cyclohexene were also present; the first compound may be the precursor of toluene. The absorptivity value used for this calculation was reported previously.[13]

The experimental results summarized in Table IV suggest that the aromatization of 1,1-dimethylcyclohexane to o-xylene proceeds stepwise, *via* the formation of *gem*-dimethylcyclohexene and cyclohexadiene and that the latter then undergoes a dehydroisomerization reaction as indicated in Table IV.

SUMMARY

(1) The effect of aluminas in the platinum-alumina catalysts have been investigated in regard to the aromatization of 1,1-dimethylcyclohexane (I) and 4,4-dimethylcyclohexene (II).

(2) The aromatization of I and II can be used as a measuring stick for the determination of acidic properties of platinum-alumina catalysts; for catalysts with weak acidic properties, compound II is recommended.

(3) High activity dehydroisomerization catalysts were prepared, even in the absence of halogen acids, when aluminas of high intrinsic acidity were used.

(4) Platinum seems to neutralize the acidic sites of aluminas.

(5) The dehydroisomerization reaction can be explained by a carbonium ion mechanism.

(6) The demethanation reaction to form toluene seems to proceed through a stepwise dehydrogenation to II and IV. The dehydrogenated species are not desorbed from the catalyst prior to demethanation. In the presence of catalyst having acidic properties the adsorbed species are probably protonated before they are aromatized.

(7) The aromatization of I and II seems to proceed in part through a ring expansion, followed by a ring contraction. This would explain the presence of m- and p-xylene and of ethylbenzene in the reaction product. The aromatization of methylcycloheptane gives data in accordance with this hypothesis.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Alumina: Catalyst and Support. VII.[1] Aromatization of n-Heptane-1-C^{14} Over Chromia-Alumina Catalysts[2,3]

HERMAN PINES AND CHAO-TUNG CHEN

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The aromatization of n-heptane-1-C^{14} over chromia alone and chromia-alumina catalysts having different intrinsic acidities was studied. The catalysts exhibited specific activity decrease patterns and the C^{14} distribution in the product toluene was found to depend on the nature of the catalysts and change with time. The results were interpreted by mechanisms involving five-, six-, and seven-membered ring intermediates of which the relative contributions depend on the nature of the catalyst and change of time. Cycloheptane was aromatized over chromia-alumina catalysts in good yields. Ethylcyclopentane was aromatized over chromia-alumina catalyst having high intrinsic acidity but not over chromia-alumina catalyst in which the alumina had low intrinsic acidity.

The mechanism of catalytic aromatization of alkanes has been the subject of considerable interest for the last twenty-five years.[4a–c] Chromia-alumina was found to be one of the best catalysts for this reaction. The mechanisms of Twigg,[5] Herington and Rideal,[6] Pitkethly and Steiner,[7] and Wheatcroft[8] would all predict 50% methyl labeled toluene from n-heptane-1-C^{14}. Recently Mitchell[9] has reported values of 27–29% in disagreement with the prediction and postulated three mechanisms to account for the low value of methyl label. These include an intermediate formation of a transanular bridge,[6] rapid five- to six-membered

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[1] For Paper VI of this series see: H. Pines and T. W. Greenlee, *J. Org. Chem.*, 26, 1052 (1961).

[2] Paper IV of the series of aromatization of hydrocarbons. For Paper III see Ref. 1.

[3] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said Fund.

[4] (a) For a review of the literature see: A. H. Steiner, "Catalytic Cyclization and Aromatization of Hydrocarbons," in *Catalysis*, Vol. IV, pp. 529–560, edited by P. H. Emmett, Reinhold, New York, 1956. (b) G. F. Ciapetta, R. M. Dobres, and R. W. Baker, "Catalytic Reforming of Pure Hydrocarbons and Petroleum Naphthas," in *Catalysis*, Vol. VI, pp. 492–692, edited by P. H. Emmett, Reinhold, New York, 1958. (c) C. Hansch, *Chem. Revs.*, 353 (1953).

[5] G. H. Twigg, *Trans. Far. Soc.*, 34, 1006 (1939).

[6] E. F. G. Herington and E. K. Rideal, *Proc. Roy. Soc.*, 184A, 434, 447 (1945).

[7] R. C. Pitkethly and A. H. Steiner, *Trans. Far. Soc.*, 35, 979 (1939).

[8] R. W. Wheatcroft, dissertation, University of California, August 1, 1949.

[9] J. J. Mitchell, *J. Am. Chem. Soc.*, 80, 5848 (1958).

ring interconversion,[10] and intermediate formation of cycloheptane species.

In none of the published papers dealing with the aromatization catalyzed by chromia-alumina is there suggestion that alumina might exert an effect upon the catalytic properties of chromia-alumina and thereby alter the consequences of the reaction.

Recent studies in our laboratory have disclosed that alumina has intrinsic acidic properties and that the strength of the acid sites depends on the methods used for the preparation of the alumina.[11] Alumina obtained by hydrolysis from aluminum isopropoxide catalyzed the isomerization of cyclohexene to methylcyclopentenes, whereas alumina prepared from potassium aluminate did not effect such isomerization. It has also been shown that aluminas of different intrinsic acidities influence the catalytic properties of chromia-alumina catalysts in aromatization reactions.[12]

The present study was undertaken to determine the effect of different chromia-alumina catalysts on the aromatization of *n*-heptane-1-C^{14} and gain a better understanding of the mechanism of aromatization reaction.

EXPERIMENTAL

Hydrocarbons. a. n-Heptane-1-C^{14} was synthesized in 70% overall yield by the carbonation of *n*-hexylmagnesium bromide with carbon dioxide-C^{14}, the lithium aluminum hydride reduction of the resulting *n*-heptanoic acid-1-C^{14}, and finally the hydrogenolysis of the resulting *n*-heptanol-1-C^{14}. A synthetic sequence of this type was described previously.[14]

b. Ethylcyclopentane, b.p. 102–103.7°, n_D^{20} 1.4192, was synthesized in 76% overall yield, by the iodine catalyzed dehydration of 1-ethylcyclopentanol followed by hydrogenation.

c. Cycloheptane, b.p. 117–118°, n_D^{20} 1.4432, was prepared by the conventional Wolf-Kishner reduction of cycloheptanone in 72% yield.

Catalysts. The catalysts used in this study were: chromia alone (20 ml., 24.2 g.); chromia-alumina A (20 ml., 17.0 g.) in which the alumina was prepared by hydrolysis of aluminum isopropoxide and is considered to have strong intrinsic acidic properties; and chromia-alumina B (15 ml., 11.0 g.), in which the alumina was prepared by precipitation from potassium aluminate and is considered to have very weak intrinsic acidic properties. The chromia-alumina catalysts were prepared by impregnation; a more detailed description of the catalysts was given in a previous paper.[13]

Apparatus and procedure. The apparatus used was that described previously.[13] The hydrocarbons were passed over the catalysts at 500°, atmospheric pressure, and hourly liquid space velocity of 0.32. The liquid products were withdrawn periodically and analyzed by infrared spectroscopy and gas chromatography using a 6-foot tricresyl phosphate on fire brick column.

The liquid product obtained from *n*-heptane-1-C^{14} was diluted with inactive toluene and chromatographed on silica gel.[14] The toluene fraction thus obtained was oxidized with alkaline potassium permanganate to benzoic acid. The weight percent of toluene in the original sample was calculated by the isotope dilution method.[14] The benzoic acid was decarboxylated by heating in quinoline with copper oxide at 265° for 3 hr. Both carbon dioxide and benzene were assayed for C^{14} to obtain the isotope distribution.

All the samples assayed were converted to gaseous carbon dioxide. The organic samples were burned by wet combustion according to the procedure of Van Slyke,[15a,b] in which the carbon dioxide produced was 100 ± 0.5% for all aromatic substances assayed. For compounds such as *n*-heptane-1-C^{14} dry combustion was preferred.[14]

The radioactivity assay was performed in a 250 ml. ionization chamber, connected to a vibrating reed electrometer. The commercially available instrument used was a Dynacon model 6000,[16] equipped with a 10 millivolt variable chart speed recorder.

DISCUSSION

The experimental results obtained from the aromatization of *n*-heptane-1-C^{14} are summarized in Table 1.

Toluene formation. Over chromia alone the toluene content starts at a high value of 70% and falls rapidly to 10%. Over chromia-alumina A (having alumina of high intrinsic acidity) the conversion to toluene starts at 45% and decreases almost linearly with the smallest slope of the three experiments. Over chromia-alumina B (prepared from potassium aluminate and having an alumina of very weak intrinsic acidity) the toluene content starts at about the same value as in Experiment 2 but decreases with a greater slope and ends with the lowest value of all. Not much may be concluded from these data concerning the mechanism, but these patterns indicate that incorporation of different aluminas in chromia-alumina produces different catalytic effects.

Distribution of C^{14}. a. Chromia. Chromia alone gave 47% methyl-labeled toluene. Mitchell[9] has found that the catalytic dehydrocyclization showed no isotope discrimination within experimental error, but that the assay of the methyl carbon involved an overall 10% isotope discrimination. As the present decarboxylation method was conducted at 265°—much higher than the temperature at which Mitchell carried out the Hunsdiecker reaction—it is expected that the isotope discrimination attending our assay of the methyl carbon is absent or at least much lower than 10%. In the present experiments benzene resulting from the decarboxylation was also assayed, and the largest deviation from 100% radioactivity recovery was 2.7%. In any event, therefore, an uncertainty of 3% may be allowed for the assay data.

It follows that the dehydrocyclization over chromia alone may be interpreted by any one of

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(10) H. Pines and R. W. Myerholtz, *J. Am. Chem. Soc.*, **77**, 5392 (1955).

(11) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

(12) C. T. Chen, W. O. Haag, H. Pines, *Chem. & Ind.*, 1379 (1959).

(13) H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **82**, 3562 (1960).

(14) H. Pines and A. W. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

(15) (a) D. D. Van Slyke, J. Folch, *J. Biol. Chem.*, **136**, 509 (1940). (b) D. D. Van Slyke, J. Plazin, and T. R. Weisiger, *J. Biol. Chem.*, **191**, 299 (1951).

(16) Nuclear-Chicago Corp.

TABLE I

TOLUENE CONTENT OF DEHYDROCYCLIZATION PRODUCT FROM n-HEPTANE-1-C^{14} AND DILUTION DATA. C^{14} DISTRIBUTION IN TOLUENE

							C^{14} Distribution in Toluene[b]		
Expt.	Catalyst	Activity of n-Heptane, μc./Mmole	Cut[a]	Product, G.	Toluene Added, G.	Toluene,[b] Wt. %	Methyl, %	Ring, %	Difference,[c] %
1	Chromia alone	2.86	1	1.293	3.644	70.2	44.7	56.9	+1.6
			3	1.594	2.190	27.2	47.3	52.3	−0.4
			5	2.019	2.017	10.3	47.4	52.3	−0.3
2	Chromia-Alumina A	2.74	1	1.283	2.635	44.5	38.7	60.7	−0.6
			3	1.592	2.716	29.8	39.8	60.0	−0.2
			6	1.877	2.354	20.3	41.7	59.3	+1.0
3	Chromia-Alumina B	2.74	1	1.583	2.551	44.1	17.5	81.0	−1.5
			3	1.787	2.419	22.3	21.7	77.0	−1.3
			5	2.089	2.603	4.1	32.1	70.6	+2.7

[a] Cuts were taken at 3-ml. intervals. [b] Calculated by isotope dilution method. Activities of benzoic acids derived from toluene samples are given in Table II. [c] Difference between 100% activity recovery and experimental value.

TABLE II

DATA ON DECARBOXYLATION OF BENZOIC ACID DERIVED FROM TOLUENE

Benzoic Acid from Expt.	Cut	Activity, μc./Mmole	Carbon Dioxide, μc./Mmole	Benzene, μc./Mmole
1	1	0.570	0.255	0.324
	3	0.472	0.223	0.247
	5	0.266	0.126	0.139
2	1	0.488	0.189	0.296
	3	0.407	0.162	0.244
	6	0.381	0.159	0.266
3	1	0.589	0.103	0.477
	3	0.387	0.0841	0.298
	5	0.0865	0.0284	0.0611

the mechanisms[5–8] which predicted 50% methyl label. However, there is another mechanism which would also give 50% methyl label. It involves the process: formation of absorbed cyclopentene by 1,5-closure of adsorbed 1- or 2-heptene and ring expansion to absorbed methylcyclohexene. Actually this is 1,6-closure carried out in two steps, but it is nonetheless different from the second postulated mechanism of Mitchell in that the cyclopentane species is formed from heptene directly but not from adsorbed methylcyclohexene. Twigg's opinion[6] that 3-heptene must isomerize to 1- or 2-heptene before undergoing cyclization may not be absolute, because 3-heptene may also undergo 1,5-closure directly, followed by ring expansion and aromatization. The relatively slow rate of toluene formation from 3-heptene may be attributed to the slow rate of the aromatization of the cyclopentene intermediate or, as Twigg has pointed out, to the necessity of first isomerizing to other heptenes, or both.

It was shown previously that chromia has intrinsic acidity as noted by its ability to cause some skeletal isomerization accompanying the aromatization of 1,1-dimethylcyclohexane.[13] The acidities, however, were considered to be insufficient to cause a deep-seated isomerization such as five- to six-membered ring interconversion, and the isomerization was explained as proceeding mainly in terms of methyl migration through a carbonium ion mechanism. In the dehydrocyclization of n-heptane over chromia alone methyl migration in the intermediate methylcyclohexane species is likely to be involved although the methyl label would not thereby be affected. The slightly lower methyl label of 45% for cut 1 might, therefore, be due to an involvement of a cycloheptane intermediate to be mentioned later.

The increase in methyl label with time is explained as due to the deactivation of dehydrogenation sites, which probably are responsible for the formation of seven carbon ring intermediates. The preferred deactivation of the dehydrogenation sites was observed previously.[13]

b. Chromia-Alumina A. That alumina modified or changes the nature of chromia and thereby alters the consequences of the reaction is revealed by the data on chromia-alumina A. The methyl label of about 40% is obviously different from 50% and must be accounted for by contribution of some side reactions which give less methyl label. These side reactions may involve those speculated by Mitchell. However, the first postulate of bicyclic intermediate may be excluded on the grounds already mentioned[12] and to be discussed in detail in a following paper of this series.[17]

The second postulate of Mitchell concerning five- to six-membered ring interconversion may not be excluded entirely if it is assumed that the olefinic species were involved and not the saturated hydrocarbons. Chromia-alumina A was able to dehydroisomerize 1,1-dimethylcyclohexane to a greater extent than chromia alone did, indicating that it possesses stronger acidic sites than the latter. The acidities were, however, considered to be still insufficient to cause six- to five-membered ring

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(17) H. Pines and C. T. Chen, paper presented before the Second International Congress on Catalysis, July 4–9, 1960, Paris, France.

interconversion in 1,1-dimethylcyclohexane but not in 4,4-dimethylcyclohexene.[13] The adsorbed cyclopentane species as intermediate could be involved to an appreciable extent at first because ethylcyclopentane over chromia-alumina A gave 20% toluene. The toluene yield decreased rapidly to 3%. The formation of alkylcyclopentanes from alkanes having five carbon atom chains were reported in the literature.[18]

The formation of cycloheptane intermediate is, however, not excluded as responsible for the less than 50% C^{14} methyl label.

c. Chromia-Alumina B. Remarkably different results were obtained with the less acidic chromia-alumina B which gave methyl label values ranging from 17.5% to 32%. Cyclopentanes were not involved in the reaction since ethylcyclopentane was not aromatized over this catalyst. Mitchell's value of 28% falls in the range of our values, although it is not known whether or not his value was a constant throughout his dehydrocyclization experiment, as he analyzed a gross sample of the product. It is inadequate to restrict oneself to those mechanisms which give 25% methyl label. It is now apparent that mechanisms which would predict an even lower value are necessary to explain the 17.5%. A methyl label value of 14.3% will result if one assumes the following processes: formation of adsorbedcy cloheptene species from adsorbed 1-heptene, rapid rolling around of the adsorbed cycloheptene, and ring contraction to adsorbed methylcyclohexene. This differs from the third speculation of Mitchell in that the seven-membered ring intermediate is formed not from the absorbed methylcyclohexene but directly from adsorbed 1-heptene, and that it rolls around the catalyst surface so much more rapidly than the subsequent ring contraction that isotopic equivalency of all of the seven carbon atoms is acquired. Although this process is necessary to account for the 17.5% methyl label, a concurrent operation of Mitchell's cycloheptene mechanism may not be excluded.

Cycloheptane gave toluene in 95% and 65% yield over chromia-alumina A and B, respectively, providing proof that the seven-membered ring compounds could be intermediates in the dehydrocyclization reaction. One may argue that chromia-alumina B gave a smaller yield of toluene from cycloheptane than chromia-alumina A, while the radiochemical data suggest a much greater contribution of the seven-membered ring intermediate over chromia-alumina B. It seems that the ability to form the adsorbed cycloheptene intermediate is a more important factor in this reaction than is the ability to destroy it. An alternative way of acquiring isotopic equivalency of the seven carbon atoms may involve simultaneous desorption and hydrogenation to cycloheptane. However, distinction between the two can not definitely be made at present.

The data obtained from the competitive aromatization of *n*-heptane and cycloheptane seem to indicate that desorbed cycloheptane is not involved in dehydrocyclization of *n*-heptane. The data in Table III show that cycloheptane disappeared faster than *n*-heptane, but the two chromia-alumina catalysts gave the same relative rate of reaction of these hydrocarbons. Decrease in mole ratio cycloheptane/*n*-heptane of starting mixture decreased the relative rate, suggesting that the two hydrocarbons were competing for the same catalyst sites. The rather small relative rate of 2:3 seems to predict a possible survival of the cycloheptane intermediate in the dehydrocyclization of *n*-heptane. Vapor phase chromatography revealed a trace of a compound having retention time intermediate between those of *n*-heptane and toluene but not exactly the same as that of cycloheptane.

TABLE III

COMPETITIVE AROMATIZATION OF *n*-HEPTANE AND CYCLOHEPTANE AT 500°

	Chromia-Alumina A	Chromia-Alumina B
Mole ratio[a]	1.01	1.01
H.L.S.V.	1.02	0.84
Rel. ratio[b]	2.6	2.7
Mole ratio[a]	0.39	0.39
H.L.S.V.	1.04	0.84
Rel. rate[b]	2.0	2.1

[a] Mole ratio cycloheptane/*n*-heptane of the charging stock. [b] Relative rate of disappearing, cycloheptane/*n*-heptane, as calculated from the mole ratio of remaining hydrocarbons.

The absence of cycloheptane in the products from the reaction of *n*-heptane is not necessarily an indication that cycloheptene species were not involved in the aromatization reaction. It is probable that adsorbed cycloheptene species were present but their relative rates of aromatization to toluene is much faster than that of cycloheptane.

CONCLUSION

The present study has added a new mechanism involving the intermediate formation of adsorbed cycloheptene. It may be concluded that the formation of toluene from *n*-heptane over a chromia catalyst may involve five-, six-, and seven-membered ring intermediates the relative contributions of which depend on the nature of the catalyst and change with time. It has been demonstrated that aluminas of different intrinsic acidities influence the behavior of chromia-alumina catalysts. The C^{14} distribution data suggest that a

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[18] A. L. Liberman, G. V. Loza, G. Min-Nan, and B. A. Kazanskii, *Proc. Acad. Sci., U.S.S.R.*, 120, 413 (1958).

larger ring is more readily formed over chromia-alumina B having low intrinsic acidity. It appears that the catalyst sites leading to the specific ring closures are plural in kind and different in number from one catalyst to another. Besides the acidic properties, the arrangement of chromia on alumina surface may be a more important factor in the dehydrocyclization reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Michael Type Additions with Nitroparaffins.[1] A Convenient Route to Nitrocyclohexanols

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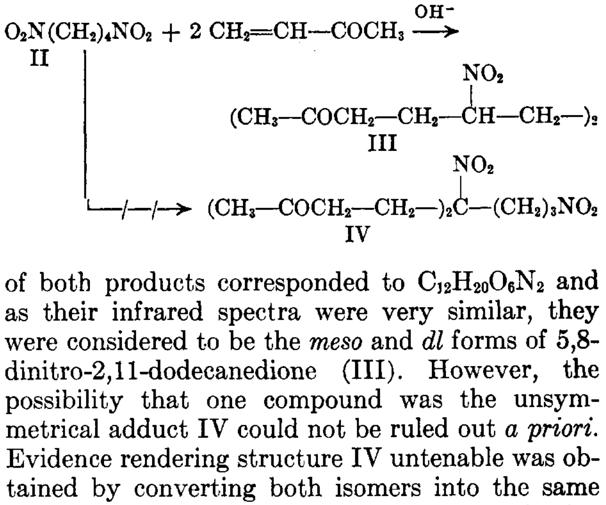
Primary nitroparaffins condense with phenyl vinyl ketone to afford monoaddition adducts. Treatment of these products with an additional equivalent of phenyl vinyl ketone yields predominantly the expected diadducts. Strong bases such as ethoxide and hydroxide cause cyclization of the initial reaction products to form substituted cyclohexanols providing a convenient synthetic route to these structures. When this Michael type reaction is applied to methyl vinyl ketone, the initial diaddition compounds cannot be isolated. Instead, cyclization occurs with the formation of cyclohexanols. The reaction of 2 equivalents of methyl vinyl ketone with α,ω-dinitroalkanes gives the symmetrical addition compound. Four equivalents of methyl vinyl ketone give the tetraaddition product. However, here also cyclization occurs concurrently with reaction so that dicyclohexanol derivatives are obtained. Dehydration of these cyclohexanols, followed by hydrogenation, opens a new route for the preparation of substituted nitrocyclohexanes.

Although the Michael type addition employing primary and secondary nitroparaffins as donors has been investigated by many workers,[2] little attention has been given to the use of α,ω-dinitroparaffins in this reaction. Only two reports[3] dealing with the Michael addition to dinitro compounds have appeared in the literature. Feuer and Leston found that disodium 2,2-dimethyl-1,3-propanedinitronate reacted in an unusual way with methyl acrylate to afford 4,4-dimethyl-5-(2′-carboxyethylidene)isoxazoline oxide, while 1,5-dinitropentane gave a 34% yield of the expected Michael adduct 5,9-dinitro-2,12-tridecanedione (I) when treated with two equivalents of methyl vinyl ketone.[3b]

α,ω-Dinitroparaffins. The present investigation was initiated by studying the reaction between 1,4-dinitrobutane (II) and two equivalents of methyl vinyl ketone. When this reaction was carried out in ethanol and in the presence of a catalytic amount of sodium hydroxide, two products, m.p. 91.5–92.5° and 61–62° were obtained. The same two compounds were secured when the full salt of compound II was employed. As the elemental analyses of both products corresponded to $C_{12}H_{20}O_6N_2$ and as their infrared spectra were very similar, they were considered to be the *meso* and *dl* forms of 5,8-dinitro-2,11-dodecanedione (III). However, the possibility that one compound was the unsymmetrical adduct IV could not be ruled out *a priori*. Evidence rendering structure IV untenable was obtained by converting both isomers into the same dibromo derivative (V) in almost quantitative yield on treatment with two equivalents of base and excess bromine. The infrared spectra of compound V, obtained in both reactions were superimposable and a mixed melting point determination showed no depression.



$$\underset{\text{II}}{O_2N(CH_2)_4NO_2} + 2\,CH_2{=}CH{-}COCH_3 \xrightarrow{OH^-} \underset{\text{III}}{(CH_3{-}COCH_2{-}CH_2{-}\overset{NO_2}{\overset{|}{C}}H{-}CH_2{-})_2}$$

$$\text{II} \;{-}/{-}/{\rightarrow}\; \underset{\text{IV}}{(CH_3{-}COCH_2{-}CH_2{-})_2\overset{NO_2}{\overset{|}{C}}{-}(CH_2)_3NO_2}$$

$$\text{III} \xrightarrow[2)\ Br_2]{1)\ OH^-} (CH_3{-}COCH_2{-}CH_2{-}\underset{\underset{Br}{|}}{\overset{\overset{NO_2}{|}}{C}}{-}CH_2{-})_2$$

V

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[1] (a) From the Ph.D. thesis of Ronald Harmetz, Purdue University, 1959; (b) presented before the Division of Organic Chemistry at the Cleveland Meeting of the American Chemical Society, April 1960.

[2] (a) M. C. Kloetzel, *J. Am. Chem. Soc.*, **69**, 2271 (1947); (b) D. E. Worrall, and C. J. Bradway, *J. Am. Chem. Soc.*, **58**, 1607 (1936); (c) E. P. Kohler, *J. Am. Chem. Soc.*, **38**, 889 (1916); (d) F. Villani and F. Nord, *J. Am. Chem. Soc.*, **69**, 2608 (1947); (e) E. P. Kohler and H. Engelbrecht, *J. Am. Chem. Soc.*, **41**, 764, 1379 (1919); (f) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943); (g) G. D. Buckley, T. J. Elliott, F. G. Hunt, and A. Lowe, *J. Chem. Soc.*, 1505 (1947); (h) G. D. Buckley, J. L. Charlish, and J. D. Rose, *J. Chem. Soc.*, 1514 (1947); (i) A. Lambert and H. A. Piggott, *J. Chem. Soc.*, **1947**, 1489; (j) for a thorough survey of the literature, reference is made to *The Michael Reaction* by E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

[3] (a) H. Feuer and G. Leston, Abstract of Papers presented at the International Congress of Pure and Applied Chemistry, Paris, July 1957, p. 24; (b) H. Feuer and C. N. Aguilar, *J. Org. Chem.*, **23**, 607 (1958).