7,11-diketo-$\Delta^{5,8(9)}$-cholestadien-3β-ol benzoate (IV) which, on reduction with acetic acid and zinc, formed 7,11-diketocholesteryl benzoate (VII). Catalytic reduction of VII yielded 7,11-diketocholestan-3β-ol benzoate (VIII) which was converted to 11-ketocholestanol (IX) by the Wolff–Kishner reaction.

Considerable research has been done on the introduction of a keto group into the 11-position of steroids with an unsubstituted C ring.[2–11] Our

(1) Takamine Research Laboratory, Sankyo Co., Ltd., Tokyo, Japan.

(2) L. F. Fieser, J. E. Herz and W.-Y. Huang, THIS JOURNAL, **73**, 2397 (1951); L. F. Fieser, J. C. Babcock, J. E. Herz, W.-Y. Huang and W. P. Schneider, *ibid.*, **73**, 4053 (1951).

(3) E. M. Chamberlin, W. V. Erickson, J. M. Chemerda, L. M. Aliminosa, R. L. Erickson, G. E. Sita and M. Tishler, *ibid.*, **73**, 2396 (1951).

(4) G. Stork, J. Romo, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 3546 (1951); C. Djerassi, O. Mancera, G. Stork and G. Rosenkranz, *ibid.*, **73**, 4496 (1951).

(5) R. C. Anderson, R. Budziarek, G. T. Newbold, R. Stevenson and F. S. Spring, *Chemistry & Industry*, 1035 (1951).

(6) H. Heusser, K. Eichenberger, P. Kurath, H. R. Dallenbach and O. Jeger, *Helv. Chim. Acta*, **34**, 2106 (1951); H. Heusser, K. Heusler, K. Eichenberger, C. G. Honegger and O. Jeger, *ibid.*, **35**, 295 (1952); H. Heusser, R. Anliker, K. Eichenberger and O. Jeger, *ibid.*, **35**, 936 (1952).

(7) (a) L. F. Fieser, W.-Y. Huang and J. C. Babcock, THIS JOURNAL, **75**, 116 (1953); (b) L. F. Fieser and J. E. Herz, *ibid.*, **75**, 121 (1953); (c) L. F. Fieser, W. P. Schneider and W.-Y. Huang, *ibid.*, **75**, 124 (1953).

(8) G. Rosenkranz, M. Velasco, C. Djerassi and F. Sondheimer, *ibid.*, **75**, 4430 (1953).

(9) G. D. Laubach, E. C. Schreiber, E. J. Angenello, E. N. Lightfoot and K. J. Brunings, *ibid.*, **75**, 1514 (1953).

(10) P. Bladon, H. B. Henbest, E. R. H. Jones, G. W. Wood, D. C. Eaton and A. A. Wagland, *J. Chem. Soc.*, 2916 (1953); P. Bladon, H. B. Henbest, E. R. H. Jones, B. J. Lovell, G. W. Wood, G. F. Wood, J. Elks, R. M. Evans, D. E. Hathway, J. F. Oughton and G. H. Thomas, *ibid.*, 2921 (1953); J. Elks, R. M. Evans, C. H. Robinson, G. H. Thomas and L. J. Wyman, *ibid.*, 2933 (1953); D. C. Burk, J. H. Turnbull and W. Wildon, *ibid.*, 3237 (1953); (a) J. Ekls, R. M. Evans, A. G. Long and G. H. Thomas, *ibid.*, 451 (1954); (b) J. Elks, R. M. Evans, J. F. Oughton and G. H. Thomas, *ibid.*, 463 (1954).

(11) J. Lemin and C. Djerassi, THIS JOURNAL, **76**, 5672 (1954).