[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Ring Enlargements. IV. Steric Influences in Diazomethane–Carbonyl Reactions. The Reaction of *cis-* and *trans*-α-Decalone with Diazomethane[1,2]

BY C. DAVID GUTSCHE AND HUGO H. PETER

RECEIVED FEBRUARY 12, 1955

To study the steric influences in the diazomethane–carbonyl reaction, *cis-* and *trans*-α-decalone (I) have been investigated. The interaction of diazomethane with these compounds results in the formation of *cis-* and *trans*-α-hexahydrobenzosuberone (II), *cis-* and *trans*-β-hexahydrobenzosuberone (III), the oxide IV and, under certain conditions, a hexahydrobenzocyclooctanone (V). All of these compounds have been obtained in a state of known purity, either by synthesis or by isolation, and provide the basis for a quantitative assay of the product from diazomethane and compound I. By means of this assay, differences in the product ratios from the reactions involving *cis*-I and *trans*-I have been measured. Also, the effect of various reaction conditions have been investigated including changes in temperature, concentration, solvent and base.

In the reaction between cyclic ketones and diazomethane to produce ring-enlarged ketones and/or oxides, steric factors are undoubtedly important and may exert an influence at two stages of the reaction: the initial attack of the diazomethane at the carbonyl group as well as the subsequent rearrangement of the resulting intermediate may be sterically-controlled. Examples of the first effect are the ring enlargements of 2-substituted cyclohexanones which, in many cases, proceed in lower yield than those involving cyclohexanones lacking 2-substituents. Thus, cyclohexanone yields 60–65% of cycloheptanone,[3] but 2-methylcyclohexanone gives a 37% yield of methylcycloheptanones,[4] and 2-cyclohexylcyclohexanone is reported to yield only 4–5% of ring-enlarged ketone.[5] Examples of the second effect are more difficult to establish, but the ratio of carbonyl product to oxide and the ratio of isomeric carbonyl products formed from unsymmetrically-substituted cycloalkanones may be determined, in part, by steric factors. For instance, the ratio of ketone to oxide is about 4:1 in the ring enlargement of cyclohexanone, but is closer to 1:1 with 3,5,5-trimethylcyclohexanone. Also, in the latter example the two isomeric trimethylcycloheptanones are not formed in equal amount.[6]

In all of these and similar examples, however, an electronic factor complicates the steric factor. Thus, alkyl groups are usually considered as electron-donating relative to hydrogen, and the lower reactivity of 2-alkylcyclohexanones might also be explained in terms of an inductive deactivation of the carbonyl group. Similarly, the decomposition of the intermediate might also be controlled by the greater electron-donating power of an RCH– group over that of a CH_2– group. In an attempt to study a system in which electronic differences are at a minimum and in which steric differences should predominate, the present investigation was undertaken. One of the simplest systems in which this requirement appeared to be satisfied was that of the *cis-* and *trans*-α-decalones, and it is with this pair of compounds that the present work deals.

cis–cis-α-Decalol was synthesized in 50% over-all yield from α-naphthol by reduction with lithium–ammonia–ethanol[7] to 5,8-dihydro-1-naphthol followed by catalytic reduction to 5,6,7,8-tetrahydro-1-naphthol[8] and then to a mixture of α-decalols from which the *cis–cis* isomer could be isolated as a solid. Oxidation with chromium trioxide-pyridine[9] gave 71% of pure *cis*-α-decalone (Ia). A mixture of α-decalols suitable for the preparation of the *trans*-ketone could be obtained in 69% yield by the Raney nickel catalyzed reduction of α-naphthol[10] or in 87% yield by a similar reduction of 5,6,7,8-tetrahydro-1-naphthol. Oxidation yielded a mixture of α-decalones which could be completely converted to *trans*-α-decalone by 12-hour refluxing with aqueous methanolic sodium hydroxide, the over-all yield from α-naphthol being 50%.

One of the major obstacles to the interpretation of diazomethane reactions on the basis of the products isolated is the formation of difficultly-separable mixtures. The amounts of the various pure compounds isolated do not necessarily represent the amounts actually formed. For this reason it was important for the present investigation to find a method of assay which would provide an accurate estimate of all of the reaction products. Previously, the method of quantitative infrared analysis had been successfully employed in a similar study[11] and it was again chosen as the most appropriate. For this method, however, it was necessary to secure pure samples of the hitherto unknown *cis-* and *trans*-α-hexahydrobenzosuberone (II), *cis-* and *trans*-β-hexahydrobenzosuberone (III) and the oxide IV.

Catalytic reduction of α-benzosuberone in the presence of Adams catalyst followed by oxidation of the product gave a 44% yield of II.

(1) This work was supported, in part, by grants-in-aid from the Monsanto Chemical Co. and the Office of Ordnance Research, Contract No. DA-23-072-ORD-767, and was presented at the XIVth International Union of Pure and Applied Chemistry, Zurich, Switzerland, July, 1955.

(2) For paper III of this series *cf.* C. D. Gutsche and H. E. Johnson, THIS JOURNAL, **77**, 109 (1955).

(3) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1057 (1939).

(4) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 181 (1939).

(5) M. Mousseron and G. Manon, *Bull. soc. chim. France*, 392 (1949).

(6) M. Stoll and W. Scherrer, *Helv. Chim. Acta*, **23**, 941 (1940).

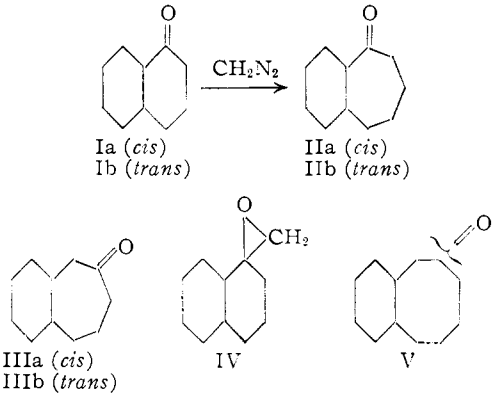
(7) *Cf.* A. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5360 (1953).

(8) This material, obtained in 90% yield, previously has been prepared from α-naphthol in *ca.* 40% yield by catalytic hydrogenation and in *ca.* 85% yield by chemical reduction. The present method has the advantage over earlier procedures both with respect to yield and to ease of manipulation.

(9) G. I. Poos, G. E. Arth, G. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

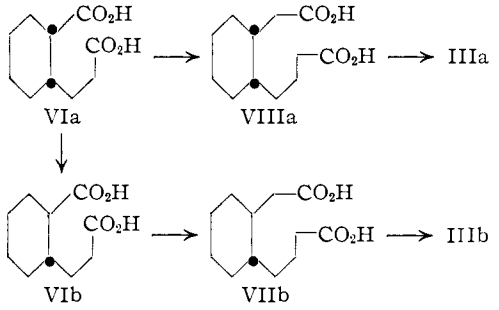
(10) As has been observed by H. E. Ungnade and co-workers, *ibid.*, **66**, 118, 1218 (1944), and by others, the extent of hydrogenolysis can be reduced by addition of base to the hydrogenation reaction mixture. It was also observed in the present case that when larger amounts of base were added, the amount of α-decalol formed was greatly reduced, the major product being 1,2,3,4-tetrahydro-1-naphthol (70%).

(11) C. D. Gutsche, THIS JOURNAL, **71**, 3513 (1949).



The pure *cis* isomer was obtained *via* the semicarbazone and it is interesting to note in this respect that IIa shows much less tendency to isomerize to IIb than does its six-membered analog Ia to Ib; thus, hydrolysis of the semicarbazone of IIa proceeds with little, if any, inversion of configuration. Similarly, catalytic reduction of α-benzosuberone in the presence of Raney nickel, oxidation of the product, treatment of the crude ketone with aqueous methanolic sodium hydroxide and purification *via* the semicarbazone yielded the pure *trans* isomer IIb.

Catalytic reduction of β-(2-carboxyphenyl)-propionic acid in the presence of Adams catalyst gave an 87% yield of *cis*-β-(2-carboxycyclohexane)-propionic acid (VIa) which could be isomerized to the *trans* isomer VIb by heating at 200° with concentrated sodium hydroxide. The *cis* and *trans* isomers of VI were subjected to bis-homologation *via* the Arndt–Eistert method to yield the *cis* and *trans* isomers of γ-(2-carboxymethylcyclohexane)-butyric acid (VII). Cyclization by pyrolysis of the corresponding thorium salts then provided the *cis* and *trans* isomers of β-hexahydrobenzosuberone (III).



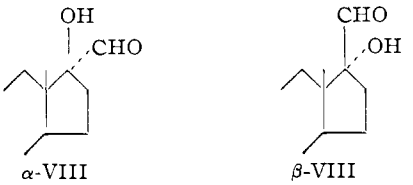
It was not possible to isolate a pure sample of the oxide IV. However, it was possible to secure its infrared spectrum by virtue of the fact that the composition of the mixture of IV and Ib (obtained from a diazomethane reaction) could be determined *via* infrared analysis for Ib and chemical analysis for IV. The infrared spectrum of the oxide could thus be obtained by difference and it, along with the spectra of the six ketones described above, provided the necessary data for the analysis of the products from diazomethane and the α-decalones.

The analysis of the reaction mixture by means of infrared followed well-established procedures.[12]

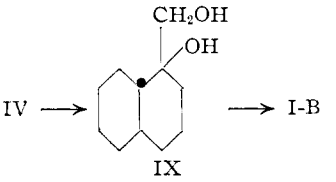
(12) *Cf.*, for example, M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950.

To test the reliability of the method a two-component mixture and a four-component mixture of known composition were assayed with the following results: A mixture known to contain 38.8% of Ia and 61.2% of Ib gave values of 39% and 61% upon infrared analysis; a mixture known to contain 8% of IV, 16% of IIb, 26% of IIb and 50% of Ib gave values of 8, 12, 30 and 50%. It is probably safe to assume, therefore, that the absolute error in the values reported in Tables I–IV is not more than ±5% and in many cases, less.

The reactions with diazomethane were carried out in two ways, designated as the *ex situ* and the *in situ* methods. The former refers to those reactions in which an ethereal solution of diazomethane is employed, while the latter refers to those reactions in which N-nitrosomethylurethan is added to a basic solution containing the ketone. Inspection of Tables III and IV reveals that under comparable conditions in the *ex situ* method, *trans*-α-decalone shows a much greater tendency to form the oxide than does *cis*-α-decalone, the ratio of ketone to oxide being about 1.5–2.0 and 20 (or greater), respectively. A similar difference has been reported for an *ex situ* reaction with the 17-epimers of 17-formyl-4-androsten-17-ol-3-one (VIII) which yields a ketone (30%) from the α-isomer and the oxide (33%) from the β-isomer.[13] Under *in situ* conditions, also (*cf.* Tables I and II) the *trans* isomer Ib forms more oxide than the *cis* isomer Ia, the ketone to oxide ratios being about 1.5 and 7, respectively. The latter value is lower than in the *ex situ* case due to the base-catalyzed inversion of Ia to Ib during the

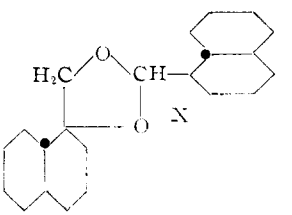


in situ reaction, a rearrangement which, it should be pointed out, *does not* occur under *ex situ* conditions. The oxide formed from Ia was shown, in fact, to be derived from Ib (hydrolysis to the glycol IX followed by periodate oxidation to Ib). The glycol IX from Ib was further characterized by acid-catalyzed rearrangement to decahydro-1-naphthylcarboxaldehyde[14] from which the known *trans*-*trans*-



(13) D. A. Prins and T. Reichstein, *Helv. Chim. Acta*, **24**, 945 (1941).

(14) The nature of the product obtained from the acid-catalyzed rearrangement of IX varied depending upon whether aqueous or methanolic sulfuric acid was used. The latter yielded the aldehyde, but the former yielded a compound which is chemically, spectrally and analytically compatible with the dioxolane X.



decahydronaphthylcarboxylic acid[15] was obtained by oxidation.

In an attempt to gain further insight into the reaction between diazomethane and cycloalkanones, the effect of certain reaction conditions was investigated. It has been stated that in the ring enlargement of cyclohexanone no effect on the ketone to oxide ratio results from changes in reaction temperature (0–50°), the nature of the base used (potassium carbonate, barium oxide, magnesium methoxide), the alcohol or the concentration of diazomethane.[3] Inspection of Tables I–IV, however, reveals that several of these factors may influence the outcome of the reaction in the present case.

TABLE I

THE REACTION OF DIAZOMETHANE (*in situ*) WITH *cis*-α-DECALONE (Ia)[a]

Temperature, °C.	0	40
Components of reaction mixture, %		
Ib[b]	27	42
IIb	24	19
IIIa	70	71
IIIb	0	0
IV	6	10

[a] The reactions were carried out in 3% methanolic potassium carbonate. The ratio of N-nitrosomethylurethan to ketone was 1.17. Duplicate analyses were accurate to ±5%. [b] The numbers in this line represent the amount of unreacted material (Ia inverted to Ib) recovered. The numbers in the remaining lines represent the amounts of products obtained, corrected for recovered Ib.

TABLE IV

THE REACTION OF DIAZOMETHANE (*ex situ*) WITH *trans*-α-DECALONE (Ib)[a]

Temp., °C.	4	35	4
CH_3OH, ml.	20	20	20
$(C_2H_5)_2O$, ml.	40	40	120
Components of reaction mixture, %			
Ib[b]	36	56	62
IIb	9	2	21
IIIb	50	66	55
IV	41	32	24

[a] The ratio of diazomethane to ketone was 1.17. Duplicate analyses were accurate to ±1%. [b] The numbers in this line represent the amount of starting material (Ib) recovered. The numbers in the remaining lines represent the amounts of products obtained, corrected for recovered Ib.

Temperature.—An increase in the reaction temperature results in all cases in a decrease in the extent of the reaction. Both in the *in situ* and the *ex situ* methods some diazomethane is lost through polymerization to polymethylene and through reaction with methanol, and apparently these side reactions are more strongly temperature dependent than is the reaction between diazomethane and the ketone. Temperature changes also affect the product ratios; with increasing temperature the *cis*-ketone (Table III) shows an increase in the IIa to IIIa ratio, while the *trans*-ketone (Tables II and IV) shows an increase in the IIIb to IIb plus IV ratio.

TABLE II

THE REACTION OF DIAZOMETHANE (*in situ*) WITH *trans*-α-DECALONE (Ib)

Temp., °C.	0	35	65	0	0	0	0	0	0	0	0
Solvent	MeOH	MeOH	MeOH	EtOH	MeOH	MeOH	MeOH	MeOH	MeOH	MeOH	MeOH
Base[a]	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	KOH	NaOH	Triton-B	Piperidine	Pyridine	NaOAc	NaOMe
Components of reaction mixture, %											
Ib[b]	26	32	60	44	32	27	36	39	56	42	34
IIb	27	19	18	25	12	12	25	25	30	26	26
IIIb	36	38	61	30	59	59	41	45	41	36	35
IV	37	43	21	45	29	29	34	30	29	38	39

[a] In all cases a 3% solution of the base in methanol was employed except in the one instance where ethanol was the solvent. In all cases the ratio of N-nitrosomethylurethan to ketone (Ib) was 1.17. [b] The numbers in this line represent the amount of starting material (Ib) recovered. The numbers in the remaining lines represent the amounts of products obtained, corrected for recovered Ib.

TABLE III

THE REACTION OF DIAZOMETHANE (*ex situ*) WITH *cis*-α-DECALONE (Ia)[a]

Temp., °C.	4	30	4	4	4	30
CH_2N_2/Ia ratio	1.17	1.17	1.17	3.34	5.85	5.85
CH_3OH, ml.	20	20	20	20	20	20
$(C_2H_5)_2O$, ml.	40	40	120	80	190	190
Components of reaction mixture, %						
Ia[b]	55	60	79	44	30	67
IIa	54	71	14	46	50	30
IIIa	46	29	86	54	50	70
IV[c]	(3)				(7)	

[a] Duplicate analyses were accurate to ±5%. [b] The numbers in this line represent the amount of starting material (Ia) recovered. The numbers in the remaining lines represent the amounts of products obtained, corrected for recovered Ia. [c] The oxide was present in such small amounts that it could not be assayed by the infrared method. Chemical assay was used to obtain the values shown in this line.

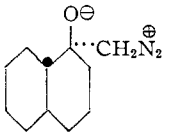
Concentration.—When the reaction mixtures are diluted with ether, the extent of the reaction decreases and certain product ratios are changed. From the *cis*-ketone the ratio of IIa to IIIa decreases (Table III) and from the *trans*-ketone the amount of IIb formed increases, largely at the expense of the oxide (Table IV).

Solvent.—A change in solvent does not appear to affect the product ratios, but it does influence the extent of the reaction. With potassium carbonate as the base the reaction proceeds very sluggishly in ethanol and fails completely in isopropyl alcohol, ethyl acetate and water (Table II). With sodium isopropoxide in isopropyl alcohol, however, the reaction takes place thus indicating that the previous failure is probably due to the insolubility of potassium carbonate in isopropyl alcohol.

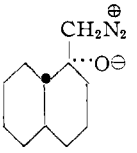
(15) W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954).

Base.—On the basis of the ratio of IIIb to IIb formed (Table II), the bases investigated can be divided into three groups: (a) those which give rise to a low IIIb to IIb ratio (*ca.* 1.3) including potassium carbonate, sodium acetate and sodium methoxide, (b) those which give rise to a high IIIb to IIb ratio (*ca.* 5) including sodium hydroxide and potassium hydroxide and (c) those which give rise an intermediate IIIb to IIb ratio (*ca.* 1.4–1.8) including trimethylbenzylammonium hydroxide, piperidine and pyridine. The amount of oxide IV formed is fairly constant in all cases.

Reactions involving aldehydes or ketones and diazomethane are usually rationalized as proceeding through a betaine (or furadiazole) intermediate resulting from the attack of a nucleophilic diazomethane molecule on the electrophilic carbon atom of the carbonyl group.[16] In an unsymmetrically-substituted carbonyl compound this attack might involve either face of the carbonyl group and lead to epimeric intermediates. *trans*-α-Decalone, for instance, could give rise to XIa or XIb. Undoubtedly, the epimeric intermediates are not formed in equal amount, nor should they necessarily decompose in the same fashion, quantitatively or even qualitatively. Thus, the differing amounts of oxide from *cis*- and *trans*-α-decalone might be interpreted in terms of a stereoselectivity in the initial addition and/or a stereoselectivity in the decomposition of the intermediate. Also, the observed temperature and concentration effects could be explained in the same fashion, some substantiation for this being the apparent lack of temperature and concentration dependence in the cyclohexanone reaction where epimeric intermediates are not possible.

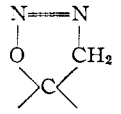


XIa

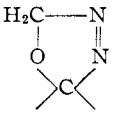


XIb

An alternative explanation which we believe cannot be overlooked, however, assumes that the oxide and ketone do not arise from the same intermediate. That a diazoalkane might attack a carbonyl group in the opposite manner to that usually postulated has been suggested by Schönberg and co-workers[17] and by Smith and Pings.[18] The latter workers, in fact, isolated several nitrogen-containing compounds from the reaction of diazomethane with duroquinone and they postulated furadiazole structures of the type XIIa and XIIb corresponding to the two modes of addition of diazomethane to the carbonyl group. The observed effects of solvent and base as well as other factors might be explainable in terms of a dual-intermediate scheme and we hope to carry out further experiments to determine the validity of this concept.



XIIa



XIIb

When *trans*-α-decalone is treated with an excess of diazomethane, a carbonyl compound different from IIb or IIIb is obtained and it undoubtedly is a hexahydrobenzocycloöctanone (V). Curiously, however, it does not appear to be formed from the hexahydrobenzocycloheptanones IIb or IIIb as such, for when IIb and IIIb are treated with diazomethane under the same conditions employed with Ib, practically no reaction takes place and starting material is recovered. A similar phenomenon has been suggested for the reaction between diazomethane and ketene where the cyclobutanone that is formed may not arise through an intermediate cyclopropanone.[19] Possibly, V arises from attack of diazomethane on the intermediate (*e.g.*, XI) involved in the formation of II and III, this attack being promoted by an excess of diazomethane.

The present work indicates that the diazomethane–carbonyl reaction is quite susceptible to steric influences, not just in the determination of the rate of the reaction but also in the determination of the various products formed. It also indicates, contrary to previous thinking, that changes in certain reaction conditions may alter the ratios of products formed, at least in the system studied. It is hoped that further investigation will illuminate the detailed mechanism of the reaction and will also suggest methods whereby a more nearly complete predetermination of the nature of the products can be achieved.

Experimental[20–22]

cis-α-**Decalone** (Ia).—Following a general method described by Wilds and Nelson,[7] a 108-g. sample of α-naphthol (Eastman Kodak Co. white label) was reduced to 106 g. (97%) of 5,8-dihydro-1-naphthol, m.p. 69–71°. Recrystallization from petroleum ether (b.p. 63–69°) gave colorless plates with m.p. 71–74° (reported[23] 71–74°); λ_{max}^{EtOH} (ε) 272.5 mμ (1980), 298 mμ (620). The crude dihydro compound was hydrogenated at 2 atmospheres pressure in the presence of palladium-on-charcoal to yield, after one recrystallization from petroleum ether (b.p. 88–98°), 96 g. (87%) of 5,6,7,8-tetrahydro-1-naphthol, m.p. 68–69° (reported[24] 68°). An 80-g. sample of this material was dissolved in 200 ml. of glacial acetic acid, treated with 3.0 g. of freshly-prepared Adams catalyst[25] and hydrogenated for 4 days at 2 atmospheres pressure. The crude product was recrystallized from petroleum ether (b.p. 63–69°) to give 49 g. (59%) of *cis-cis*-α-decalol, m.p. 92–93° (reported[26] 93°). Oxidation with chromium trioxide in pyridine[9] yielded 35 g. (71%) of *cis*-α-decalone after purification through the bisulfite compound: b.p. 120–121° (20 mm.). $n^{25}D$ 1.4910 (reported[26] $n^{25}D$ 1.4936); $\bar{\nu}_{max}^{liquid}$ in cm.$^{-1}$ 828.

(16) For references *cf.* C. D. Gutsche, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364.

(17) A. Schönberg, A. Mustafa, W. I. Awad and G. E. Moussa, THIS JOURNAL, **76**, 2273 (1954).

(18) L. I. Smith and W. B. Pings, *J. Org. Chem.*, **2**, 95 (1937).

(19) Sj. Kaarsemeker and J. Coops, *Rec. trav. chim.*, **70**, 1033 (1951).

(20) All melting points are corrected; all boiling points are uncorrected.

(21) The microanalyses were performed by Miss Charlotte Peterson, Washington University, and by Drs. Weiler and Strauss, Oxford, England.

(22) The infrared spectra were determined in a Perkin–Elmer model 21 spectrophotometer. The ultraviolet spectra were determined in a Beckman model DU spectrophotometer.

(23) A. B. Birch, *J. Chem. Soc.*, 430 (1944).

(24) P. Jacobsen and A. Turnbull, *Ber.*, **31**, 897 (1898).

(25) R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 463.

(26) W. Hückel, *Ann.*, **441**, 1 (1925).

878, 986, 1008, 1051, 1102, 1132, 1152, 1185, 1225, 1318, 1375, 1426, 1443, 1458, 1710, 2840, 2890.

The 2,4-dinitrophenylhydrazone of *cis*-α-decalone was prepared at 0° to avoid inversion to the *trans* isomer and was obtained, after one recrystallization from ethyl acetate–petroleum ether (b.p. 88–98°) as light orange needles, m.p. 176–177°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07. Found: C, 57.87; H, 5.90.

***trans*-α-Decalone** (Ib).—The crude α-decalone obtained by chromic acid oxidation of 116 g. of the mixture of α-decalols resulting from the catalytic reduction of α-naphthol or 5,6,7,8-tetrahydro-1-naphthol was refluxed for 12 hours with 100 g. of sodium hydroxide in 150 ml. of water and 200 ml. of methanol. The product from this treatment was converted to the bisulfite compound from which 78 g. (68%) of *trans*-α-decalone was obtained, b.p. 58° (0.8 mm.), $n^{20}D$ 1.4852 (reported[26] $n^{20}D$ 1.4849), m.p. 31–32° (reported[26] 32°); $\tilde{\nu}_{max}^{liquid}$ in cm.$^{-1}$ 812, 906, 941, 982, 1040, 1108, 1138, 1175, 1197, 1243, 1302, 1312, 1375, 1452, 1710, 2840, 2890.

The 2,4-dinitrophenylhydrazone of *trans*-α-decalone was obtained as fine, dark orange-red needles after recrystallization from ethyl acetate–petroleum ether (b.p. 88–98°); m.p. 238–239° (reported 222–222.5°,[27] 225.2–227.8°,[15] 234–235°[7]).

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07. Found: C, 57.86; H, 6.00.

Synthesis of the α-Hexahydrobenzosuberones II

***cis*-α-Hexahydrobenzosuberone** (IIa).—53.3 grams of benzosuberone in 200 ml. of glacial acetic acid was treated with 3 g. of Adams catalyst and hydrogenated for 10 days at 2 atmospheres at which time a total of four mole equivalents of hydrogen had been absorbed. Distillation of the crude product through a 20-inch, glass-helix packed column yielded 33.4 g. (61%) of α-hexahydrobenzosuberol, b.p. 85–88° (0.8 mm.), $n^{25}D$ 1.5075. In hydrogenations which proceeded at a faster rate the yield of alcohol was reduced; one reduction requiring just 6 hours, for instance, gave only 33% of alcohol. Oxidation of the hexahydrobenzosuberol with chromium trioxide in pyridine[9] gave 24.3 g. (44% overall from benzosuberone) of ketone with b.p. 70–75° (0.7 mm.), $n^{25}D$ 1.5050. Conversion to the semicarbazone followed by cleavage with aqueous oxalic acid at room temperature yielded a ketone with b.p. 92–94° (1 mm.), $n^{25}D$ 1.4973; $\tilde{\nu}_{max}^{liquid}$ in cm.$^{-1}$ 769, 839, 917, 949, 983, 1044, 1125, 1142, 1161, 1240, 1290, 1315, 1348, 1446, 1703, 2846, 2908.

Anal. Calcd. for $C_{11}H_{18}O$; C, 79.47; H, 10.84. Found: C, 79.38; H, 10.80.

The semicarbazone of IIa was obtained as colorless needles after several recrystallizations from aqueous ethanol; m.p. 205–206°.

Anal. Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48. Found: C, 64.37; H, 9.35.

The 2,4-dinitrophenylhydrazone of IIa was obtained as orange prisms after several recrystallizations from ethanol; m.p. 146–147°.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40. Found: C, 58.75; H, 6.15.

***trans*-α-Hexahydrobenzosuberone** (IIb).—A 40.0-gram sample of benzosuberone was mixed with 2 teaspoonsful of Raney nickel catalyst[23] and 1.0 g. of potassium hydroxide, and the mixture was hydrogenated for 2 hr. at 2500 p.s.i. and 225°. The crude product, consisting of 38.7 g. (92%) of material, was oxidized with chromium trioxide in pyridine[9] to yield 32.9 g. of an amber-colored oil. This was dissolved in 150 ml. of ethanol, treated with 40 g. of sodium hydroxide in 50 ml. of water, and the solution was refluxed for 12 hr. The resulting product was distilled through a 12-inch glass-helix packed column to yield 3.15 g. (9%) of a mixture of benzosuberan and hexahydrobenzosuberan with b.p. 49–52° (0.8 mm.) and 21.7 g. (52%) of *trans*-α-hexahydrobenzosuberone with b.p. 75–78° (0.8 mm.). Further purification of the latter through a Piros–Glover spinning band column gave a center cut with b.p. 107° (5 mm.), $n^{25}D$ 1.4893; $\tilde{\nu}_{max}^{liquid}$ in cm.$^{-1}$ 749, 802, 837, 965, 1008, 1053, 1155, 1172, 1240, 1315, 1342, 1446, 1705, 2840, 2908.

(27) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 817 (1937).

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.84. Found: C, 79.45; H, 10.82.

The semicarbazone of IIb was obtained as colorless needles after several recrystallizations from aqueous ethanol; m.p. 222–223°.

Anal. Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48. Found: C, 64.58; H, 9.49.

The 2,4-dinitrophenylhydrazone of IIb was obtained as fine orange needles after several recrystallizations from ethyl acetate–petroleum ether (b.p. 88–98°); m.p. 176.5–177°.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40. Found: C, 58.92; H, 6.45.

Synthesis of the β-Hexahydrobenzosuberones III

***cis*-γ-(2-Carboxymethylcyclohexane)-butyric Acid** (VIIa).—β-(2-Carboxyphenyl)-propionic acid was prepared by peracetic acid oxidation of β-naphthol to *o*-carboxycinnamic acid[28] followed by reduction with Raney nickel alloy in aqueous sodium hydroxide.[29] The product, obtained in *ca.* 65% over-all yield (m.p. 164–165°), was dissolved in glacial acetic acid and hydrogenated at room temperature and 2 atmospheres pressure in the presence of Adams catalyst.[26] Purification of the reduction product by recrystallization from water gave an 87% yield of *cis*-β-(2-carboxycyclohexane)-propionic acid (VIa) as colorless needles with m.p. 101.5–102.5° (reported[30] 103°). A 10.10-g. sample of this material was converted to the bis-acid chloride by the action of oxalyl chloride on the dry sodium salt,[31,32] the bis-acid chloride was treated with diazomethane to yield the bis-diazoketone, and the bis-diazoketone was rearranged in methanol solution in the presence of silver benzoate[33] to yield 7.20 g. (58%) of the dimethyl ester of VIIa with b.p. 121–125° (0.5 mm.) and $n^{25}D$ 1.4660.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44. Found: C, 65.85; H, 9.78.

Saponification of the ester yielded 92% of the corresponding dicarboxylic acid (VIIa) with m.p. 122–125°, which, after several recrystallizations from ethyl acetate–petroleum ether (b.p. 88–98°), was obtained as fine, colorless needles, m.p. 129–130°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.03; H, 8.82.

***trans*-γ-(2-Carboxymethylcyclohexane)-butyric Acid** (VIIb).—A 50.0-g. sample of *cis*-β-(2-carboxycyclohexane)-propionic acid (*cf.* above) was treated with 50 ml. of water and 50 g. of sodium hydroxide and heated for 24 hours in an autoclave at 200°. The crude product consisted of 48.2 g. (96%) of a tan solid with m.p. 131–134° which, after several recrystallizations from water, yielded 29.6 g. (59%) of *trans*-β-(2-carboxycyclohexane)-propionic acid with m.p. 142–143° (reported[30] 143°). For the preparation of large amounts of VIb it proved easier to convert β-(2-carboxyphenyl)-propionic acid to the diester, hydrogenate the diester to the hexahydro compound in the presence of Raney nickel catalyst at 225°, and saponify the product to a mixture of VIa and VIb. The base treatment outlined above then provided pure VIb. The free acid VIb failed to undergo smooth hydrogenation under these conditions. The Arndt–Eistert homologation of VIb as described above for the *cis* isomer yielded 78% of the dimethyl ester of VIIb as a colorless oil, b.p. 121–125° (0.8 mm.), $n^{25}D$ 1.4651.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44. Found: C, 65.14; H, 9.49.

Saponification of the ester yielded 98% of the corresponding dicarboxylic acid VIIb with m.p. 132–134° which, after several recrystallizations from ethyl acetate–petroleum ether (b.p. 88–98°), was obtained as colorless needles, m.p. 138–139°. A mixed m.p. with the *cis* isomer was 116–125°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 62.90; H, 8.87.

(28) F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).

(29) E. Schwenk, *et al.*, *J. Org. Chem.*, **7**, 587 (1942); *ibid.*, **9**, 1, 175 (1944).

(30) A. Windaus and W. Hückel, *Ber.*, **56**, 91 (1923).

(31) R. Adams, *et al.*, THIS JOURNAL, **40**, 424 (1918); **42**, 599 (1920).

(32) A. L. Wilds and C. H. Shunk, *ibid.*, **70**, 2427 (1948).

(33) M. S. Newman and P. F. Beal, *ibid.*, **72**, 5163 (1950).

The dihydrazide of VIIb was obtained as colorless, glistening needles after several recrystallizations from ethyl acetate–petroleum ether (b.p. 88–98°); m.p. 172–173°.

Anal. Calcd. for $C_{12}H_{24}N_4O_2$: C, 56.22; H, 9.44. Found: C, 56.13; H, 9.16.

cis-β-**Hexahydrobenzosuberone** (IIIa).—An 8.14-g. sample of *cis*-γ-(2-carboxymethylcyclohexane)-butyric acid (VIIa) was converted to the thorium salt which was mixed with iron powder and pyrolyzed at 350–400° to yield 4.56 g. (77%) of crude ketone. Purification *via* the semicarbazone yielded 1.34 g. (23%) of pure ketone as a colorless oil, b.p. 69–71° (0.1 mm.), $n^{25}D$ 1.4975; $\tilde{\nu}_{max}^{liquid}$ in cm.$^{-1}$ 821, 842, 870, 908, 920, 940, 977, 1006, 1058, 1172, 1195, 1226, 1260, 1343, 1374, 1409, 1453, 1706, 2840, 2900.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.84. Found: C, 79.77; H, 10.76.

The semicarbazone of IIIa was obtained as colorless plates after recrystallization from aqueous ethanol; m.p. 196–197°.

Anal. Calcd. for $C_{17}H_{22}N_3O$: C, 64.54; H, 9.48. Found: C, 64.41; H, 9.52.

The 2,4-dinitrophenylhydrazone of IIIa was obtained as yellow-orange prisms after recrystallization from ethanol; m.p. 128–129°.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40. Found: C, 59.15; H, 6.16.

trans-β-**Hexahydrobenzosuberone** (IIIb).—An 11.40-g. sample of *trans*-γ-(2-carboxymethylcyclohexane)-butyric acid (VIIb) was converted to 5.04 g. (60%) of crude ketone by pyrolysis of the thorium salt. Purification of the ketone via the semicarbazone yielded 1.32 g. (16%) of a colorless oil, b.p. 70–72° (0.2 mm.), $n^{25}D$ 1.4899, $\tilde{\nu}_{max}^{liquid}$ in cm.$^{-1}$ 732, 918, 958, 1000, 1051, 1075, 1124, 1142, 1246, 1281, 1323, 1411, 1450, 1706, 2840, 2900.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.84. Found: C, 79.40; H, 10.99.

The semicarbazone of IIIb was obtained as colorless needles after recrystallization from aqueous ethanol; m.p. 210.5–211.5°.

Anal. Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48. Found: C, 65.00; H, 9.43.

The 2,4-dinitrophenylhydrazone of IIIb was obtained as fine, bright yellow prisms after several recrystallizations from ethyl acetate–petroleum ether (b.p. 88–98°); m.p. 166–167°.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40. Found: C, 59.08; H, 6.36.

β-Benzosuberone was prepared in the hope of using it for the synthesis of III. Tarbell and Page[34] obtained γ-(2-carboxymethylphenyl)-butyric acid from β-(2-carboxyphenyl)-propionic acid by reduction to the diol, conversion to the dinitrile *via* the dichloride followed by hydrolysis. Arndt-Eistert homologation *via* the Newman–Beal method,[33] however, proceeded smoothly and gave the pure acid in *ca.* 60% over-all yield. When the acid was cyclized by pyrolysis of the thorium salt, considerable degradation ensued and the β-benzosuberone produced was contaminated with as much as 25% of α-tetralone. Similar degradations during cyclization have been noted previously[35] although to a lesser extent. Probably the aromatic ring is responsible for its high incidence in the present case. The Dieckmann cyclization is the preferred method in this instance.[34]

Ring Enlargement Experiments

Quantitative Procedure. (a) *in situ* **Method.**—2.0-g. of *cis*- or *trans*-α-decalone was dissolved in 20 ml. of 3% anhydrous potassium carbonate in methanol (prepared by shaking 30 g. of anhydrous potassium carbonate with 1000 ml. of methanol until solution is complete—*ca.* 10 hr.) and was treated, with stirring, with N-nitrosomethylurethan. After the appropriate reaction time, the solvent and volatile products were removed under reduced pressure on the steam-bath, and the residue was taken up in ether and washed with water. Evaporation of the ether yielded the material on which the quantitative infrared measurements were made.

(b) *ex situ* **Method.**—A 2.0-g. sample of *cis*- or *trans*-α-decalone was dissolved in 20 ml. of methanol and treated with an ethereal solution of diazomethane. The product was isolated as described above.

Ring Enlargement of *cis*-α-Decalone.—A 26.7-g. sample (0.175 mole) of *cis*-α-decalone was dissolved in 250 ml. of 3% methanolic potassium carbonate and was treated with 27 g. (0.204 mole) of N-nitrosomethylurethan, added dropwise over a period of 15 minutes. After 1 hour the volatile components were removed under vacuum on the steam-bath, and the residue was treated with 200 ml. of 0.5% sulfuric acid and shaken at room temperature for 12 hours. The resulting product was distilled through a Piros–Glover spinning band column to give: (a) 5.1 g. of *trans*-α-decalone, b.p. 67–84° (3.6 mm.); (b) 9.5 g. of a mixture of *trans*-α-hexahydrobenzosuberone and *cis*-β-hexahydrobenzosuberone, b.p. 84–86° (3.6 mm.); (c) 1.6 g. of a mixture of *cis*- and *trans*-β-hexahydrobenzosuberone, b.p. 87–94° (3.6 mm.); (d) 1.2 g. of hexahydrobenzocycloöctanone, b.p. 94–98° (4 mm.). The identity of the various fractions was based on the 2,4-dinitrophenylhydrazone derivatives isolated from them. The distillation residue (8.0 g.) was recrystallized from ethyl acetate–petroleum ether (b.p. 88–98°) to yield 4.0 g. of colorless needles, which did not change in m.p. upon further recrystallization; m.p. 111–112°. This product was shown to be *trans*-1-hydroxy-1-hydroxymethyldecalin (IX) (*cf.* below).

Ring Enlargement of *trans*-α-Decalone.—A 32.5 g. sample of *trans*-α-decalone was ring enlarged under the conditions described above for the *cis* isomer. The crude product was distilled directly, without prior hydrolysis, through a 15-inch glass helix-packed column to yield: (a) 19.7 g. of a mixture of starting material and oxide, b.p. 65–68° (1.6 mm.); (b) 3.5 g. of a mixture of starting material and *trans*-α-hexahydrobenzosuberone, b.p. 68–69° (1.6 mm.); (c) 3.5 g. of a mixture of *trans*-α-hexahydrobenzosuberone and *trans*-β-hexahydrobenzosuberone, b.p. 70–80° (1.6 mm.); (d) 4.9 g. of *trans*-β-hexahydrobenzosuberone, b.p. 80–82° (1.6 mm.).

trans-**1-Hydroxy-1-hydroxymethyldecahydronaphthalene** (IX).—The same glycol was obtained by hydrolysis of the ring enlargement product from both *cis*- and *trans*-α-decalone (*cf.* above for *cis*). It consisted of colorless needles with m.p. 111–112°.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.94; H, 10.71.

Oxidation of a 0.74-g. sample of the glycol by means of sodium metaperiodate in methanol gave 0.60 g. (98%) of *trans*-α-decalone.

Rearrangement of a 2.0-g. sample of the glycol by refluxing for 30 minutes with 5 ml. of concentrated sulfuric acid in 30 ml. of methanol gave 1.0 g. of *trans–trans*-decahydro-1-naphthylcarboxaldehyde with b.p. 50–60° (0.03 mm.), $n^{32}D$ 1.4840. The aldehyde was identified as the *trans–trans* isomer by oxidation to the known *trans–trans*-decahydro-1-naphthoic acid of m.p. 101.5–102.5° (reported[15] 102°) and transformation to the corresponding amide of m.p. 223–224° (reported[15] 223°). The 2,4-dinitrophenylhydrazone of the aldehyde was obtained, after recrystallization from ethanol, as bright yellow needles with m.p. 170–171.5°. This m.p. differs considerably from the reported value of 203–204°[15] for this isomer.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40. Found: C, 58.56; H, 6.23.

The semicarbazone of *trans–trans*-decahydro-1-naphthylcarboxaldehyde was obtained, after several recrystallizations from aqueous ethanol, as fine, colorless needles with m.p. 194–195°. The reported value for the *trans–cis* isomer of the aldehyde[15] is 176–176.5° while no derivative has been reported for the *trans–trans* isomer.

Anal. Calcd. for $C_{12}H_{14}N_3O$: C, 64.54; H, 9.48. Found: C, 64.51; H, 9.28.

trans-**Hexahydrobenzocycloöctanone** (V).—The crude product obtained from the ring-enlargement of 5.0 g. (0.033 mole) of *trans*-α-decalone with 25 g. (0.19 mole) of N-nitrosomethylurethan was converted to the 2,4-dinitrophenylhydrazone. Recrystallization from ethanol yielded 1.20 g. of material with m.p. 172–176° which upon further recrystallization gave 0.80 g. of the 2,4-dinitrophenylhydrazone as fine, orange needles, m.p. 179–180°.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.88; H, 6.74; N, 15.70.

(34) D. S. Tarbell and G. A. Page, THIS JOURNAL, **75**, 2053 (1953).

(35) L. Ruzicka and W. Brugger, *Helv. Chim. Acta*, **9**, 339 (1926).

The pure 2,4-dinitrophenylhydrazone was converted to the ketone by the procedure of Martin and Demaeker.[36] The crude ketone was evaporatively distilled at 45–55° (0.03 mm.) and obtained in 83% over-all yield as a colorless oil, $n^{32}D$ 1.4974.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.44; H, 11.22.

The semicarbazone of V was obtained as small, colorless needles after recrystallization from ethanol; m.p. 201–202° dec.

Anal. Calcd. for $C_{13}H_{23}N_3O$: C, 65.78; H, 9.77. Found: C, 65.73; H, 10.14.

2-(Decahydro-1-naphthyl)-octahydrospiro[1,3-dioxolane-4,1′(2′*H*)-naphthalene] (X).[37]—A 2.0-g. sample of the glycol IX described above was refluxed for 20 minutes with 20 ml. of 20% sulfuric acid. Several evaporative distillations of the product yielded a very viscous oil, b.p. 130–140° (0.02 mm.), $n^{25}D$ 1.5150.

Anal. Calcd. for $C_{22}H_{36}O_2$: C, 79.46; H, 10.92. Found: C, 78.85; H, 10.75.

Prolonged refluxing of the above material with 2,4-dinitrophenylhydrazine hydrochloride in ethanol yielded the 2,4-dinitrophenylhydrazone of *trans-trans*-decahydro-1-naphthylcarboxaldehyde, m.p. 170–171.5°.

Infrared Analysis.—The quantitative infrared analyses were carried out in carbon disulfide solution in 0.1-mm. thick cells. A Perkin–Elmer model 21 double-beam instrument was used without compensation for the solvent, and corrections for solvent absorption were applied to the calculations.

ST. LOUIS, MISSOURI

(36) R. H. Martin and J. Demaeker, *Nature*, **173**, 266 (1954).

(37) We are indebted to Dr. Leonard T. Capell of *Chemical Abstracts* for information concerning the nomenclature of this compound.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Polynuclear Aromatic Hydrocarbons. IV.[1] Benzo[c]phenanthrenes

BY DONALD D. PHILLIPS AND A. WILLIAM JOHNSON

RECEIVED JUNE 9, 1955

A new method for the preparation of benzo[*c*]phenanthrene derivatives has been developed. Advantage is taken of the polyfunctional nature of the readily available β-methallylsuccinic anhydride (I) which, when treated with benzene in the Friedel–Crafts reaction, gives rise to keto acids II and III, both of which may be converted in good over-all yield to the *gem*-dimethyl derivative XIII, and thence to 5-methylbenzo[*c*]phenanthrene (XVIII). Compounds analogous to XIII are of interest as potential carcinogenic agents and may prove useful in establishing the role of coplanarity in carcinogenesis among polynuclear aromatic hydrocarbons.

One of the most intriguing problems in the study of carcinogenic hydrocarbons has been the correlation between chemical structure and biological activity. Numerous theories have been published[2] on this subject but as yet none has been found satisfactory in all respects.

Although coplanarity has been suggested as a requirement for carcinogenic activity,[3] the importance of this structural feature *per se* has not been fully investigated. Badger[4] has found that partial hydrogenation of several carcinogenic hydrocarbons destroys their activity and has ascribed this to a disruption in the coplanarity of the molecule. The recent important discovery by Miller[5] that 3,4-benzpyrene is rapidly bound to protein in the epidermal fraction of mouse skin indicates that some kind of complex formation takes place and the relative importance of coplanarity in this reaction takes on added significance.

As one approach to this problem we have selected for study the benzo[*c*]phenanthrene (*cf.* XVIII) ring system. Our choice was based on the fact that several of its derivatives are known to be carcinogenic[6] and suitably substituted benzo[*c*]-phenanthrenes are non-planar because of steric interference between carbons 1 and 12.[7] These would be particularly interesting to examine for activity because they still possess the important[8] 9,10-phenanthrene double bond which was absent in most of the reduced hydrocarbons previously tested.[4,9]

Several synthetic routes to the benzo[*c*]phenanthrene ring system have been reported in the recent literature[10,16] but none of them seemed practical for preparing both the hindered and partially reduced derivatives that we wished to investigate. Moreover, we hoped to devise a synthesis based on readily available starting materials so that a variety of substituted benzo[*c*]phenanthrenes could be examined. In this respect, β-methallylsuccinic anhydride (I) seemed eminently suited to our purpose because of its polyfunctional nature and ease of preparation from maleic anhydride and isobutylene.[11] When condensed with benzene in the pres-

(1) Paper III, D. D. Phillips and E. J. McWhorter, THIS JOURNAL, **77**, 3856 (1955).

(2) For an excellent review on the subject of chemical constitution and carcinogenic activity see G. M. Badger in "Advances in Cancer Research," Vol. 2, Academic Press Inc., New York, N. Y., 1954, pp. 73–127.

(3) (a) Reference 2, p. 98. (b) Coplanarity is an important feature in the currently popular "electron density hypothesis" theory as applied to carcinogenic hydrocarbons; see A. Pullman, *Ann. chim.*, **2**, 5 (1947); P. Daudel and R. Daudel, *Biol. méd.*, **39**, No. 4, 1 (1950), and ref. 2, p. 101.

(4) G. M. Badger, *Brit. J. Cancer*, **2**, 309 (1948).

(5) E. C. Miller, *Cancer Research*, **11**, 100 (1951). For proof that the binding is covalent in nature see P. M. Bhargava, H. I. Hudler and C. Heidelberger, THIS JOURNAL, **77**, 2877 (1955).

(6) Reference 2, p. 86.

(7) F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3302 (1954); M. S. Newman and W. B. Wheatley, THIS JOURNAL, **70**, 1913 (1948).

(8) R. Robinson, *Brit. Med. J.*, **I**, 943 (1946); ref. 2, pp. 95–97.

(9) M. J. Shear, *Am. J. Cancer*, **28**, 334 (1936); **33**, 439 (1938); J. L. Hartwell, "Survey of Compounds which Have Been Tested for Carcinogenic Activity," 1st and 2nd Ed., Public Health Service Publication, Washington, D. C., 1940 and 1951.

(10) M. S. Newman, H. V. Anderson and K. H. Takemura, THIS JOURNAL, **75**, 347 (1953); J. Szmuszkovicz and E. J. Modest, *ibid.*, **70**, 2542 (1948); **72**, 566 (1950); C. Djerassi and T. T. Grossnickle, *ibid.*, **76**, 1741 (1954); A. L. Wilds and R. G. Werth, *J. Org. Chem.*, **17**, 1154 (1952); S. M. Mukherji, V. S. Gaind and P. N. Rao, *ibid.*, **19**, 328 (1954); G. T. Tatevosyan and V. O. Babayan, *J. Gen. Chem.*, **22**, 1421 (1952).

(11) K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76B**, 47 (1943).