JOURNAL OF CATALYSIS 10, 52–59 (1968)

Intermediate Steps in Autoxidation

III. Reactions of Mn^{III} Acetate in Acetic Acid with Benzene, Chlorobenzene, and Toluene

R. E. VAN DER PLOEG, R. W. DE KORTE, AND E. C. KOOYMAN*

From the Laboratory of Organic Chemistry, Leiden University, The Netherlands

Received July 11, 1967; revised October 12, 1967

Product data on the reactions of manganic acetate in glacial acetic acid with benzene (100°C), chlorobenzene, or toluene (110°C) indicate that HOOC–$CH_2\cdot$ radicals are the primary intermediates. Presumably, these are formed from manganic acetate and acetic acid in a concerted step. In the absence of benzene derivatives, they react with manganic acetate to form acetoxyacetic acid or dimerize to succinic acid; acetoxyacetic acid is further degraded to methylene diacetate.

Benzene, chlorobenzene, or toluene add on HOOC–$CH_2\cdot$radicals, forming phenylacetic acid(s); these in turn are further degraded to benzyl acetate(s), benzal diacetate(s) and benzaldehyde(s) which are the main products, accounting for more than 60% of the oxidizing agent. In the presence of potassium bromide, toluene reacts at a much higher rate; products then are mainly benzyl acetate and benzyl bromide. Rates of reduction of Mn^{III} acetate in the presence of manganous acetate are not affected by large proportions of benzene or chlorobenzene; toluene has a slight accelerating effect.

Products and mechanisms are compared with those obtaining in oxidations by manganic acetate in which electron transfer is the primary step.

INTRODUCTION

Parts I and II of this series (*1*, *2*) dealt with enolization as the rate-determining step in the manganese-catalyzed autoxidation of acetophenones in glacial acetic acid solution. Evidence was presented demonstrating that the enols are rapidly oxidized by manganic acetate to produce the chain-carrying phenacyl radical. In earlier work manganic acetate in glacial acetic acid was found to be an effective oxidizing agent for many organic substrates, viz., dihydroanthracene, anthracene, triphenylmethane, 2,6-di-*tert*-butyl-*p*-cresol, and anthrone (*3*) as well as α-hydroxy acids (*4*), thioanisoles, and dimethylanilines (*5*).

In the present paper, we discuss the reactions of manganic acetate with benzene, chlorobenzene, and toluene in glacial acetic acid solution. They appear to belong to a group characterized by product formation through subsequent reactions of HOOC–$CH_2\cdot$radicals formed in the primary thermolysis of the oxidizing agent—in contrast to the former group where direct interactions are predominant.

Exploratory work by one of us on the oxidation of toluene (*4*) yielded as the main products, accounting for more than 65% of the manganic acetate decomposed, *o*-, *m*-, and *p*-methylbenzyl acetate besides a small proportion of the plausible benzyl acetate, benzaldehyde, and bibenzyl. The origin of the methyl group in the methylbenzyl acetates was not accounted for.

After the present investigation had been

---

* To whom inquiries should be sent.

completed, Dewar and several co-workers reported on the oxidations of anisoles, benzanthracene, and other more or less "basic" substrates by means of manganic acetate dihydrate in glacial acetic acid (*6*). Their interpretations were based on direct interaction between the organic substrate and manganic acetate, leading to electron transfer [see ref. (*3*)].

Recently, we obtained evidence that anhydrous manganic acetate in glacial acetic acid is a trimeric rather than a monomeric species; for simplicity, however, reactions of manganic acetate will be represented here as proceeding through $Mn(OAc)_3$. An analytical study of manganic acetate, including the important spectroscopical changes occurring upon the addition of manganous acetate will be published shortly (*7*).

METHODS

1. Starting materials. Benzene, chlorobenzene, toluene, and glacial acetic acid were analytical grade commercial samples checked by means of gas-liquid chromatography. Manganic acetate (*4, 8*) was prepared by oxidation of anhydrous manganous acetate in glacial acetic acid containing 7% of acetic anhydride by shaking with finely ground potassium permanganate at room temperature for 15 min, followed by 15 min at 40°C. The solution was evaporated to 40% of its original volume; after 3 days the crystals were collected, washed with glacial acetic acid and diethyl ether, and finally dried over solid potassium hydroxide in an evacuated desiccator. Found: 74.5% acetate (7), 23.0% Mn^{III} (iodometrically). Calculated for $Mn(OAc)_3$:76.3% acetate, 23.7% Mn^{III}.

Manganic propionate (*9*) was synthesized by dissolving manganous carbonate in an excess of propionic acid at reflux temperature; the solution was then oxidized at room temperature with the equivalent amount of finely ground potassium permanganate after addition of 5% of propionic anhydride. It was concentrated to about one-third of its original volume; after the addition of petroleum ether (b.p. 120°), manganic propionate precipitates and is collected after a few days' standing. The product is washed with dry diethyl ether and dried over phosphorus pentoxide in a desiccator. On the basis of iodometric titration, it contained 93% Mn^{III} propionate.

2. Standard samples used in product identifications. Benzyl acetate, tolualdehydes, chlorotoluenes, and chlorobenzaldehydes were pure commercial samples (Fluka), checked by means of gas-liquid chromatography.

The benzaldehydes were converted to the corresponding diacetates, acids, and carbinols by standard methods; benzyl acetates were obtained by acetylation of the carbinols or via the corresponding bromides. Further data are recorded in Table 1.

3. Analytical methods. Manganic acetate was determined iodometrically; for low concentrations, the absorption band at 462 mμ was used. In gas-liquid chromatography, Carbowax, Apiezon, asphalt (with temperature programming), fluorinated silicon oil, or Porapak Q columns were used. Separation of meta and para isomers was often incomplete; the ortho/(meta + para) ratios checked well with the infrared data. NMR data also led to o/m + p ratios of isomers. All analyses were based on standard samples of the pure compounds. Carbon dioxide and methane were collected by means of a gas burette and determined mass spectrometrically.

4. Kinetic runs. Typical intakes were 0.15 mmoles of manganic and of manganous acetate, 20 mmoles of the benzene derivative (if any) and 870 mmoles (50 ml) of glacial acetic acid. Flasks were completely immersed in thermostated oil baths and trivalent manganese determined at various intervals.

5. Preparative runs. These were run on a larger scale, and with a higher proportion of the benzene derivative; no manganous acetate was added. As in the kinetic runs, oxygen was excluded.

A typical run had the following intake: Glacial acetic acid, 2500 ml (about 42 moles); manganic acetate, 92.8 g (400 m.at. of Mn^{III}) and 433 g of toluene (4.7

TABLE 1
STANDARD SAMPLES USED IN PRODUCT IDENTIFICATIONS

Compound	M.p.[a] (°C)	B.p.[a] (°C/mm Hg	Elementary analysis		NMR[b] (ppm)	Infrared (Characteristic peaks, cm^{-1})
			Found	Calculated		
o-Cl-benzyl acetate[c]	—	72°/0.8	19.5% Cl	19.2% Cl	5.13	756
m-Cl-benzyl acetate[d,e]	—	80°/1.1	19.2% Cl	19.2% Cl	4.97	—
p-Cl-benzyl acetate	—	78°/1 (240°[f])	18.9% Cl	19.2% Cl	4.97	1017
o-Cl-benzal diacetate	52–53° (51–53°[g])	157°–158°/10	14.6% Cl	14.6% Cl	7.83	—
m-Cl-benzal diacetate	64–65° (65°[h])	—	14.3% Cl	14.6% Cl	7.50	—
p-Cl-benzal diacetate	81–82° (82°[h])	—	14.6% Cl	14.6% Cl	7.50	—
o-Cl-phenylacetic acid	93–94° (95°[i])	—	20.8% Cl	20.8% Cl	—	768, 759
m-Cl-phenylacetic acid	74° (76°[j])	—	20.8% Cl	20.8% Cl	—	1073
p-Cl-phenylacetic acid	102–103° (105°[i])	—	20.6% Cl	20.8% Cl	—	804
o-Methylbenzyl acetate	—	104–105°/13 (228–230°[k])	73.4% C; 7.5% H	73.2% C; 7.3% H	5.02	744
m-Methylbenzyl acetate	—	110°/15 (226°[l])	73.1% C; 7.3% H	73.2% C; 7.3% H	4.93	780
p-Methylbenzyl acetate	—	103–104°/13 (121°/18[m,n])	73.6% C; 7.4% H	73.2% C; 7.3% H	4.93	807

[a] Values in parentheses are from the literature.

[b] Peaks due to α-C–H (Varian A 60, CCl_4 solvent) relative to TMS.

[c] Häring, M., *Helv. Chim. Acta* **43,** 104 (1960).

[d] Davies, D. I., *J. Chem. Soc.* p. 2351 (1963).

[e] Fieser, L. F., Clapp, R. C., and Daudt, H. W., *J. Am. Chem. Soc.* **64,** 2052 (1964).

[f] Beilstein, F., and Kuhlborg, A., *Ann.* **147,** 345 (1868).

[g] Sherlin, S. M., *J. Gen. Chem.* (*USSR*) **6,** 508 (1936).

[h] German Patent, 173.020 (Kl. 39 b).

[i] Mehner, H., *J. Prakt. Chem.* (2) **62,** 554 (1900).

[j] Kenner, J., and Morton, F., *J. Chem. Soc*, p. 679 (1934).

[k] Grignard, M. V., *Bull. Soc. Chim. France* **29,** 953 (1903).

[l] Vollrath, A., *Ann.* **144,** 262 (1867).

[m] Thiele, J., and Balhorn, H., *Ber.* **37,** 1463 (1904).

[n] Stephen, H., Short, W. F., and Gladding, G., *J. Chem. Soc.*, p. 520 (1920).

moles). After 24 hr at 110° trivalent manganese had completely disappeared.

Neutral products were isolated by pouring the reaction mixture into an excess of water; the mixture was extracted several times with diethyl ether. The ethereal solution was extracted with sodium bicarbonate solution and dried over anhydrous $MgSO_4$. Ether was then carefully removed on a 10-plate column, the residue being unconverted toluene and neutral reaction products. This residue was separated by fractional distillation into a series of cuts, which were separately analyzed by GLC, infrared, and NMR.

Acidic aromatic products were obtained via the above bicarbonate extract as well as via separate runs worked up by distillation of excess toluene (benzene or chlorobenzene) and acetic acid. The residue was then poured into water and the mixture extracted with diethyl ether; the aqueous layer was evaporated to dryness and then treated with concentrated HCl solution. The acids liberated were extracted with benzene. Benzene and ether extracts were combined and the acids isolated via extraction with alkali.

Results and Discussion

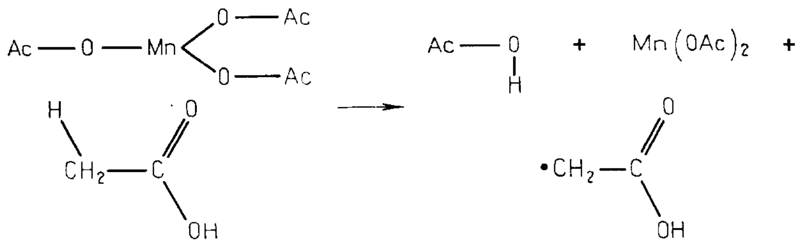
A. *Decomposition of Manganic Acetate in Glacial Acetic Acid*

The main products based on conversion of manganic to manganous acetate (% molar) were carbon dioxide (14.6%), acetoxyacetic acid (20%), succinic acid ($\leq 2\%$), and methylene diacetate; methane (2%) and methyl acetate were detected in low proportions. The chromotropic acid test for formaldehyde was positive, which may have been partly due to methylene diacetate.

These data indicate that little decomposition takes place by the direct loss of an acetoxy fragment [Eq. (1)]:

$$\mathrm{Mn(OAc)_3} \rightarrow \mathrm{Mn(OAc)_2} + [\mathrm{CH_3CO_2}\cdot] \qquad (1)$$

This would require the formation of 100% carbon dioxide as well as large proportions of methane, derived from solvent attack by methyl radicals resulting from the highly unstable acetoxy fragment. It is preferred, therefore, to ascribe product formation to the generation of $HOOC{-}CH_2\cdot$radicals. These species might arise from a concerted decomposition of the oxidizing agent and a molecule of the acetic acid solvent, without the formation of a kinetically free acetoxy radical, e.g.,



(2)

The following set of subsequent reactions starting from $HOOC{-}CH_2\cdot$radicals is proposed:

$$\mathrm{HOOC{-}CH_2\cdot} + \mathrm{Mn(OAc)_3} \rightarrow \mathrm{HOOC{-}CH_2{-}OAc} + \mathrm{Mn(OAc)_2} \qquad (3)$$

$$2\mathrm{HOOC{-}CH_2\cdot} \rightarrow \mathrm{HOOC{-}CH_2{-}CH_2{-}COOH} \qquad (4)$$

$$\mathrm{HOOC{-}CH_2{-}OAc} + \mathrm{Mn(OAc)_3} \rightarrow \mathrm{AcO{-}CH_2{-}COO{-}Mn(OAc)_2} + \mathrm{HOAc} \qquad (5)$$

$$\mathrm{AcO{-}CH_2{-}COO{-}Mn(OAc)_2} \rightarrow \mathrm{AcO{-}CH_2\cdot} + \mathrm{CO_2} + \mathrm{Mn(OAc)_2} \qquad (6)$$

$$\mathrm{AcO{-}CH_2\cdot} + \mathrm{Mn(OAc)_3} \rightarrow \mathrm{AcO{-}CH_2{-}OAc} + \mathrm{Mn(OAc)_2} \qquad (7)$$

Reactions (3) and (7) may be visualized as an induced decomposition of manganic acetate, resembling that of diacyl peroxides, viz., addition of a radical to the carbonyl oxygen atom, forming an ester plus manganous acetate in a single step. (Oxidation of the radical to form a carbonium ion, e.g., $HOOC{-}CH_2^+$, would seem to be less plausible because of the high energy of ionization required in such a process.)

Ligand exchange (5) constitutes a very plausible reaction. In fact, when dissolving manganic acetate in propionic acid formation of acetic acid was observed to occur readily at room temperature as shown by GLC.

Decarboxylation (6) may be a multiple fission process, metal–oxygen and carbon–carbon bond rupture occurring simultaneously. Such a reaction should be facilitated by resonance stabilization of the carbon radical formed, i.e., it should be easier for the group $-OOC-CH_2-OAc$ than for $-OOC-CH_3$. It may be noted that the $AcO-CH_2\cdot$ radical resembles the intermediates formed from vinyl acetate in radical polymerization.

An alternative pathway for decarboxylation would be that the radical $AcO-\dot{C}H-COOH$ is formed (analogous to the formation of the radical $HOOC-CH_2\cdot$); a type (5) reaction would then lead to diacetoxyacetic acid which could decarboxylate to methylene diacetate (*10*).

The above scheme appeared to be consistent with product formation observed when benzene, chlorobenzene, or toluene were present (Section B) as well as with kinetic data.

Rates of Reduction

The Mn^{III} reduction rate showed a first order behavior up to 60–70% conversion only when a molar proportion of manganous acetate had been added. Otherwise, deviations were observed, initial rates (up to 25% conversion) then being appreciably higher. Starting from concentrations of tri- and bivalent manganese acetate of about 0.3% molar, first order rate constants were found to be 0.028 hr^{-1} at 90°C and 0.19 hr^{-1} at 108°C. From these two data, the Arrhenius energy of activation is computed to be about 28 kcal/mole. The deviation at high conversions may be attributable to contributions of steps (5)–(7).

The important effect of manganous acetate on the reduction rate is believed to be due to the formation of a new complex, containing both trivalent and divalent manganese, from the original trimer.

Exploratory work (*9*) on the thermolysis of manganic *propionate* has led to somewhat higher rates of reduction in propionic acid as the solvent, viz., 0.19 hr^{-1} at 90°. Similar results were obtained when starting from the acetate in the same solvent. In contrast to manganic acetate, the propionate appeared to be soluble in benzene or chlorobenzene; in these solvents, the rate of disappearance of Mn^{III} was, however, more than ten times lower than in propionic acid. The phenomenon is taken as evidence for a direct interaction between the manganic compound and the carboxylic acid solvent; the increase of rate when going from acetate to propionic acid is probably attributable to the lower α-C–H bond strength in the latter. Decomposition of the propionate in benzene and in chlorobenzene led to appreciable proportions (>5%) of ethylbenzene and of ethylchlorobenzenes, respectively; this suggests that, in the absence of propionic acid, ethyl radicals are formed, presumably by a type (1) reaction. (Cf. the data on *methylated* products ($ArCH_3$) in Table 2.)

B. *Decomposition of Manganic Acetate in Glacial Acetic Acid Containing Benzene, Chlorobenzene, and Toluene*

Results of preparative runs are given in Tables 2 and 3.

Percentages of carbon dioxide were somewhat higher in the benzene runs (22%) than with chlorobenzene (17%); in the absence of the benzene derivatives it amounted to 15%. This trend suggests that CO_2 arises from decarboxylation of $ArCH_2COOH$ (see Table 2), which are intermediates in the formation of the benzyl acetates; further oxidation of the latter could then lead to benzaldiacetates and benzaldehydes. Nuclear substituents are derived from the acetic acid. Isomer distributions are characterized by appreciable proportions of meta isomers. The data further indicate that the trace amounts of $ArCH_3$ found cannot have been precursors of the benzyl acetates, etc. They must have arisen from a pathway different from that responsible for the formation of the other products, presumably nuclear methylation following a very small contri-

TABLE 2

Aromatic Products from Mn^{III} Acetate in Glacial Acetic Acid and Benzenes

Aromatic compound (ArH)	Products[a]					% Mn^{III} accounted for
	$ArCH_3$[b]	$ArCH_2COOH$	$ArCH_2OAc$	$ArCH(OAc)_2$	ArCHO	
Benzene	+	8	51	9	18	86
Chlorobenzene	+	13	21	17	11	62
Toluene	—	—	67	—	7	87[c]

[a] Runs with benzene at 101°, otherwise at 110°. Figures refer to the percentage of Mn^{III} required for formation of the various compounds.

[b] Toluene as well as the chlorotoluenes were positively identified, amounts being of the order of 0.5%; xylenes could not be detected (<0.1%).

[c] Toluene gave also benzyl acetate (10%), benzaldehyde (3%) and a trace of bibenzyl; no attempts were made to detect $ArCH_2COOH$ or $ArCH(OAc)_2$.

bution of type (1) decomposition of manganic acetate.

A preparative run with phenylacetic acid as the substrate led to benzyl acetate, benzal diacetate, and benzaldehyde, i.e., the same products as when starting from benzene. Rates of reduction of Mn^{III} were appreciably higher, however, viz. $k = 0.58$ hr^{-1} at 80°. Carbon dioxide formation amounted to 43% based on Mn^{III} consumed. Earlier, it had been found that a very large excess of phenylacetic acid reacts with manganic acetate to form the benzyl ester of phenylacetic acid (*4*). These data support the formation of the esters via decarboxylation of the free acids. Formation of phenylacetic acid was demonstrated by Ikeda to occur in good yields when treating benzene derivatives such as chlorobenzene or anisol with diacetylperoxide in glacial acetic acid (*11*). In this case, the reactions must have proceeded through the $HOOC\text{–}CH_2\cdot$ radical.

Accordingly, the present results can be rationalized in terms of the following reactions, starting from $HOOC\text{–}CH_2\cdot$ generated by a type (2) process:

$$2HOOC\text{—}CH_2\cdot + ArH \xrightarrow{\text{Two steps}} ArCH_2COOH + HOAc \quad (8)$$

$$ArCH_2COOH + 2Mn(OAc)_3 \xrightarrow{\text{Two steps}} ArCH_2\text{—}OAc + 2Mn(OAc)_2 + CO_2 + HOAc \quad (9)$$

In this scheme (8) consists in the well-established nuclear substitution sequence, the fact that all *three* isomers were formed from chlorobenzene or toluene being consistent with a radical rather than an electrophilic attack. Sequence (9) is analogous to that postulated for acetoxyacetic acid, a benzyl radical being formed simultaneously with carbon dioxide. The alternative route for decarboxylation mentioned for the formation of methylene diacetate seems improbable here, *o*-acetyl mandelic acid being quite stable in refluxing acetic acid.

TABLE 3

Isomer Ratios[a] of Nuclear Substitution Products Formed from Toluene and Chlorobenzene with Manganic Acetate (110°)

From chlorobenzene	*o*	*m*	*p*	From toluene	*o*	*m*	*p*
Chlorobenzyl acetates	46	+	+	Methylbenzyl acetates	58	23	19
Chlorobenzaldehydes	39	+	+	Tolualdehydes	39	+	+
Chlorophenylacetic acids	≃40	+	+				
Chlorobenzal diacetates	≃30	+	+				

[a] Percentages; + refers to positive identification, but incomplete separation (GLC, NMR) of meta and para isomers, formed in comparable amounts.

Rates of Disappearance of Manganic Acetate

In the presence of benzene or chlorobenzene the manganic acetate disappearance rate showed a first order behavior and approximately the same rate constants (108°C) as in the absence of these compounds, viz. 0.20 and 0.21 hr^{-1}, respectively. With toluene, the rate of reduction of manganic acetate was nearly doubled, viz. 0.40 hr^{-1}. The addition of an equimolar proportion of potassium bromide (relative to Mn^{III}) led to appreciable rate enhancement ($k = 0.12$ hr^{-1} at 39.5°). Preparative runs with this system gave benzyl acetate, benzyl bromide, benzaldiacetate, and benzaldehyde as the main products; methylbenzyl acetate could not be detected (*4*)! Apparently, a different reaction obtains, bromine atoms being formed which then attack the side chain. The use of (inorganic) bromides as co-catalyst in autoxidations of alkylbenzenes is mentioned in several recent patents (*12*); their effectiveness is probably attributable to the high reactivity of bromine atoms with regard to side-chain attack.

C. *Some Mechanistic Considerations*

The fact that even large proportions of benzene or chlorobenzene do not affect the rate of Mn^{III} reduction suggests that direct interactions between the aromatic ring and the oxidizing agent do not contribute to the reduction process. Product formations can be satisfactorily explained in terms of $HOOC–CH_2\cdot$ radicals as the primary intermediates. The acceleration observed with toluene might be due to a contribution from electron transfer; however, in the preparative runs, a 12 times lower proportion of toluene—relative to Mn^{III}—was used and, accordingly, electron transfer, eventually leading to benzyl acetate could have been only a minor product-forming step. Moreover, part of the latter compound may have been formed by side chain attack, $HOOC–CH_2\cdot$ forming acetic acid and a benzyl radical. The relatively rapid oxidations of dihydroanthracene and of triphenylmethane reported earlier (*3*) probably proceed by mechanisms similar to that proposed by Dewar *et al.* (*6*) for *p*-methylanisole and related compounds, i.e., by electron transfer as the primary step, followed by loss of a proton to form the benzyl-type radical; the latter may then react by a type (5) reaction to give the acetate.

The presence of two molecules of water of crystallization per atom of manganese may cause a certain stabilization of Mn^{III} acetate. Thus, the half-life reported by Dewar *et al.* for manganic acetate in the presence of a half-molar proportion of anisole (950 min at 100°C) is even greater than that observed by us for Mn^{III} in glacial acetic acid alone. The American authors did not determine the half-life of their manganic acetate as such, beyond stating that decomposition was slow. In our hands, the rate of reduction of anhydrous manganic acetate ($k_{90°} = 0.03$ hr^{-1}) was not affected by a molar proportion of anisole; an eightfold acceleration ($k'_{90} = 0.23$ hr^{-1}) was observed when using as much as 130 moles per atom of manganese.

In this connection, it is of interest to note that Dewar *et al.* detected *p*- and *o*-methoxybenzyl acetate—via crystalline derivatives of the corresponding benzylalcohols—after the reaction with anisole; meta isomers were not excluded, however. Product formation was attributed to electrophilic formylation by formaldehyde; if little effect of anisol on rates of Mn^{III} reduction also takes place with manganic acetate dihydrate, our present data would suggest that the *three* isomeric methoxybenzyl acetates are formed, electrophilic formylation merely leading to para- and ortho-isomers.

ACKNOWLEDGMENT

Our thanks are due to Dr. H. van Zwet for helpful suggestions.

REFERENCES

1. DEN HERTOG, H. J., JR., AND KOOYMAN, E. C., *J. Catalysis* **6**, 347 (1966).
2. DEN HERTOG, H. J., JR., AND KOOYMAN, E. C., *J. Catalysis* **6**, 357 (1966).
3. VAN HELDEN, R., AND KOOYMAN, E. C., *Rec. Trav. Chim.* **80**, 57 (1961).

4. De Korte, R. W., Thesis, Leiden, The Netherlands, 1964.
5. Bronsdijk, J. W., Thesis, Leiden, The Netherlands, 1965.
6. Andrulis, P. J., Jr., Dewar, M. J. S., Dietz, R., and Hunt, R. L., *J. Am. Chem. Soc.* **88,** 5473 (1966); Aratani, T., and Dewar, M. J. S., ibid., p. 5479; Andrulis, P. J., Jr., and Dewar, M. J. S., ibid., p. 5483.
7. Hessel, L. W., de Klein, W. J., and Kooyman, E. C., to be published.
8. Van der Ploeg, R. E., Thesis, Leiden, The Netherlands, 1967.
9. Steggerda, W. A., and Van der Ploeg, R. E., work carried out in this Laboratory.
10. Kharasch, M. S., Friedlander, H. V., and Urry, W. H., *J. Org. Chem.* **16,** 538 (1951).
11. Ikeda, Y., *Chem. Abstr.* **54,** 4507c, 5557c (1960); *Nippon Kagaku Zasshi* **79,** 1110, 1223 (1958).
12. U. S. Patents 2,963,508, and 3,069,462, for example.