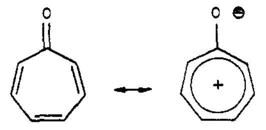
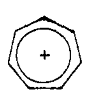
the sum of the values assumed for ΔH_1, ΔH_2 and ΔH_3 in the heptafulvene treatment (−159.0 kcal./mole). The difference between these two figures gives an approximate value of 28 kcal./mole for the resonance energy of heptafulvalene.

Hydrogenation of dihydroheptafulvalene (III) proceeded smoothly in acetic acid solution with absorption of six molar equivalents of hydrogen and a heat evolution of 138.81 ± 0.20 kcal./mole or 69.4 kcal. per cycloheptatriene ring. The latter value is in good agreement with the cycloheptatriene result (−70.5 kcal./mole)[3] if account is taken of non-bonded interactions in the reduction product involving one ring and hydrogen atoms of the other. Comparison of the results obtained for dihydroheptafulvalene and for heptafulvalene (hydrogen uptake, 6 molar equivalents) indicates that the resonance energy involved in the coupling of two cycloheptatriene rings in the latter compound amounts to about 8.0 kcal./mole. It is of interest to note that this figure is approximately twice the value of 4.2 kcal./mole obtained for conjugation of the cycloheptatriene ring and exocyclic double bond in heptafulvene.

Tropone.—Of interest as the oxygen analog of heptafulvene and as the next simpler member of the tropolone system, tropone has been treated theoretically by Brown[49] and has recently been synthesized.[9,50] The basicity of this substance and its chemical stability in acid have led to the formulation of the conjugate acid as a hydroxycycloheptatrienylium ion and to the formulation of tropone itself as cycloheptatrienylium oxide (IV). The considerable stability of the cycloheptatrienylium ion (V), which is regarded as the symmetrical parent of the seven-membered aromatic system, has been clearly demonstrated by Doering and Knox.[51]

The heat of hydrogenation of tropone to cycloheptanone over palladium-on-barium sulfate in acetic acid solution is −67.58 ± 0.30 kcal./mole. Assuming a planar structure for this molecule and using tropilidene (heat of hydrogenation, −70.49 ± 0.39 kcal./mole)[3] as the model for a tropone in which there is no interaction of the carbonyl group with the ring, the extra resonance energy in tropone resulting from this interaction is calculated as 2.9 kcal./mole. Although this stabilization can be rationalized in terms of contributing structures of type IVb, a larger value might have been expected in view of the large resonance energy (3.00 β) calculated for V. It is clear, however, that the stabilization achieved in IVb is accomplished at the expense of considerable electrostatic work of charge separation, which has the effect of reducing the measurable resonance energy.


IVa IVb


V

It should be noted, finally, that the resonance energy associated with coupling of the tropilidene system with a carbonyl group (2.9 kcal./mole) is somewhat less than that derived from coupling with an olefinic linkage (4.2 kcal./mole in heptafulvene). This result finds a parallel in the benzene series where it has been shown that styrene possesses a higher resonance energy (38.2 kcal./mole)[52] than benzaldehyde (35 kcal./mole).[52] A further analogy is provided by the observation that the heat of hydrogenation of pentadiene-1,3 to pentene-1 is 1.1 kcal. lower than that of crotonaldehyde to butyraldehyde.[2c]

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[49] R. D. Brown, *J. Chem. Soc.*, 2670 (1951).

[50] H. J. Dauben and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951).

[51] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[52] The styrene and benzaldehyde values given here are calculated by comparable methods from combustion data (see ref. 24, pp. 98, 99).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Heats of Hydrogenation. IV. Hydrogenation of Some *cis*- and *trans*-Cycloölefins[1]

BY RICHARD B. TURNER AND W. R. MEADOR

RECEIVED FEBRUARY 25, 1957

The heats of hydrogenation of the *cis*- and *trans*-cycloöctenes, cyclononenes and cyclodecenes have been measured in acetic acid solution at 25°. The values (kcal./mole) obtained for these olefins are as follows: *cis*-cycloöctene, −22.98 ± 0.10, *trans*-cycloöctene, −32.24 ± 0.21; *cis*-cyclononene, −23.62 ± 0.07, *trans*-cyclononene, −26.49 ± 0.14; *cis*-cyclodecene, −20.67 ± 0.08, *trans*-cyclodecene, −24.01 ± 0.09.

The heats of hydrogenation of cyclopentene, cyclohexene, cycloheptene and of *cis*-cycloöctene were measured several years ago in the gas phase by Kistiakowsky and his associates. The results of this work (Table I) were correlated by Conn, Kistiakowsky and Smith,[2] who advanced a consistent interpretation of the data based upon consideration of non-bonded repulsions appearing in the products of the various hydrogenation processes. An important outcome of the investigation was the demonstration that the heat of hydrogenation of cyclopentene is 1.7 kcal./mole *lower* than that of cyclohexene, despite the fact that strain of the cyclopentene double bond is clearly *greater* than that of the olefinic linkage in cyclohexene. Al-

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[1] The work reported in this paper was supported by the Eli Lilly Co., Indianapolis.

[2] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **61**, 1868 (1939).

TABLE I

HEATS OF HYDROGENATION OF CYCLOÖLEFINS (GAS PHASE)

Compound	$-\Delta H$(82°, kcal./mole)
Cyclopentene	26.92 ± 0.01[a]
Cyclohexene	28.59 ± .01[b]
Cycloheptene	26.52 ± .02[c]
cis-Cycloöctene[d]	23.53 ± .04[c]

[a] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, THIS JOURNAL, 59, 831 (1937). [b] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, 58, 137 (1936); [c] Data from reference 2. [d] The cycloöctene was prepared by E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, 61, 1057 (1939), by dehydration of cycloöctanol with β-naphthalenesulfonic acid. Material obtained by this route is substantially pure *cis*-cycloöctene.

though the hydrogenation data do not conform with predictions based on strain effects in these molecules, an entirely satisfactory explanation of the results was provided by the observation that the C–H bonds in cyclopentane are extensively eclipsed, whereas those in cyclohexane are staggered.[3] It was thus concluded that the enthalpy difference associated with repulsive interactions arising in the reduction products, cyclopentane and cyclohexane, is sufficiently large to obscure the difference in enthalpy resulting from variations of strain in the corresponding olefins. Calculations of "total strain energy" in the cyclohexane, cyclopentane, cyclohexene and cyclopentene molecules carried out by Pitzer[4] are consistent with this interpretation. The hydrogenation results have been further verified by combustion experiments, which show that the difference between the heats of formation (ΔH°_f, 25°, gas phase) of cyclohexane and cyclopentane (−10.97 kcal./mole)[5] is greater than the difference between the heats of formation of cyclohexene and cyclopentene (−9.57 kcal./mole)[6] by a factor of 1.4 kcal./mole.

In their summarizing paper, Conn, Kistiakowsky and Smith[2] also directed attention to the fact that the heats of hydrogenation of cycloölefins decrease progressively in the series cyclohexene, cycloheptene, *cis*-cycloöctene in a manner suggestive of increased internal crowding in the larger cycloparaffins. The crowding hypothesis is now supported by evidence from a variety of sources which indicates that congestion in the "medium-sized" (8- to 12-membered) rings is severe. Maximum hindrance probably is attained in the cyclodecane system, although this point has not been established with certainty. An excellent summary of work in this field up to 1950 has been given by Prelog.[7] Considerable additional information bearing on the problem of internal hindrance in cyclic systems has appeared more recently. Evidence establishing the close proximity of hydrogen atoms and ring carbon atoms in medium-sized cycles is provided by the remarkable transannular hydride shifts that occur in reactions of cycloöctene,[8] cyclononene,[9] cyclodecene[10] and of cycloundecene[11] with performic acid.[12] Studies of the rates of solvolysis of various cycloalkyl *p*-toluenesulfonates have revealed a marked acceleration of rate in the 7- to 11-membered derivatives, which is attributed to relief of steric strain in the transition states in these instances.[13] Maximum acceleration of solvolysis is observed in the case of cyclodecyl *p*-toluenesulfonate.

Mention should be made finally of the precision combustion measurements of Kaarsemaker and Coops (Table II),[14] which demonstrate that in the cycloparaffin series heats of combustion per methylene group increase in order from the C_6- to the C_9-compounds. Although the numerical differences observed in this series are small, the variations nevertheless fall outside the limits of experimental error.

TABLE II

HEATS OF COMBUSTION OF CYCLOPARAFFINS (GAS PHASE, 25°)

Compound	$-\Delta H$, kcal./methylene group
Cyclopentane	158.7
Cyclohexane	157.4
Cycloheptane	158.3
Cycloöctane	158.7
Cyclononane	158.9
Cyclodecane	*158.6*[a]

[a] Older data of (W. Hückel, A. Gercke and A. Gross, *Ber.*, 66, 563 (1933).

In view of continued interest in the properties of cycloölefins possessing medium-sized rings, and especially in the behavior of the highly strained *trans* isomers,[15] we have measured the heats of hydrogenation of the *cis*- and *trans*-cycloöctenes, cyclononenes and cyclodecenes in acetic acid solution at 25°. The results of this investigation are listed in Table III. For purposes of comparison, the

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(3) This view, which was apparently first expressed in the present connection by V. Schomaker, has since been amply confirmed. *Cf.* W. G. Dauben and K. S. Pitzer, Chapter 1 in "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, and references cited therein.

(4) K. S. Pitzer, *Science*, **101**, 672 (1945).

(5) "Selected Values of Properties of Hydrocarbons," Circular C461 of the National Bureau of Standards (1952).

(6) M. B. Epstein, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **42**, 379 (1949).

(7) V. Prelog, *J. Chem. Soc.*, 420 (1950).

(8) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

(9) V. Prelog, K. Schenker and W. Kung, *Helv. Chim. Acta*, **36**, 471 (1953).

(10) V. Prelog and K. Schenker, *ibid.*, **35**, 2044 (1952); see also V. Prelog, H. J. Urech, A. A. Bothner-By and J. Würsch, *ibid.*, **38**, 1095 (1955).

(11) V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955).

(12) Considerable interest is attached to the fact that *cis*-1,4-cycloheptanediol has been obtained as a minor product in the solvolysis of cycloheptene oxide [A. C. Cope, T. A. Liss and G. W. Wood, *Chemistry & Industry*, 823 (1956)] and that *trans*-1,4-cyclohexanediol has been identified among the products of the reaction of cyclohexene with performic acid [A. C. Cope, H. E. Johnson and J. S. Stephenson, THIS JOURNAL, **78**, 5599 (1956)]. The yields of these substances are, however, exceedingly small. The reaction of cyclododecene with performic acid appears to proceed normally [V. Prelog and M. Speck, *Helv. Chim. Acta*, **38**, 1786 (1955)].

(13) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955); H. C. Brown and G. Ham, THIS JOURNAL, **78**, 2735 (1956).

(14) Sj. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

(15) The preparation and chemistry of the *trans*-cycloölefins has been discussed by: (a) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950); K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kühlhorn and J. Schneider, *ibid.*, **589**, 122 (1951); (b) A. T. Blomquist, R. E. Burge and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952); A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952); (c) A. C. Cope, R. A. Pike and C. F. Spencer, *ibid.*, **75**, 3212 (1953); A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955); (d) V. Prelog, K. Schenker and H. H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952), and reference 9.

solution values for cyclohexene and for cycloheptene[16] are included also.

TABLE III

HEATS OF HYDROGENATION OF CYCLOÖLEFINS (ACETIC ACID SOLUTION)

Compound	Mmoles	PtO_2, mg.	$-\Delta H$(25°, kcal./mole)
cis-Cycloöctene	4.598	100.6	22.88
	4.526	100.5	23.08
		Average	22.98 ± 0.10[a]
trans-Cycloöctene	2.487	99.7	32.44
	2.436	99.6	32.04
		Average	32.24 ± 0.21
cis-Cyclononene	3.517	100.8	23.67
	2.516	99.7	23.56
		Average	23.62 ± 0.07
trans-Cyclononene	3.484	100.7	26.62
	3.609	99.3	26.36
		Average	26.49 ± 0.14
cis-Cyclodecene	3.553	99.3	20.63
	3.937	99.2	20.60
	3.960	100.0	20.77
		Average	20.67 ± 0.08
trans-Cyclodecene	3.744	99.8	23.92
	3.751	99.3	24.07
	3.773	100.7	24.05
		Average	24.01 ± 0.09
Cyclohexene		Average	27.10 ± 0.08[b]
Cycloheptene		Average	25.85 ± 0.09[b]

[a] Deviations include uncertainty in the heat of hydrogenation of the catalyst. [b] Data from reference 16.

Although the data are largely self-explanatory, the following points may be singled out for special comment. It will be noted first that the values obtained for the *cis*-olefins show a decrease of 6.4 kcal. in passing from cyclohexene (−27.1 kcal./mole) to *cis*-cyclodecene (−20.7 kcal./mole). The general trend established for the series cyclohexene to *cis*-cycloöctene (Table I) is thus projected at least as far as the 10-membered ring derivative. While it would appear that increased steric compression in the higher cycloparaffins plays a dominant role in lowering the heats of hydrogenation of the larger cycloölefins, it is clear that differences in angular and repulsive strains in the unsaturated compounds cannot be disregarded. The fact that the heat of hydrogenation of *cis*-cyclononene is higher than that of *cis*-cycloöctene, whereas the inverse relation might have been expected in view of the combustion data of Table II, can best be explained on the basis of such considerations.

In each *cis–trans* isomer pair for which data are given, the *trans* modification possesses the higher heat of hydrogenation and hence the lower stability. The heats of isomerization (*trans* → *cis*) calculated for the 8-, 9- and 10-membered olefins from the hydrogenation results are −9.2, −2.9 and −3.3 kcal./mole, respectively, as compared with the value of −1.0 kcal./mole reported by Kistiakowsky[17] for the heat of isomerization of *cis*-butene into *trans*-butene. Conclusions regarding isomer stability that have been drawn from qualitative studies of the equilibrium behavior of the cyclic olefins in the presence of acid[15] are thereby confirmed and are placed on a quantitative basis. The difference of 9 kcal. observed in the heats of hydrogenation of *cis*- and of *trans*-cyclooctene is the largest yet obtained for any pair of *cis–trans* isomers and reflects the severe strain that accompanies incorporation of a *trans* double bond in the eight-membered ring. The question of the point in the cyclic series at which the *trans* isomer may become more stable than the *cis*, as in open-chain olefins, presents an interesting problem for future investigation.[18]

With reference to the data for *cis*-cyclodecene, mention should finally be made of the fact that the heat of hydrogenation of this substance is the lowest yet recorded for a compound possessing an isolated double bond.[19] The highest such value thus far encountered is that obtained for *cis*-di-*t*-butylethylene (−35.5 kcal./mole).[20] The spread of almost 15 kcal. in the heats of hydrogenation of these two *cis*-disubstituted olefins provides a striking demonstration of the extent to which environmental factors may be implicated in chemical transformations.

Experimental

The calorimetric procedure followed in this investigation was that described in Paper I.[16] Acetic acid was employed as the solvent in all cases, and platinum oxide was used as the catalyst throughout.

Samples of *cis*-cycloöctene, n^{25}_D 1.4690, b.p. 74–75° (84 mm.), and of *trans*-cycloöctene, n^{25}_D 1.4742, b.p. 75° (78 mm.), were kindly supplied by Prof. A. C. Cope. In view of the instability of *trans*-cycloöctene, the specimen of this substance was shipped to us in Dry Ice by air express. Upon receipt, the material was sealed in evacuated ampoules, which were stored at −15°. Measurements were carried out on the two days following arrival of the sample, and at the end of the experiment a spare ampoule was broken and the contents examined in the infrared. The absorption spectrum proved to be identical with that of pure *trans*-cycloöctene showing that no polymerization or isomerization to the *cis* isomer had occurred. Professor Cope has informed us that *trans*-cycloöctene is completely stable in acetic acid solution at room temperature for periods up to 2 hr. Careful examination of the calorimetric time–temperature curves before and after dissolution of the sample, but prior to initiation of the hydrogenation reaction, has confirmed this view.

The cyclononene and cyclodecene samples, which were generously provided by Prof. V. Prelog, possessed the following constants: *cis*-cyclononene, n^{20}_D 1.4791; *trans*-cyclononene, n^{19}_D 1.4789; *cis*-cyclodecene, n^{21}_D 1.4849, b.p. 90.3° (33 mm.); *trans*-cyclodecene, n^{20}_D 1.4799, b.p. 198–199° (760 mm.). The specimens of *cis*-cyclononene and of *cis*-cyclodecene absorbed only 95.3 and 98.0%, respectively, of the theoretical amount of hydrogen. Since both compounds were prepared by partial hydrogenation of the corresponding cycloalkynes, the most likely contaminant would appear to be cycloparaffin. Although impurities of this type would have no effect on heats of hydrogenation

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(16) R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

(17) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935).

(18) The conclusion of N. L. Allinger, *Experientia*, **10**, 328 (1954), derived from correlations of boiling points densities and refractive indices, that *trans*-cyclodecene should be more stable than the corresponding *cis* isomer has been revised in the light of other considerations (N. L. Allinger private communication).

(19) In systems possessing a high degree of resonance stabilization low heats of hydrogenation are, of course, expected. Thus benzene, with a resonance energy of 36 kcal./mole, has a heat of hydrogenation (gas phase) of 16.6 kcal. per "double bond" [G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **58**, 146 (1936)].

(20) Paper VI of this series (forthcoming).

calculated on the basis of hydrogen uptake, the presence of any appreciable amounts of unreduced acetylenes (which would, however, lead to high hydrogen uptake values) would be more serious. Careful scanning of the infrared absorption spectra of the two compounds, however, revealed no trace of acetylenic absorption.

It is a pleasure to acknowledge the considerable contribution made to this work by Professors Prelog and Cope, whose coöperation in supplying samples has been of the greatest assistance.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Reaction of Cyanogen Halides with the Silver Salts of Carboxylic Acids

BY PIERRE H. PAYOT, WILLIAM G. DAUBEN AND LANNY REPLOGLE

RECEIVED SEPTEMBER 4, 1956

The reaction of cyanogen halides with the silver salts of carboxylic acids was studied. The major products were found to be the corresponding nitrile, acid and anhydride. The yields of these three compounds varied with the solvent employed, the yield of nitrile being highest (32%) in acetonitrile, the yield of acid being highest (82%) in nitromethane and the yield of anhydride (88%) in trichloroethylene. It is postulated that an intermediate acyl cyanate is formed and this material reacts further to give rise to nitrile and anhydride.

The silver salt–bromine degradation of Hunsdiecker has been widely used to prepare alkyl halides.[1] Recently, this reaction has been employed in the preparation of complex C^{14}-carboxyl labeled acids according to the following sequence (eq. 1).[2] Considering the relative ease by

$$\mathrm{RCOOH} \xrightarrow[2,\ \mathrm{Br_2}]{1,\ \mathrm{Ag}^{\oplus}} \mathrm{RBr} \xrightarrow{\mathrm{C^*N}^{\ominus}} \mathrm{RC^*N} \xrightarrow{\mathrm{H_2O}} \mathrm{RC^*OOH} \quad (1)$$

which C^{14}-labeled cyanogen halides can be prepared from labeled alkali metal or silver cyanides[3] and the similarity of such compounds with a halogen molecule, a modification and extension of the Hunsdiecker reaction using cyanogen halides instead of bromine was studied. Other than the usual chemical interest in the reaction of pseudohalogens, it also was of interest to see if replacement of an unlabeled carboxyl group by a labeled cyanide group could be achieved in one step (eq. 2).

$$\mathrm{R{-}COOAg} + \mathrm{C^*NX} \longrightarrow \mathrm{R{-}C^*N} + \mathrm{AgX} + \mathrm{CO_2} \quad (2)$$

In 1947,[4] Zappi and Bouso described a similar reaction, and in their work solid alkali metal salts of carboxylic acids were pyrolyzed in the presence of cyanogen halides at temperatures between 200–300° and nitriles were isolated in variable yields. When this reaction was performed with C^{14}-carboxyl labeled benzoic acid, Douglas, Eccles and Almond[5] observed that no displacement occurred, the evolved carbon dioxide was not labeled and the generated benzonitrile was labeled. On the other hand, when a carboxyl labeled aliphatic acid was used in the pyrolysis reaction, the carbon dioxide was labeled and the nitrile was not radioactive.[5] Evaluation of these conflicting results must await further work.

It was obvious that the drastic conditions used in this alkali metal salt and cyanogen halide reaction would limit the usefulness of the reaction to acids of simple structure if, indeed, displacement did occur. If, however, the reaction could be run with the silver salts of carboxylic acids under the conditions of the silver salt–bromine degradation of Hunsdiecker, the reaction might become a valuable method for the introduction of C^{14} into organic compounds. In line with this concept are the findings of Haszeldine and Jander[6] who report that when the silver salt of an aliphatic trifluorocarboxylic acid is allowed to react with nitrosyl chloride under the conditions of the Hunsdiecker reaction, an alkylnitroso compound and carbon dioxide are obtained.

Although the mechanism of the Hunsdiecker reaction is not clearly understood,[1] the most likely route would involve the reaction of a bromine cation, $\mathrm{Br}^{\oplus}$, with the silver salt to form an acylhypohalite which, in turn, would decompose to alkyl halide and carbon dioxide. From what is known of the chemistry of the cyanogen halides,[7] it is clear that under certain conditions these compounds do generate $\mathrm{CN}^{\oplus}$, and it appears that cyanogen chloride would be more likely to do this than cyanogen bromide and the bromide more likely than the iodide.[8] In the present work, cyanogen bromide was utilized since it is easier to handle than the gaseous cyanogen chloride and the easily subliming cyanogen iodide. Furthermore, since the main aim of the study was to obtain a good yield of nitrile, most experiments were not performed under identical conditions. The acid chosen for the most investigations was γ-phenylbutyric acid since this acid shows the features of both an aromatic ring and an aliphatic acid.

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(1) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956); C. H. F. Allen and C. V. Wilson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 578.

(2) S. Bergström, K. Pääbo and M. Rottenberg, *Acta Chem. Scand.*, **6**, 1127 (1952); S. Bergström, M. Rottenberg and J. Voltz, *ibid.*, **7**, 481 (1953); S. Bergström, K. Pääbo and M. Rottenberg, *ibid.*, **7**, 1001 (1953); D. R. Howton, R. H. Davis and J. C. Nevenzel, THIS JOURNAL, **76**, 4970 (1954).

(3) S. Graf, M. Engelman, H. B. Gillespie and A. M. Graf, *Cancer Research*, **11**, 388 (1951); F. Weygand and H. Simon in Houben-Weyl, "Methoden der Organischen Chemie," Vol. IV, part 2, Georg Thieme Verlag, Stuttgart, 1955, p. 558.

(4) E. V. Zappi and O. Bouso, *Ann. asoc. quim. Argentina*, **35**, 137 (1947).

(5) D. E. Douglas, J. Eccles and A. E. Almond, *Can. J. Chem.*, **31**, 1127 (1953).

(6) R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 4172 (1953).

(7) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 97; D. T. Mowry, *Chem. Revs.*, **42**, 189 (1948).

(8) G. Lord and A. A. Woolf, *J. Chem. Soc.*, 2546 (1954); T. Kikindai, *Bull. soc. chim. France*, **18**, 799 (1951).