[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ROCHESTER]

4-Carboxytropolone and Related Compounds

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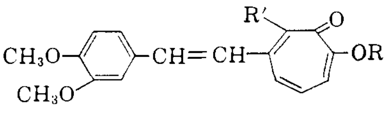
4-Carboxytropolone and several other 4-substituted tropolones and 4-substituted 2-aminotropones have been prepared from purpurogallin through the 4-styryltropolones. The key step is represented by the oxidation of 4-styryltropolone to 4-formyltropolone by the osmium tetroxide-catalyzed periodate procedure. A stable acid chloride has been prepared from 2-acetamino-4-carboxytropone. 4-Formyltropolone has been condensed with malonic acid to yield 4-(β-carboxyvinyl)-tropolone.

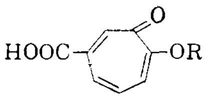
In connection with some projected syntheses in the tropolone field, it was necessary to obtain 4-carboxytropolone (IV) and some of its derivatives by practical procedures. The preparation of this compound has been reported by several procedures,[1-4] but all are long and the yields are unsatisfactory. Our re-examinations of some of them failed to give a feasible method of preparation, and we have therefore developed a new synthesis of 4-carboxytropolone and various related compounds by the oxidation of 4-styryltropolone.

Initial attempts to oxidize 4-styryl-3-carboxytropolone[2,5] and the 4-styryltropolone[6] were unpromising, and attention was directed toward the corresponding 3,4-dimethoxy series, I. Oxidation of the methyl ether methyl ester Ia by permanganate in aqueous suspension at room temperature in the presence of magnesium sulfate gave about 25% yield (after sublimation) of the anhydride III,[2] which was decarboxylated to the acid IV by heating in aqueous solution in a bomb.[2] The acid was converted into the new crystalline benzoate IVa by benzoyl chloride and pyridine. This sequence of reactions was not satisfactory because of the number of stages and the low yields in some of them.

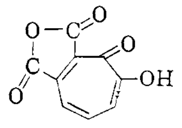
Because in all of the oxidations tried, including the neutral permanganate method described above, the tropolone ring appeared to be oxidized more readily than the styryl double bond, we investigated more specific oxidation procedures for carbon–carbon double bonds. Ozonization[7] of 4-styryltropolone was unsuccessful, and the permanganate–periodate procedure[8] was also. However, the osmium tetroxide-catalyzed periodate procedure[9] gave an 84% yield of purified 4-formyltropolone when applied to 4-styryltropolone (V). The 4-formyltropolone (VIII) was oxidized to the 4-carboxytropolone (IV) with fresh silver oxide[1,10] in basic solution in 53% yield. The attempted preparation of the acid chloride of IV with thionyl chloride failed, as expected, as tropolones are known to react with this reagent to form 2-chlorotropones[11] and also with acid chlorides to give esters. The benzoate IVa suffered decomposition when treated with oxalyl chloride.[12] As O-acyltropolones are vinylogs of acid anhydrides, it is not surprising that they are unstable.



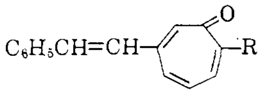
I, $R = H$, $R' = COOH$
Ia, $R = CH_3$, $R' = COOCH_3$
Ib, $R = H$, $R' = COOCH_3$
II, $R = R' = H$
IIa, $R = COC_6H_5$, $R' = H$



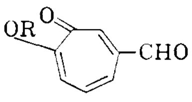
IV, $R = H$
IVa, $R = COC_6H_5$



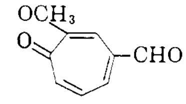
III



V, $R = OH$
Va, $R = OCH_3$
Vb, $R = OCOCH_3$
Vc, $R = OCOC_6H_5$
VI, $R = NH_2$
VIa, $R = NHCOH_3$
VII, $R = NHNH_2$



VIII, $R = H$
VIIIa, $R = CH_3$



IX

In order to circumvent this instability of the acylating agents derived from 4-carboxytropolone, various methods of protecting or altering the tropolone hydroxyl group were investigated. Methylation of 4-styryltropolone with diazomethane yielded the known[1] ether Va, m.p. 142°; the noncrystalline residue evidently contained the isomeric ether X, because oxidation of these residues by the osmium tetroxide–periodate procedure yielded 2-methoxy-4-formyltropone IX which has been de-

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[1] R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, 561 (1951).

[2] W. D. Crow, R. D. Haworth and P. R. Jefferies, *ibid.*, 3705 (1952).

[3] J. R. Bartels-Keith and A. W. Johnson, *Chemistry & Industry*, 677 (1950); J. R. Bartels-Keith, A. W. Johnson and W. I. Taylor, *J. Chem. Soc.*, 2352 (1951).

[4] Y. Kitahara, *Sci. Repts. Tohoku Univ.*, **40**, 74 (1956).

[5] (a) T. Nozoe, Y. Kitahara, K. Doi and M. Endo, *Proc. Japan Acad.*, **28**, 32 (1952); (b) D. S. Tarbell, R. F. Smith and V. Boekelheide, THIS JOURNAL, **76**, 2470 (1954).

[6] T. Nozoe, Y. Kitahara, K. Doi and S. Masamune, *Proc. Japan Acad.*, **28**, 291 (1952).

[7] *Cf.* C. E. Kaslow and R. D. Stayner, THIS JOURNAL, **67**, 1716 (1945), for the ozonization of styryl heterocycles to the corresponding carboxylic acids.

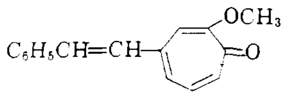
[8] E. von Rudloff, *Can. J. Chem.*, **33**, 1714 (1955).

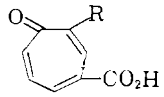
[9] R. Pappo, D. S. Allen, Jr., R. U. Lemieux and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

[10] I. A. Pearl, THIS JOURNAL, **68**, 429 (1946).

[11] W. von E. Doering and L. H. Knox, *ibid.*, **74**, 5683 (1952).

[12] Roger Adams and L. H. Ulich, *ibid.*, **42**, 599 (1920).


X

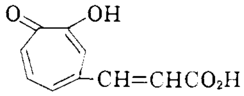

XI, R = OCH_3
XII, R = NH_2
XIII, R = $NHCOCH_3$

scribed and oriented by Haworth.[1,13] Similar oxidation of the crystalline methyl ether X yielded 2-methoxy-6-formyltropone (VIIIa), the orientation of which was based on exclusion. By relation to VIIIa the orientation of the crystalline styryl methyl ether Va is known as are the orientations of its derivatives VI, VIa and VII (see Experimental). The orientations of the tropolone esters are not known.

Treatment of the isomeric aldehydes VIIIa and IX with fresh silver oxide in cold basic solution resulted in the hydrolysis of the former to 4-formyltropolone and oxidation of the latter to 2-methoxy-4-carboxytropone(XI). As this compound yielded an unstable acid chloride when treated, as the potassium salt, with oxalyl chloride, further alteration of the tropolone hydroxyl function of 4-carboxytropolone was necessitated.

Treatment of 2-methoxy-4-carboxytropone (XI) with liquid ammonia in a sealed tube at room temperature gave the crystalline 2-amino-4-carboxytropone (XII) which was converted to the acetamino compound XIII. This was in turn changed to its relatively stable acid chloride, with oxalyl chloride, and characterized by its *p*-bromoanilide.

4-Formyltropolone reacts, in the normal manner of aromatic aldehydes, with malonic acid and piperidine catalyst in pyridine solution to give 4-(β-carboxyvinyl)-tropolone (XIV).


XIV

Experimental[14]

3-Carboxy-4-carboxymethyltropolone was prepared by oxidation of purpurogallin[15] following Haworth's procedure,[1] with some modifications.[16] The use of purpurogallin which had been purified by crystallization from anisole gave yields of 52–57%; crude purpurogallin gave much lower yields, in the 20–30% range, and the results were frequently erratic.

3-Carboxy-4-(3,4-dimethoxystyryl)-tropolone (I).—A mixture of 9 g. of 3-carboxy-4-carboxymethyltropolone, 80 ml. of acetic acid and 6 ml. of acetic anhydride was stirred at 70° for 1.5 hr., and then cooled to 40°. The dark red solution was treated with 3 ml. of pyridine and 6.6 g. of veratraldehyde, and stirring was continued for 3 hr. at 40–50°. The mixture was heated briefly to 70°, then it was allowed to cool slowly to about 20°. The orange solid that separated was filtered and washed with ethanol to yield 7.4 g. (56%) of product, melting with decomposition at 195–197°. It gave an immediate red color with ferric chloride in ethanol. In other experiments the product was obtained melting with decomposition at 208–210°. The lower melting sample was not converted into the higher melting one by warming with four portions of ethanol. Both samples gave the same infrared spectrum and yielded the same methyl ether methyl ester Ia.

Anal. (210° sample). Calcd. for $C_{19}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.67; H, 4.95.

Methyl Ether Methyl Ester[17] Ia of I.—A mixture of 6.56 g. of 3-carboxy-4-(3,4-dimethoxystyryl)-tropolone, 8 g. of dimethyl sulfate, 8.8 g. of powdered anhydrous potassium carbonate and 250 ml. of dry acetone were refluxed with stirring for 23 hr. The mixture was cooled, filtered and the filtrate was freed of acetone. The residue was rubbed with 25 ml. of dilute ammonium hydroxide to decompose the excess dimethyl sulfate. The resulting yellow solid was collected, dissolved in 60 ml. of methanol, the methanol solution was diluted with 400 ml. of water, and the resulting solid was collected, redissolved in methanol and reprecipitated with water. The yield was 6.6 g. (93%) of material melting at 75–79°. When this solid was heated at 108° for 30 min. or was recrystallized from methanol, the m.p. was raised to 137–138°. Both products gave a negative ferric chloride test and were insoluble in cold saturated bicarbonate solution.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found (m.p. 75–79°): C, 67.14; H, 5.58. Found (m.p. 137–138°): C, 67.38; H, 5.75.

The infrared spectra of these two samples indicate that the higher-melting sample has a *cis*-disubstituted double bond (sharp bands at 947, 792 and 785 cm.$^{-1}$); the lower-melting compound is probably a mixture of *cis* and *trans* forms (weak, broad band at 944–962 cm.$^{-1}$, no absorption at 780–795 cm.$^{-1}$). The starting acid I has a sharp band at 965 cm.$^{-1}$, indicating that it, like its analogs,[5b] has a *trans* double bond.

Treatment of I in dioxane with ethereal diazomethane yielded a small amount of the above dimethyl compound, m.p. 75–79°, which was characterized by mixed m.p. and its infrared spectrum. The use of ether instead of dioxane in this reaction yielded a yellow solid, m.p. 171–173°, which gave a positive ferric chloride test and hence was the *methyl ester Ib*; this was supported by the analysis.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.67; H, 5.30. Found: C, 67.01; H, 5.41.

Several unsuccessful attempts to oxidize the stilbene-type double bond of 3-carboxy-4-styryltropolone, 3-carboxy-4-(3,4-dimethoxystyryl)-tropolone (I), 4-styryltropolone (V) and of their benzoates were made. These included ozonation, peracid oxidation, permanganate–periodate oxidation, Prevost oxidation, nitric acid oxidation and chromic acid oxidation.

Tropolone-3,4-dicarboxylic Acid Anhydride (III).—To a suspension of 4 g. of the methyl ether of 3-carbomethoxy-4-(3,4-dimethoxystyryl)-tropolone (Ia) in 180 ml. of water containing 2 g. of magnesium sulfate was added a solution of 4.48 g. of potassium permanganate in 320 ml. of water. The addition was complete in 15 min. and the purple permanganate color was gone in an additional 15 min. The mixture was stirred for 1 hr. and the manganese dioxide and the unreacted starting material were removed by filtration. The neutral filtrate was extracted for 4 hr. with 250 ml. of ether, was acidified to congo red with concentrated hydrochloric acid and was then extracted continuously with ether for 16 hr.

The extract from the neutral solution afforded 2.5 g. of a yellow oil, which yielded a red 2,4-dinitrophenylhydrazone shown to be that of veratraldehyde by a mixed m.p.

The extract from the acidified solution was freed of ether, the residue was triturated with 5 ml. of ether, and the resulting dark orange solid (850 mg.) was sublimed at 120–160° (0.2 mm.); this yielded 500 mg. (23%) of the yellow anhydride, m.p. 253–255° with decomposition. Although the carbon and hydrogen analysis was not very satisfactory, the agreement of the m.p. and the infrared spectrum with those reported[2] indicated that it was the anhydride.

Decarboxylation in water[2] at 170–180° for 40 min. gave a 46% yield of 4-carboxytropolone, m.p. 217–218°, in agreement with the reported value.[1,2]

Benzoate of 4-Carboxytropolone (IVa).—A solution of 50 mg. of 4-carboxytropolone in 0.3 ml. of anhydrous pyri-

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[13] P. Akroyd, R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, 3427 (1951).

[14] Microanalyses are by Miss Annette Smith, W. Manser, T. Montzka and the Micro-Tech. Laboratories, Skokie, Ill. Melting points are uncorrected.

[15] T. W. Evans and W. M. Dehn, THIS JOURNAL, **52**, 3647 (1930).

[16] R. F. Smith, Ph.D. Thesis, University of Rochester, 1953.

[17] The position of the methyl ether group in this compound is not rigorously proved; it may be derived from the tautomeric form of the tropolone ring (*cf.* Va and X).

dine was treated with one drop of benzoyl chloride, heated briefly on the steam-bath, acidified, and the resulting solid was collected by centrifugation. Recrystallization from dilute ethanol yielded 45 mg. of product, m.p. 187–190°, which showed two peaks, at 1750 and 1742 cm.$^{-1}$, in the infrared. The analytical sample was prepared by three more crystallizations from dilute ethanol, followed by drying *in vacuo*.

Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.67; H, 3.73. Found: C, 66.62; H, 3.89.

4-(3,4-Dimethoxystyryl)-tropolone (II).—A mixture of 3.4 g. of 3-carboxy-4-(3,4-dimethoxystyryl)-tropolone (I), 22 ml. of quinoline and 0.5 g. of copper chromite was heated at 140° until bubbling ceased, then at 165° for 15 min. The mixture was taken up in 1*N* mineral acid, filtered and the filtrate was extracted with four 60-ml. portions of chloroform. The extracts, after washing with hydrochloric acid, yielded a residue, which was recrystallized from dilute methanol and gave 1.2 g. (41%) of yellow crystals, m.p. 108–109°; the compound gave a red ferric chloride color. The analytical sample was prepared by using copper powder in place of copper chromite; the decarboxylation was also carried out by sublimation at 210° (0.5 mm.).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.60; H, 5.67.

The benzoate was prepared with benzoyl chloride in pyridine, and melted, after recrystallization from ethanol, at 157.5–158°.

Anal. Calcd. for $C_{24}H_{20}O_5$: C, 74.21· H, 5.19. Found: C, 74.25; H, 5.44.

3-Carboxy-4-styryltropolone.—The published procedure[5b] was modified as follows. A mixture of 24 g. of 3-carboxy-4-carboxymethyltropolone, 17 ml. of acetic anhydride and 300 ml. of glacial acetic acid was heated at 80–90° with stirring for 30 min. The deep red solution was cooled to 40°, and 12 ml. of benzaldehyde was added, followed by 8 ml. of dry pyridine. The mixture was maintained at 40–45° for 1 hr., was then raised to 60°, the heat source was removed, and stirring was continued for 3.5 hr. The yellow-brown solution was then poured over 1 kg. of ice in 600 ml. of 10% hydrochloric acid with stirring. Cold water (1 l.) was added to ensure complete separation of the product. The yellow solid was collected, washed with cold water, dissolved in 600 ml. of hot 6*N* acetic acid, treated with charcoal and filtered. Addition of 200 ml. of boiling water to the filtrate yielded 17 g. (59%) of yellow-brown product, of indefinite melting point.

4-Styryltropolone (V).—A mixture of 33 g. of once recrystallized 3-carboxy-4-styryltropolone and 3 g. of copper powder in 100 ml. of dry quinoline (Eastman Kodak Co. technical grade) distilled from zinc dust was heated with stirring at about 150° for 1 hr., and cooled. Ether (300 ml.) was added and stirring was continued for 30 min The solution was acidified with about 1 l. of 10% hydrochloric acid and extracted thoroughly with ether; the solution was dried, the solvent was removed, and the residue was recrystallized from 1 l. of heptane to give 17.2 g. of orange-yellow crystals, m.p. 90–91°; the reported[6] m.p. is 90.5–91°. An additional 1.2 g. (total yield 18.4 g., 67%) was obtained by concentrating the filtrate to 200 ml. and treating with charcoal.

The acetate Vb was prepared with acetic anhydride and pyridine, and melted, after three crystallizations from dilute ethanol, at 99–99.5°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.31. Found: C, 76.63; H, 5.30.

The benzoate Vc was prepared with benzoyl chloride in pyridine, and melted, after crystallization from dioxane or ethanol, at 183–184°.

Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.92. Found: C, 80.67; H, 5.01.

4-Formyltropolone (VIII) by Periodate-Osmate Oxidation of 4-Styryltropolone (V).—To a stirred solution of 4.5 g. (0.02 mole) of 4-styryltropolone and 14 mg. of osmic acid in 100 ml. of a mixture of three volumes of dioxane to one volume of water was added 9.0 g. (0.042 mole) of powdered sodium metaperiodate during a 30-min. period. The mixture was stirred for an additional 2 hr., during which time sodium iodate precipitated out. The mixture was filtered, the filter cake was washed with ether, and the combined filtrate and washings were taken to dryness with a rotary evaporator; the ether, dioxane and water were removed by the water-pump and the benzaldehyde, which was formed in the oxidation, with an oil-pump. The brown residue was sublimed at 150° (0.5 mm.) to give 2.5 g. (84%) of yellow 4-formyltropolone, m.p. 154–157°. A second sublimation or recrystallization from benzene raised the m.p. to 158–160°; the reported[1] value is 159–160°.

4-Formyltropolone Oxime.—To a solution of 0.3 g. of 4-formyltropolone in 3 ml. of 95% ethanol was added a solution of 0.15 g. of hydroxylamine hydrochloride in a mixture of 4 ml. of water and 1.6 ml. of 2*N* sodium hydroxide. The mixture was allowed to stand overnight, was then acidified with acetic acid, and the resulting solid was collected, washed with water and recrystallized from ethanol to give 0.21 g. (64%) of pale yellow plates of m.p. 205°. Two more crystallizations from ethanol raised the m.p. to 207–209° (sealed tube).

Anal. Calcd. for $C_8H_7NO_3$: C, 58.18; H, 4.28. Found: C, 58.31; H, 4.50.

4-Formyltropolone Benzoate.—To a stirred solution of 1.64 g. of 4-styryltropolone benzoate and 50 mg. of osmic acid in 50 ml. of a mixture of 75% dioxane–25% water was added 2.25 g. of sodium metaperiodate over a half-hour period. Heating at 50° and stirring were continued for 4.5 hr., then the mixture was stirred at room temperature for an additional 16 hr. Water (50 ml.) was added to dissolve the sodium iodate, the mixture was filtered, and the solid was washed thoroughly with water; the product weighed 0.6 g. (50%) and melted, after crystallization from ethanol, at 137.5–138.5°.

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.87; H, 3.97. Found: C, 71.18; H, 4.11.

2-Methoxy-6-styryltropone (Va) **and 2-Methoxy-4-styryltropone** (X).—The ethereal diazomethane solution from 17.1 g. (0.08 mole) of N-methyl-N-nitroso-*p*-toluenesulfonamide was distilled directly into a solution of 9 g. (0.04 mole) of 4-styryltropolone in 50 ml. of acetone, kept in an ice-bath, with shaking. After standing for 15 min. 2.38 g. of yellow crystalline 2-methoxy-6-styryltropone separated out and was filtered off. It melted at 141–142°. The filtrate was evaporated and the residual oil was rubbed with a mixture of ethyl acetate and ether to give 2.9 g. of solid, m.p. 120–122°. This material was recrystallized from ethyl acetate to yield about half its weight of yellow needles, m.p. 142°, which was identical with the material obtained above. The recrystallization of the 122° material also gave some additional red oil which was rubbed with ethyl acetate and ether to give more 122° material, which was recrystallized as above. The procedure was repeated until no more crystalline material could be obtained. All of the filtrates were combined and evaporated to give the crude oily isomeric methyl ether 2-methoxy-4-styryltropone.

The total yield of 142° material was 4 g. (42%). The reported[18] m.p. was 138°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.68; H, 6.24.

2-Methoxy-6-formyltropone (VIIIa).—2-Methoxy-6-styryltropone (4.76 g.) was oxidized with 16 mg. of osmic acid and 9 g. of sodium metaperiodate, in 100 ml. of 3:1 dioxane–water, as described above for 4-styryltropolone. The product was recrystallized from benzene, in total yield of 2.6 g. (79%). The analytical sample melted, after crystallization from benzene, at 137–138°.

Anal. Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 66.07; H, 5.31.

The compound was hydrolyzed to 4-formyltropolone very quickly by warm 3% hydrochloric acid, warm 5% sodium carbonate and warm 3% hydrogen peroxide. Attempts to oxidize it with peroxide and a trace of silver ion in aqueous acetic acid gave only 4-formyltropolone.

Oxidation of 2-Methoxy-4-styryltropone (X) **to 2-Methoxy-4-formyltropone** (IX).—To a stirred solution of 2.4 g. of crude 2-methoxy-4-styryltropone and 10 mg. of osmic acid in 50 ml. of a 3:1 dioxane–water mixture was added 4.5 g. of powdered sodium metaperiodate over 15 min. Stirring was continued for 1.5 hr. during which time the reaction became slightly exothermic (40–50°); external cooling was not effected however. The precipitated sodium iodate was fil-

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(18) T. Nozoe, *et al.*, *Sci. Repts. Tohoku Univ., First Series*, **38**, 257 (1954); *C. A.*, **50**, 2532 (1956).

tered off and washed well with chloroform and the combined washings and filtrates were evaporated to dryness with the rotary evaporator. The brown solid residue was extracted with 100 ml. of boiling benzene, the benzene evaporated and the residue recrystallized from methanol to give 0.8 g. (50%) of pale yellow needles of 21-methoxy-4-formyltropone of m.p. 183–184°. The reported m.p. was 182–183°.

2-Methoxy-4-carboxytropone (XI).—To a cold basic suspension of fresh silver oxide, prepared by adding 6.8 g. (0.04 mole) of silver nitrate to a solution of 2.8 g. (0.07 mole) of sodium hydroxide dissolved in 100 ml. of water, was added 3.3 g. (0.02 mole) of 2-methoxy-4-formyltropone over 15 min. with stirring. The mixture was allowed to stand at ice-bath temperature for an additional half-hour then warmed to room temperature over one-half hour. The silver was filtered off and washed with water and the solution acidified with cold 10% hydrochloric acid. The precipitated acid was filtered off and recrystallized from 25% methanol in water to give 2.5 g. (70%) of pale yellow needles of 2-methoxy-4-carboxytropone, m.p. 253–254°. The reported m.p.[1] was 258°.

2-Amino-4-carboxytropone (XII).—2-Methoxy-4-carboxytropone (1.7 g.) and liquid ammonia (20 ml.) were sealed in a glass tube and the tube was stored in a steel bomb for 3 days at room temperature. (On some of the runs the tube exploded inside of the bomb. This could be largely prevented by charging the bomb with about 150 p.s.i. of N_2 after introducing the frozen (Dry Ice) tube and later cooling the entire apparatus to Dry Ice temperature before opening the bomb.) The contents of the tube were then transferred to a beaker and the ammonia was allowed to evaporate (caution: splattering). The solid residue was taken up in 25 ml. of water and acidified with 10% hydrochloric acid. The precipitated acid was filtered off and weighed 1.45 g. (93%). Three recrystallizations from aqueous ethanol gave the analytical sample as small orange needles, m.p. 280° d. (sealed tube).

Anal. Calcd. for $C_8H_7O_3N$: C, 58.18; H, 4.28. Found: C, 57.93; H, 4.41.

2-Acetamino-4-carboxytropone (XIII).—Treatment of 2-amino-4-carboxytropone with excess acetic anhydride in pyridine on the steam-bath for 45 min. followed by acidification with 10% hydrochloric acid in ice gave a yellow-brown solid. Two recrystallizations from ethanol with decolorizing charcoal gave a pale yellow powder of m.p. 230° dec. (sealed tube).

Anal. Calcd. for $C_{10}H_9O_4N$: C, 57.97; H, 4.38. Found: C, 57.50; H, 4.50.

Acid Chloride of 2-Acetamino-4-carboxytropone.—To a stirred suspension of 0.25 g. of the dry potassium salt of 2-acetamino-4-carboxytropone in 10 ml. of benzene was added 0.1 ml. of oxalyl chloride in 5 ml. of benzene. Stirring was continued for 3 hr. at room temperature during which time a gas was evolved and the solution became yellow. The mixture was filtered and evaporated to dryness on the rotary evaporator to give the crude acid chloride as a yellow solid. Treatment with *p*-bromoaniline in benzene gave the *p*-bromoanilide derivative which melted, after two recrystallizations from benzene, at 225–227°.

Anal. Calcd. for $C_{16}H_{13}O_3N_2Br$: C, 53.20; H, 3.63; Found: C, 53.52; H, 3.89.

2-Amino-6-styryltropone (VI).—A mixture of 1.5 g. of 2-methoxy-6-styryltropone (Va) and 30 ml. of liquid ammonia was allowed to stand in a sealed tube at room temperature for 45 hr. After evaporation of the ammonia the product was recrystallized from 100 ml. of benzene to give 0.85 g. of orange plates, m.p. 135–136°. An additional 0.35 g. was obtained by treating the filtrate with decolorizing charcoal and evaporating to 20 ml. The total yield was 1.2 g. (86%). Three more crystallizations from benzene (with charcoal treatment) gave the analytical sample as sparkling golden plates, m.p. 137–138°.

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87. Found: C, 80.24; H, 5.80.

The acetyl derivative VIa was prepared with acetic anhydride and pyridine, and melted, after three crystallizations from heptane containing 5% of benzene, at 179.5–181°.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70. Found: C, 76.96; H, 5.98.

2-Hydrazino-6-styryltropone (VII).—To a suspension of 0.238 g. of 2-methoxy-6-styryltropone in 1 ml. of methanol and 1 ml. of dioxane was added 0.1 g. of 95% hydrazine. The mixture was warmed on the steam-bath for 5 min. and cooled; the crystals were collected (0.21 g., 88%) and after three crystallizations from methanol gave brilliant red crystals, m.p. 162.5–163.5°.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92. Found: C, 75.91; H, 5.79.

4-(β-Carboxyvinyl)-tropolone (XIV).—A mixture of 0.75 g. of 4-formyltropolone, 0.52 g. of malonic acid, 1 ml. of piperidine and 20 ml. of pyridine was heated on the steam-bath for 12 hr. The resulting solution was poured over ice and acidified with 10% hydrochloric acid and the acidic solution was continuously extracted with ether for 24 hr. Evaporation of the dried ether solution and recrystallization of the solid residue from ethanol gave yellow needles of 4-(β-carboxyvinyl)-tropolone, m.p. 226.5–227.5° dec. (sealed tube). The compound gave an immediate green-brown color with ethanolic ferric chloride solution.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.60; H, 4.20. Found: C, 62.84; H, 4.37.

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The Beckmann Rearrangement of the Acetoxime of $\Delta^{5,16}$-Pregnadien-3β-ol-20-one Acetate with Boron Trifluoride

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Beckmann rearrangement of $\Delta^{5,16}$-pregnadien-3β-acetoxy-20-acetoximino (Ib) with boron trifluoride etherate in benzene afforded dehydro epiandrosterone acetate (IIb), whereas in acetic anhydride the rearrangement followed a different course and two products were isolated: 17β-methyl-18-nor-$\Delta^{5,13(14)}$-isopregnadien-3β,16α-diol-20-one diacetate (IIIa) and 16-acetyl-17-acetylamino-$\Delta^{5,16}$-androstadien-3β-ol acetate (VIIa); several derivatives are described.

The Beckmann rearrangement of $\Delta^{5,16}$-pregnadien-3β-ol-20-one 3-acetate 20-oxime (Ia) has been studied by G. Rosenkranz, *et al.*[1] Using *p*-acetamidobenzenesulfonyl chloride as catalyst, the reaction afforded dehydroepiandrosterone (IIa) and working under appropriate conditions the intermediate amide VI could be isolated. In view of the current interest in this degradation of Δ^{16}-20-ketones to androstane derivatives we considered the use of boron trifluoride as catalyst in this reaction. Recently Hauser and Hoffenberg[2] have used boron trifluoride in the Beckmann rearrange-

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(1) G. Rosenkranz, O. Mancera, F. Sondheimer and C. Djerassi, *J. Org. Chem.*, **21**, 520 (1956).

(2) Ch. R. Hauser and D. S. Hoffenberg, THIS JOURNAL, **77**, 4885 (1955).