hydrogen chloride, as might be predicted on the basis of the straight-forward reaction mechanism $(C_3H_7O)_2POH + HCl \rightarrow C_3H_7OP(OH)_2 + C_3H_7Cl$ under conditions of a large excess of phosphite.

Table I

Cleavage of Diisopropyl Phosphite by Hydrogen Chloride

Time, hours	First-order rate constant[a] $K = \frac{1}{t} \ln \frac{C_0}{C}$ $\times 10^5$	Second-order rate constant[a] $K = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_0}\right)$ $\times 10^6$
	At room temperature (25°)	
0	...	...
1	...	...
2	8.09	6.18
19	2.34	1.88
25	2.18	1.79
140.3	1.64	1.89
165.3	1.53	1.85
192	1.48	1.92
259	1.34	1.98
	Average of six values[b]	1.89
	At 40°	
0	...	...
1	20.1	10.9
3	10.9	6.1
5.5	15.7	9.7
6.4	15.3	9.7
7	15.0	9.6
24	11.6	10.5
26	11.2	10.4
28	10.9	10.4
30	10.7	10.6
31	10.5	10.6
	Average of eight values[b]	10.2

[a] Calculated from densities of $(C_3H_7O)_2POH$ of 0.992 and 0.978, and neglecting volume and weight changes due to HCl and reaction products. Units of specific rate constants are sec.$^{-1}$ and liter mole^{-1} sec.$^{-1}$. [b] Values of K at times of less than three hours were not averaged since experimental errors show a comparatively great effect during the initial period of reaction. It may also be that attainment of the equilibrium suggested below is a factor.

That the alkyl phosphites form complexes with hydrogen halides is generally accepted; the hydrogen halides dissolve in dialkyl phosphites with considerable evolution of heat, and are difficult to remove by application of reduced pressure or by sweeping with an inert gas. We observed a heat of solution of 10.7 kcal./mole for the solution of hydrogen chloride in an excess of diisopropyl phosphite (mole ratio of *ca.* $^1/_{160}$) at 25 to 30°.

If it is assumed that dealkylation of the dialkyl phosphites takes place by attack of hydrogen halide on a phosphite–hydrogen halide complex, second-order kinetics in respect to hydrogen chloride might be expected: Assume

$$(RO)_2POH + HCl \rightleftarrows (RO)_2POH \cdot HCl$$

$$(RO)_2POH \cdot HCl + HCl \longrightarrow ROP(OH)_2 \cdot HCl + RCl$$

Then, letting $[HCl]_F$ and $[HCl]_T$ represent the concentrations of free and total hydrogen chloride, respectively,

$$-d[HCl]_F/dt = K[(RO)_2POH \cdot HCl][HCl]_F$$

and

$$K_e = [(RO)_2POH \cdot HCl]/[(RO)_2POH]_F[HCl]_F$$

so

$$-d(HCl)_F/dt = KK_e[(RO)_2POH]_F[HCl]^2{}_F$$

Since

$$[(RO)_2POH] >> [HCl]$$

it is essentially constant and

$$-d[HCl]_F/dt = K'[HCl]^2{}_F$$

Then

$$[HCl]_T = [(RO)_2POH \cdot HCl] + [HCl]_F$$
$$[HCl]_T = K_e[(RO)_2POH]_F[HCl]_F + [HCl]_F$$
$$[HCl]_T = [HCl]_F(K'')$$

and

$$-d[HCl]_T/dt = K'''[HCl]^2{}_T$$

The condition of an excess of dialkyl phosphite in our experiments not only permits simplification in deriving the kinetics for the proposed mechanism, but also tends to minimize the effects of two complicating factors: (1) the consecutive reaction

$$ROP(OH)_2 + HCl \rightleftarrows ROP(OH)_2 \cdot HCl \xrightarrow{HCl} P(OH)_3 + RCl$$

and (2) the equilibrium[4]

$$(RO)_2POH + P(OH)_3 \rightleftarrows 2ROP(OH)_2$$

Employing the Arrhenius equation and the specific rate constants determined at 25° and at 40°, the energy of activation for the cleavage of diisopropyl phosphite by hydrogen chloride is calculated to be 20.9 kcal. per mole.

We wish to thank Dr. G. B. Kistiakowsky for his helpful suggestions.

[4] D. H. Chadwick, P. A. Sanguinetti and E. E. Hardy, presented at the 122nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1952.

St. Louis, Missouri

Air Oxidation of Hydrocarbons. IV. The Effects of Varying Solvent and the Mechanism of Uninhibited Chain Termination

By Charles E. Boozer, George S. Hammond, Chester E Hamilton and Conrad Peterson

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In the previous papers in this series we have shown that in benzene and chlorobenzene the inhibition of cumene and tetralin oxidation can be accommodated by a consistent picture as to the mechanism of the inhibition reactions. In the course of this study we have made other observations, mainly concerned with oxidation in other solvents, which are less complete but are considered to be of sufficient interest to be reported at the present time. The results include some interesting deviant behavior for which no good explanation can be offered at the present time.

Results and Discussion

Rates of Uninhibited Oxidation.—The rate of initiated oxidation at partial pressures of oxygen which are high enough to make the reaction zero order with respect to oxygen and in the absence of added inhibitors is given by the following kinetic law.[1]

$$-\frac{dO_2}{dt} = 2ak_i\,[\text{AIBN}] + \frac{(ak_i)^{1/2}k_3[\text{AIBN}]^{1/2}[\text{RH}]}{k_t^{1/2}} \quad (1)$$

where

$2ak_i[\text{AIBN}]$ = the rate of initiation by azo-bis-isobutyronitrile
k_3 = the rate constant for the reaction of $RO_2\cdot$ with the substrate, RH
k_t = the rate constant for chain termination by bimolecular reaction of two $RO_2\cdot$

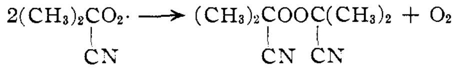
There is no really good information as to the nature of the chain-terminating step[2] so there is no basis for an *a priori* judgment as to the behavior of oxidation rates as solvents are varied. The development of methods for the measurement of initiation rates[3] enables us to correct the observed rates of oxidation of tetralin for variations in the rate of initiation. When this is done, as is shown by the data in Table I, it is found that there is relatively little variation in the ratio $k_3/k_t^{1/2}$. Since k_3 is the rate constant for the propagating hydrogen abstraction reaction it would not be expected to show any great sensitivity to medium effects unless alkylperoxy radicals are in some way complexed with the solvents. Since the ratios of the constants for termination and propagation are nearly constant it is implied that the solvents are not intimately concerned in either the propagation or termination reactions. This is by no means an inescapable conclusion and other lines of reasoning, some of which are given below, lead us to believe that judgment on this question should be reserved at the present time. Similar, but less complete observations, have been made concerning the oxidation of other substrates but are not reported in detail.

TABLE I

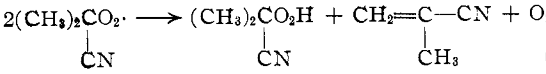
EFFECT OF SOLVENT ON THE RATE OF OXIDATION OF TETRALIN AT 62.5°

Solvent	$k_3/k_t^{1/2} \times 10^3$, $l.^{1/2}$ mole$^{-1/2}$ sec.$^{-1/2}$
Chlorobenzene	9.5
o-Dichlorobenzene	10.5
Nitrobenzene	10.3
Nitromethane	14.2
Carbon tetrachloride	9.4
Diphenyl ether	9.6
66% Trimethylpentane–17% chlorobenzene	9.4

Oxidation of the Initiator.—The oxidation of the initiator in the absence of a substrate should provide some information concerning the chain-terminating step since there is, presumably, no propagation step. The oxygenation of initiator fragments must produce an $RO_2\cdot$ species and these radicals should be destroyed either by reaction with each other or with solvent. Two conceivable reactions for their mutual destruction are



$$2(CH_3)_2\underset{\displaystyle CN}{C}O_2\cdot \longrightarrow (CH_3)_2\underset{\displaystyle CN}{C}OO\underset{\displaystyle CN}{C}(CH_3)_2 + O_2 \quad (2)$$



$$2(CH_3)_2\underset{\displaystyle CN}{C}O_2\cdot \longrightarrow (CH_3)_2\underset{\displaystyle CN}{C}O_2H + CH_2{=}\underset{\displaystyle CH_3}{C}{-}CN + O_2 \quad (3)$$

Since both of these reactions involve the evolution of oxygen the rate of oxygen uptake during the decomposition of the initiator in chlorobenzene was measured and compared with the known rates of efficient production of radicals. The results are not highly precise because of the small volume changes involved. However, it is found that the oxygen uptake exceeds by a small amount the rate of nitrogen evolution. Since the efficiency of AIBN decomposition in chlorobenzene is 0.65 it would be expected that an expansion of the total gas volume should occur if radical destruction were by way of either reaction 2 or 3. A further indication of the same fact is found in the observation that in the oxidation of the initiator in the presence of 2,6-di-*t*-butyl-*p*-cresol slightly less oxygen is consumed than in the absence of the inhibitor. It may be inferred from the nature of the isolated products of this reaction[4] that each reactive fragment produced from the initiator is oxygenated. The experimental data are best presented graphically as in Fig. 1.

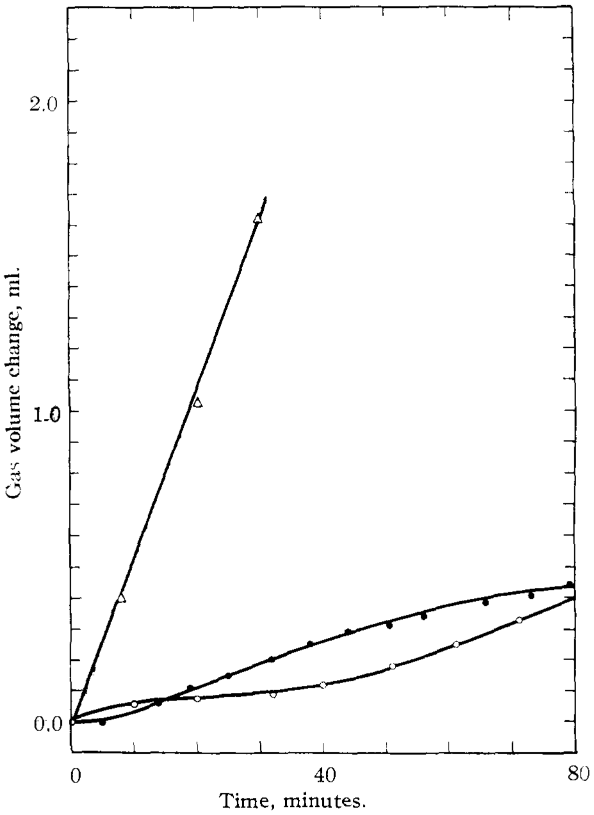


Fig. 1.—Oxidation of 6.1 × 10^{-4} mole of AIBN at 62.5° in chlorobenzene: ●, no added inhibitor; ○, in presence of 3 × 10^{-6} mole of di-*t*-butyl-*p*-cresol; Δ, nitrogen *evolution* in absence of oxygen.

A large batch of the initiator was oxidized in chlorobenzene without definitive results. A maximum of 4.2% conversion of the radicals produced

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(1) Part III, G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3238 (1955).

(2) L. Bateman, *Quart. Revs.*, **8**, 147 (1954).

(3) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(4) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955).

efficiently from the initiator[3] were converted to titratable peroxidic materials. Since iodometric assays were about twice as high in the presence of hydrochloric acid as in the absence of mineral acid, this material was probably part hydroperoxide and part peroxide. Tetramethylsuccinonitrile was isolated along with an oil which showed both carbonyl (1740 cm.$^{-1}$), nitrile (2240 cm.$^{-1}$) and olefinic (1680 cm.$^{-1}$) bands in the infrared. A white, amorphous solid which resembled polymethacrylonitrile and methacrylonitrile–oxygen copolymer also was isolated. A considerable amount of hydrogen cyanide was produced during the reaction. It seems likely that some breakdown of primary products occurs and that the inference of the nature of the reactions which destroy the peroxy radicals will be aided relatively little by a more exhaustive study of the reaction products.

It has been difficult for us to visualize any reaction of two $(CH_3)_2C(CN)O_2\cdot$ radicals which does not involve any third body and which does not lead to the release of oxygen. It is, however, possible that reaction 3 occurs and that more oxygen subsequently is fixed by the oxidation of methacrylonitrile. It can be stated rather unequivocally that the oxygen displacement, reaction 2, does not occur to any significant extent. Another possibility, which should be kept in mind, is that the solvents may become involved in the chain termination step.

Solvent Effects on Inhibitor Stoichiometry.—In Table II the results of a large number of variations in reaction conditions of inhibited oxidations are summarized. The table is organized in such a way as to group the results with a given inhibitor together.

TABLE II

THE EFFECTS OF VARIATION OF SOLVENT AND SUBSTRATE ON STOICHIOMETRIC FACTORS OF THE INHIBITORS

Inhibitor	Substrate	Solvent	Stoichiometric factor
2,6-Di-*t*-butyl-*p*-cresol	Tetralin	CCl_4	1.98
	Methacrylonitrile	CCl_4	1.0
	1-Me-cyclohexene	TMP–$C_6H_5Cl^a$	2.0
	Methacrylonitrile	CH_3NO_2	1.0
	Cumene	$C_6H_5NO_2$	1.9
	Methacrylonitrile	$C_6H_5NO_2$	2.1
4-*t*-Butylcatechol	Cumene	CCl_4	2.06
	Cumene	C_6H_6	2.00
	Tetralin	CCl_4	2.06
	Methacrylonitrile	CCl_4	1.00
	Cumene	TMP–$C_6H_5Cl^a$	2.0
	Tetralin	TMP–$C_6H_5Cl^a$	2.0
	1-Me-cyclohexene	TMP–$C_6H_5Cl^a$	1.0^b
	Methacrylonitrile	CH_3NO_2	2.02
	Tetralin	CH_3NO_2	1.65
	Cumene	$C_6H_5NO_2$	1.4
	Tetralin	$C_6H_5NO_2$	1.8
	Methacrylonitrile	$C_6H_5NO_2$	2.6
	Tetralin	*o*-$C_6H_4Cl_2$	2.0
Diphenylamine	Cumene	C_6H_5Cl	2.8
	Tetralin	C_6H_5Cl	3.5
p-Hydroxydiphenylamine	Cumene	C_6H_5Cl	2.0
	Methacrylonitrile	CCl_4	1.35
	Methacrylonitrile	CH_3NO_2	1.96
N,N,N′,N′-Tetramethyl-*p*-phenylenediamine	Cumene	C_6H_5Cl	1.8
	Tetralin	CH_3NO_2	2.4

[a] Solvent consisting of 80% 2,2,4-trimethylpentene-1 and 20% chlorobenzene. [b] Period of mild retardation follows well defined induction period.

It will be noted that stoichiometric factors vary with both substrate and solvent and the very consistent picture built up to describe inhibition in chlorobenzene and benzene is no longer realized. There is very little regularity in the results obtained with methacrylonitrile as a substrate. This substance oxidizes rapidly and the oxidation is, at least in part, due to oxygen copolymerization rather than to exclusive allylic oxidation. This is evidenced by the isolation of a polymeric material which decomposes on heating. This deviant behavior may be related in some way to the large stoichiometric variations observed.

Another variable which was scrutinized with interest was the aromatic nature of the solvents. This was prompted by the view that in aromatic solvents it is conceivable that $RO_2\cdot$ radicals exist largely as complexes similar to those involved in inhibition.[1] As has already been pointed out the rates of oxidation may be interpreted as indicative of the fact that free $RO_2\cdot$ is involved in both the propagation and termination reactions. The indication is by no means a rigorous proof and, furthermore, it would be possible that radicals are reversibly complexed by the solvent with propagation and termination still involving the uncomplexed radicals which are in equilibrium with complexes. Except with acrylonitrile as the substrate no serious deviations in stoichiometry are observed in carbon tetrachloride or nitromethane solutions. In order to obtain a non-aromatic solvent which was as unreactive toward radicals as possible an attempt was made to use a hydrocarbon. It was found that 2,2,4-trimethylpentene-1 was not a good enough solvent for the initiator and the inhibitors to permit its use. A 4:1 mixture with chlorobenzene was used and showed no important deviations with cumene and tetralin as substrates. Since these compounds are themselves aromatic, an oxidizable olefin, 1-methylcyclohexene, was used as a substrate. This additional reduction in the aromatic content of the medium, which still contained a small amount of chlorobenzene, did change the inhibitory behavior of 4-*t*-butylcatechol. Under these conditions this compound showed two stage inhibition similar to that observed previously in aromatic solvents by 2,5-di-*t*-butylhydroquinone.[4] Whether this change is actually due in any way to the change in the aromatic nature of the medium or is actually a function of the variation in the structure of $RO_2\cdot$ cannot be ascertained. It is interesting to note that 2,6-di-*t*-butyl-*p*-cresol still shows a stoichiometric factor of two in this system.

The study of both solvent effects and the uninhibited chain termination is being continued.

Experimental

Materials.—Many of the materials are described in other places.[1,4] The 2,4,4-trimethylpentene-1 boiled at 101–102°. The methylcyclohexene was prepared in connection with another project and it was not purified further. Methacrylonitrile, a gift from the Shell Development Corp., was fractionally distilled.

Inhibition Periods and Oxidation Rates.—The procedures used were the same as those described before.[4]

Oxidation of AIBN.—Fifteen grams (0.0987 mole) of AIBN was dissolved in 77 ml. of chlorobenzene in a three-necked, round-bottom flask which was fitted with a stirrer, a Friedrich condenser and a gas dispersing delivery tube. An oxygen pressure was applied through the condenser and the mixture was placed in a 62.2° thermostat and stirred for six days. At five different times during the run three 1-ml. samples were removed from the mixture for peroxide assay. In the later samples the use of hydrochloric acid increased the titer by about a factor of two over that obtained in acetic acid with no added mineral acid. The final titer was, however, equivalent to only 2.1% of radicals produced in the decomposition. At the end of the run the gas above the reaction mixture was drawn into aqueous silver nitrate and gave a copious precipitate of silver cyanide. Extensive attempts to isolate other products by fractional recrystallization and solvent extraction using petroleum ether, methylene chloride, alcohol and various solvent mixtures led to the isolation of only tetramethylsuccinonitrile and a white, amorphous solid. The latter showed strong infrared absorption at 2240, 1740 and 1680 cm.$^{-1}$ and, in general, had a spectrum similar to that of polymethacrylonitrile.

Acknowledgment.—We are very grateful for the generous support of this study by the B. F. Goodrich Co.

AMES, IOWA

The Configurations of the 3-Methylcyclopentanones and Related Compounds

BY E. J. EISENBRAUN[1] AND S. M. MCELVAIN

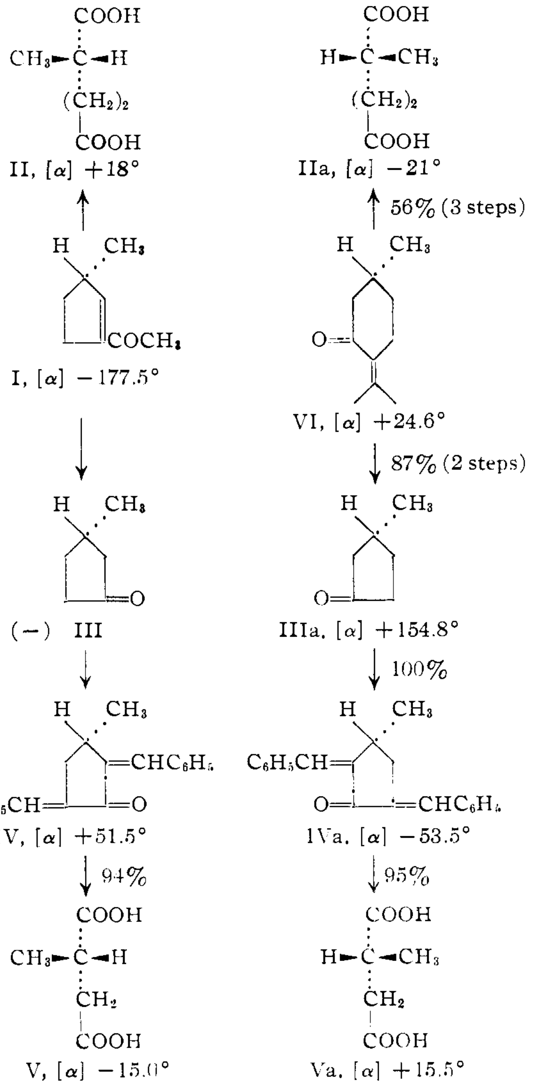
RECEIVED FEBRUARY 21, 1955

In a recent paper[2] the degradation of nepetonic acid *via* (−)3-methylcyclopentenyl methyl ketone (I) to (+)α-methylglutaric acid (II) and to a 3-methylcyclopentanone (III), which formed a (+)-dibenzylidene derivative IV, was reported. The configuration of II and its relationship to (−)lactic acid has been established by Fredga[3] by his method of quasi-racemates. The configurations of III and IV follow from that of II. The preparation of the enantiomorphs of these compounds from pulegone shows that the latter compound and the principal component of oil of catnip have opposite configurations at the ring carbon carrying the methyl substituent.

Pulegone (VI) was converted to (−)α-methylglutaric acid (IIa) *via* the ozonolysis of the (−)dibenzylidene derivative of (+)3-methylcyclohexanone; also VI was transformed *via* (+)β-methyladipic acid to (+)3-methylcyclopentanone (IIIa), which yielded the (−)dibenzylidene derivative IVa. The equivalence of the magnitudes of the rotations of the enantiomorphs IV and IVa indicates their optical purity and the rotations of IIIa, IVa and IV establish the direction of rotation of III as (−). The ozonolyses of IV and IVa to the corresponding methylsuccinic acids, V and Va, confirm an earlier[4] configurational relationship of (+)β-methyladipic acid to Va and verify Fredga's conclusion that the methylsuccinic acids and α-methylglutaric acids of opposite rotations have the same configurations.[3,5]

The configuration III assigned to (−)3-methylcyclopentanone is in accord with the calculated configuration of this ketone.[6] It is, however, the reverse of that assigned to this ketone by Hückel.[7]

The orientations of the 2- and 3-substituents relative to the 1-methyl substituent on the cyclopentane nucleus of nepetonic acid and its precursors, nepetalic acid and nepetalactone, have been determined.[2] Consequently, the assignment of configuration III to the 3-methylcyclopentanone derived from these compounds establishes the absolute configurations of their ring substituents as the opposite of those shown in the recent paper.[2]



Experimental

(−)α-Methylglutaric Acid (IIa).—A 26.3-g. sample of (+)pulegone (VI), boiling at 102–102.5° (17 mm.), $n^{24.8}_D$ 1.4853, $\alpha^{25.5}_D$ +22.47° (*l* 1 dm., neat), $[\alpha]^{26.5}_D$ + 24.6° (*c* 2.88, $CHCl_3$), $\lambda^{95\%\ EtOH}_{max}$ 252 mμ, log ε 3.85,[8] whose infrared spectrum agreed with the literature[8] and whose red 2,4-dinitrophenylhydrazone melted at 148–149°[8] was hy-

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[1] Wisconsin Alumni Research Foundation Research Assistant (1952–1954); Carbide and Carbon Chemicals Company Fellow (1954–1955).

[2] S. M. McElvain and E. J. Eisenbraun, THIS JOURNAL, **77**, 1599 (1955).

[3] A. Fredga, *Arkiv. Kemi, Mineral. Geol.*, **24A**, No. 32 (1947).

[4] J. von Braun and F. Jostes, *Ber.*, **59**, 1091 (1926).

[5] *Cf.* also V. H. T. James, *Chemistry and Industry*, 1388 (1953).

[6] (a) J. F. Lane, *Science*, **113**, 577 (1951); (b) W. J. Kauzmann, J. E. Walter and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); (c) *cf.* also D. S. Noyce and D. B. Denny, THIS JOURNAL, **76**, 768 (1954).

[7] W. Hückel, "The American FIAT Review I," Vol. 34, M. H. Davidson Co., New Haven, Conn., 1951, p. 79, assigns configuration III to (+)3-methylcyclopentanone; *cf.* also A. Fredga and J. K. Miettinen, *Acta Chem. Scand.*, **1**, 371 (1947).

[8] W. Kuhn and H. Schinz, *Helv. Chim. Acta*, **36**, 161 (1953).