The dechlorination of the trichloroethylene copolymer shows fair agreement with (8) in the range from 0 to 20% conversion (see Fig. 4). In every case, however, the reaction seemed to go faster in the conversion range beyond 20% than would be expected from (6) or (7). Furthermore, the anticipated dependence on the amount of zinc was not realized, as may be seen from the last column of Table II. It is obvious that the proposed mechanism is not entirely adequate.

The failure to achieve 100% dechlorination in the case of the dichloroethylene copolymer requires some comment. It was found that when either copolymer was heated in solution in the absence of zinc, HCl was formed. This reaction was too slow to compete with the dechlorination by zinc of the trichloroethylene copolymer, but may very well take place to a measurable extent during the dechlorination of the dichloroethylene copolymer. The removal of one molecule of HCl between two adjacent chlorinated carbon atoms will cause the remaining chlorine atom to be inert. Hence the dechlorination will not go to completion.

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BROOKLYN, N. Y.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Racemization of *d*(+)-3-Methylhexane[1]

BY HOWARD E. HELLER[2,3]

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The racemization and isomerization of *d*(+)-3-methylhexane in the presence of aluminum bromide and various promoters at 23–24° have been studied. Racemization proceeds more rapidly than isomerization, and the ratio of the two rates is not constant. The implications of these data are discussed in terms of the carbonium ion theory.

A study of the reactions of paraffins begun several years ago has been interrupted before completion. However, because of the close relationship between the results obtained by this author and the recent findings of other workers, it seems desirable to note some of the results at this time. Some of the findings of a study of the racemization and isomerization of optically active 3-methylhexane in the presence of promoted aluminum bromide are summarized here.

Experimental

Reagents.—Fractional distillation of U. S. I. "Refined Amyl Alcohol" through Podbielniak Heligrid columns yielded *d*(−)-2-methyl-1-butanol of the following characteristics after three passes: $n^{20}\mathrm{D}$ 1.4102, d^{23}_{4} 0.814, $\alpha^{23}\mathrm{D}$ −4.62°, $[\alpha]^{23}\mathrm{D}$ −5.68°.

Saturation of the alcohol under reflux with anhydrous hydrogen bromide at 100° and atmospheric pressure for 24 hours yielded *d*(+)-2-methyl-1-bromobutane. The product, washed twice with water, dried over potassium carbonate, and passed twice through towers of silica-gel, had the properties: $n^{20}\mathrm{D}$ 1.4450, d^{23}_{4} 1.220, $\alpha^{23}\mathrm{D}$ +3.70°, $[\alpha]^{23}\mathrm{D}$ +3.03°. Fractional distillation was attempted and abandoned, because even at reduced pressure (48 mm.) isomerization to the tertiary halide occurred.

Synthesis of *d*(+)-3-methylhexane was accomplished by two different methods:

(a).—By action of the Grignard reagent on diethyl sulfate: Diethyl sulfate (1.0 mole) diluted with about an equal volume of ether was added rapidly to an ether solution of the Grignard reagent prepared from 0.44 mole of active amyl bromide in 5.6 times its volume of ether. Careful drying of all reagents and apparatus, and an atmosphere of pure nitrogen were employed. After refluxing overnight with vigorous stirring, the reaction mixture was decomposed with dilute hydrochloric acid. The ether layer was dried with potassium carbonate and distilled. Yields were 55–60% of crude 3-methylhexane and 5–10% of optically active diamyl. Difficulties in stirring reduced yields in larger scale runs.

(b).—Through the malonic ester synthesis: Active amyl malonic ester was prepared according to the procedure of Adams and Kamm[4] for *n*-butylmalonic ester. The product, stripped of low boiling impurities by vacuum distillation, was treated by the method of Vliet, Marvel and Hsueh[5] to give γ-methylcaproic acid.

Lithium aluminum hydride reduction of the crude acid gave a poor yield of 4-methyl-1-hexanol. The recovered acid was converted to its ethyl ester by saturating a thirty-one volume per cent. solution of the acid in absolute ethanol with anhydrous hydrogen chloride and warming to 80° for eight hours. The mixture poured onto ice, washed with water, and dried with calcium chloride, yielded the ester. Reduction of the ester followed standard methods.[6]

Crude 4-methyl-1-hexanol heated with seven times its volume of concentrated hydriodic acid for eight hours with stirring at 90° yielded the corresponding iodide. This was separated, washed with water, dried with potassium carbonate, and used without further purification.

The iodide in twice its volume of ether was reduced to 3-methylhexane by addition to a fourfold excess of lithium aluminum hydride solution containing 1.79 moles of hydride per liter.[7,8]

Early purification work on the hydrocarbon, keeping separate the material prepared by the two paths, indicated the presence of a common impurity not removable by any of the ordinary hydrocarbon purification methods.[9] On exhaustive application of those methods, the ultraviolet absorption of both samples approached the same limiting "tail" below 2500 Å., and the optical rotation approached the same limiting value, +5.51°. The combined samples were hydrogenated over one-twentieth their total weight of platinum oxide at 45 pounds pressure and room temperature for 24 hours. The ultraviolet transparency increased over the former limit, but repeating the procedure gave no further improvement. No racemization appeared to occur during this process.

The hydrocarbon, sealed with one-seventh its weight of

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[1] The material presented herein is abstracted from the Ph.D. thesis of Howard E. Heller, the University of Chicago, 1949.

[2] Naval Research Laboratory Fellow, 1945–1947.

[3] Photo Products Department, E. I. du Pont de Nemours and Company, Parlin, New Jersey.

[4] R. Adams and R. M. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 250.

[5] E. B. Vliet, C. S. Marvel and C. M. Hsueh, *ibid.*, Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 416.

[6] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[7] L. W. Trevoy and W. G. Brown, unpublished work.

[8] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

[9] W. G. Brown and M. H. Reagan, *ibid.*, **69**, 1032 (1947).

silica-gel under high vacuum conditions in an ampule, was immersed in a −80° bath.(10) Both reagents had been thoroughly out-gassed prior to sealing-off. After several days standing with occasional shaking, the ampule was opened cold, and a portion of the hydrocarbon was decanted and stored over reagent sodium hydroxide. The ultraviolet transmission of the 3-methylhexane after this treatment was the highest encountered by the writer. The values were 100% above 2300 Å., 93% at 2200 Å., and 60% at 2080 Å., which was the lower limit of operation of the spectrophotometer used. Other physical constants of the 3-methylhexane thus obtained were: b.p. 91.9°, n^{20}_D 1.3886, d^{23}_4 0.6855, α^{23}_D +5.51°, $[\alpha]^{23}_D$ +8.02°. The literature values are: b.p. 91.95°,(11) n^{20}_D 1.38865,(11) d^{20}_4 0.6870,(11) $[\alpha]^{25}_D$ +9.12°.(12) In addition, the infrared absorption spectrum appeared to superimpose exactly on that of a sample of 3-methylhexane of an estimated 99.7% purity supplied by the National Bureau of Standards. Unless otherwise noted, 3-methylhexane of the above characteristics was used in this work.

Eimer and Amend aluminum bromide, sublimed three times and sealed in an ampule under high vacuum conditions, was removed to a dry-box filled with pure nitrogen and transferred to a standard taper capped container stored in the box.

Olefin used in one experiment was 5-methyl-1-hexene, b.p. 85–86°.

Hydrogen chloride generated from concentrated hydrochloric and sulfuric acids was passed into an evacuated storage vessel on the vacuum line through a drying tower of phosphorus pentoxide-coated glass beads.

Apparatus.—The vacuum line was a generalized type employing Stock valves wherever aluminum bromide was to be handled. It contained no novel features and will not be described further.

A Fric polarimeter and a 2-decimeter-long 1.8-ml. capacity tube was generally used in measuring the optical rotation. However, in one experiment testing the extent of change occurring in quenching $AlBr_3$–3-methylhexane mixtures in water, a special tube attached to the vacuum line was used. This tube, of all-glass construction except for liberal external coatings of Glyptal cement holding the optical flats in place, adjoined the line through a small condenser allowing transfer of the hydrocarbon into the tube for measurement. The estimated precision was ±0.10°.

A Perkin–Elmer 12-C spectrometer was employed in infrared studies of structural isomerization. Preliminary study showed identifiable quantities of methylhexanes only. Synthetic mixtures of 2-methyl- and 3-methylhexane at intervals of 5 volume % were prepared from samples supplied by the National Bureau of Standards. Comparison of spectra of known and unknown mixtures allowed estimation of the composition of the latter to within about 2%.

A Beckman quartz spectrophotometer was used for determining the ultraviolet transparency of 3-methylhexane during purification.

Procedures.—Aluminum bromide and 3-methylhexane were mixed in the arbitrary mole ratio, $^1/_{21}$, and desired catalyst-promoters were added. Standard high vacuum methods(13) were employed, extreme precautions being taken to avoid contamination by air or moisture. Transfers outside the vacuum line were conducted under pure nitrogen. The reaction ampule was sealed, removed from the line, brought to room temperature (23–24°), and shaken for the desired period. The vessel was then opened, the mixture quenched in water, and the organic material separated and dried over reagent sodium hydroxide before analysis.

Loss of optical activity during the quenching process was determined by allowing the reaction vessel to remain attached to the line during reaction. The hydrocarbon layer was then distilled to the special polarimeter tube, and the rotation measured. The mixture was returned to the reaction vessel, sealed off, warmed to room temperature, and immediately quenched in the usual manner. For 3-methylhexane having an initial rotation of +5.36° (an impure sample was used here to conserve the purest material), the rotation after reaction was +4.43°, and after quenching was +4.34°. The difference is barely at the limit of experimental error.

In a crude attempt to test the stereochemistry of the halogen–hydrogen interchange,(14) 5 ml. each of 3-methylhexane and *t*-butyl bromide were mixed and treated under nitrogen with about 0.1 g. of aluminum bromide. An immediate violent reaction ensued with much evolution of gas, and most of the product was lost. The mixture was quenched within about 10 seconds after mixing (10 seconds was the shortest time in which the vessel could be removed from the dry-box), and the rotation was measured. The initial value of +3.16° for the mixture had shrunk to 0.00°. Organically bound halogen appeared to be present since a positive Beilstein test resulted even after numerous washings with water. Insufficient product remained to permit closer identification. The very limited availability of *d*(+)-3-methylhexane prevented repeating the experiment on a large enough scale to allow this to be accomplished.

The experimental data are summarized in Table I.

TABLE I

RACEMIZATION AND ISOMERIZATION DATA

(1) Run[a]	(2) Promoter	(3) α_i[b]	(4) α_f[c]	(5) Loss of activity, %	(6) Isomerized,[d] %
3	X[e]	5.51	4.86	12	<5
4	X[e]	5.51	2.16	61	. . .[f]
5	X[e]	5.51	4.62	16	. . .
10	X[e]	5.51	3.49	37	. . .
11[g]	X[e]	5.51	3.76	32	. . .
12[h]	X[e]	5.51	3.23	41	. . .
13[i]	X[e]	5.51	1.85[k]	66	5
14[j]	X[e]	5.51	2.86	48	. . .
15	X + HCl[l]	5.51	3.60	35	. . .
16	X + olefin[m]	5.51	0.00	100	53
17	X + air[n]	5.51	0.86	84	18
18	X	3.60[o]	2.26	37	. . .
19	X + HCl[l]	5.51	0.38	93	8

[a] Unless otherwise noted, all runs were of 15 minutes duration. [b,c] Initial and final observed rotations, respectively. The information desired can be obtained from these without calculating specific rotations. [d] Determined as 2-methylhexane. [e] Designation given unknown catalyst promoters. [f] The lack of data here is due to the limited access to the I.R. spectrometer. [g,h,i,j] Reactions were of 5 min., 60 min., 30 min. and 30 min. duration, respectively. [k] A faulty joint allowed air to pass over the catalyst for a few seconds before the line was sealed. [l] The results with HCl were ambiguous, since 15 is practically identical in result with 10, 11 or 18, while 19 is far different from any of the other mixtures. The HCl was in equimolar proportions with the $AlBr_3$. [m] One volume per cent. of 5-methyl-1-hexene was added to this mixture. [n] Air pressure in the ampule at sealing-off was 135 mm. at liquid nitrogen temperature. [o] The starting material here was the product from 15. The run was performed thusly to determine whether the offending impurities could be removed through $AlBr_3$ contact, following Pines and Wackher.(15) The results indicate that such is not the case.

Discussion

Racemization and isomerization of *d*(+)-3-methylhexane proceed rapidly at 23–24° in the

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(10) The silica-gel used here was the most active chromatographic purification medium available at the time, and had been used in the "ordinary" purifications mentioned above. Early in the work, a more effective sample of silica-gel had been used, but this had been exhausted by the time the main batches of hydrocarbon were to be treated, and no other sample possessing that activity could be obtained.

(11) American Petroleum Institute Research Project 44, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons and Related Compounds," Table No. 2a (Part 2)—Paraffins, C_7, December 31, 1948.

(12) G. S. Gordon, III, and R. L. Burwell, THIS JOURNAL, **71**, 2355 (1949).

(13) See for example, R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(14) P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1531 (1944).

(15) H. Pines and R. C. Wackher, *ibid.*, **68**, 595, 599 (1946).

presence of promoted aluminum bromide. Racemization is generally faster than isomerization. Both reactions were strongly promoted by air and olefin, in agreement with the findings of Pines and Wackher on butanes and pentanes.[15] Additional unidentified promoters appeared to operate since the results of attempted control experiments and runs in which HCl was added were quite erratic. Disproportionation was apparently negligible in all but the strongly promoted reactions, since only when air, olefin or alkyl halide were added were detectable amounts of "lower-layer complex" formed. Complete loss of optical activity results when a mixture of *d*(+)-3-methylhexane and *t*-butyl bromide is treated with aluminum bromide. The data support an ion-chain mechanism for racemization and isomerization.[12,16,17]

(1) Chain initiation (and racemization)

$$R^+ + (+)(C_3H_7)(C_2H_5)(CH_3)CH = RH + (\pm)(C_3H_7)(C_2H_5)(CH_3)C^+$$

(2) Chain transfer (and racemization)

$$(\pm)(C_3H_7)(C_2H_5)(CH_3)C^+ + (+)3MH = (\pm)(C_3H_7)(C_2H_5)(CH_3)C^+ + (\pm)3MH$$

(3) Intramolecular hydride migration

$$(\pm)(C_3H_7)(C_2H_5)(CH_3)C^+ = (\pm)(C_3H_7)(CH_3C^+H)(CH_3)CH$$

(4) Isomerization

$$(\pm)(C_3H_7)(CH_3C^+H)(CH_3)CH = (C_4H_9)(CH_3)_2C^+$$

(5) Alternate chain transfer (and racemization)

$$(C_4H_9)(CH_3)_2C^+ + (+)3MH = 2MH + (\pm)(C_3H_7)(C_2H_5)(CH_3)C^+$$

The nature of the chain initiator, R^+, has been discussed by other workers.[15,18] The present results accord generally with their views, although the erratic behavior observed when no known promoters were added is unaccounted for. The purity of the 3-methylhexane is discussed later in this connection. Another possibility is that the catalyst may have been exposed to air in spite of the precautions taken during the transfer from dry-box to vacuum line. If this were the case, however, it appears that air may operate as a promoter by more than one mechanism. The accepted view[15,18] is that bromine is liberated by action of oxygen on the catalyst. The bromine attacks the hydrocarbon, and the resulting alkyl bromide serves as a source of carbonium ions.

That mechanism seems reasonable only for Run 17 of the present series, however, for the following reasons: In all other runs, the residual pressure of either oxygen or bromine measured less than 10^{-4} mm. This corresponds to a mole fraction of about 10^{-8}. Comparing the rates of isomerization observed here ($\simeq$5% in 30 minutes in "unpromoted" reactions), with those of Pines and Wackher[19] (9.5% in four hours with relatively twice as much catalyst and 10^6 times as much promoter as used here), it is hard to see how the same mechanism could be operative in both cases, even if allowance is made for the greater ease of isomerization of branched chain heptanes as compared to straight chain butanes.

An alternative suggestion is that substantial amounts of the solid reaction product of aluminum bromide and oxygen was carried into the reaction vessel during sublimation. Beeck and co-workers[20] have shown that alumina impregnated with aluminum chloride is active for both hydrogen exchange and isomerization. Something of this sort may have been responsible for the results obtained here.

Chain transfer between 3-methylhexane molecules (proportional to pure racemization) is substantially more rapid than isomerization. Aluminum bromide at room temperature is a more active catalyst for both processes than sulfuric acid at 60°,[17] and in addition gives a higher ratio of racemization to isomerization. It seems more nearly like chlorosulfonic acid in these respects, although not so reactive as that catalyst.[12]

The stereochemistry of the chain transfer is in doubt. It might be expected that an attacking group as bulky as the tertiary ions involved here would shield the molecule attacked so that as it in turn became ionized, its *attacking* side would be that opposite its *attacked* side. On this basis, an optically active heptyl bromide might have been expected from the exchange between *t*-butyl bromide and *d*(+)-3-methylhexane. That none was obtained in the experiment here does not rule out the possibility, however, since Bartlett, Condon and Schneider[14] found that the primary process occurs within a very small fraction of a second. Any optically active primary product might reasonably be expected to have racemized by the time the mixture was quenched in the present case. It is regretted that insufficient quantities of active hydrocarbon prevented further exploration of this point.[21]

Evering and Waugh have made a thorough study of hexane isomerization,[22] and find substantial differences in the rate at which various types of isomerization occur. The detection of methylhexanes only on examination of the products here is in agreement with their finding that methyl group migration along a chain was much faster than introduction or removal of branches.[23,24] Presumably the reaction times chosen here were too short to allow appearance of detectible quantities of more highly branched products.

In terms of the carbonium ion theory, the rate of loss of optical activity in mixtures rich in the original *d*(+)-3-methylhexane ought to be a rough

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[16] H. S. Bloch, H. Pines and L. Schmerling, THIS JOURNAL, **68**, 153 (1946).

[17] R. L. Burwell and G. S. Gordon, III, *ibid.*, **70**, 3128 (1948).

[18] A. G. Oblad and M. H. Gorin, *Ind. Eng. Chem.*, **38**, 822 (1946).

[19] Reference 15, p. 601.

[20] C. D. Wagner, O. Beeck, J. W. Otvos and D. P. Stevenson, *J. Chem. Phys.*, **17**, 419 (1949).

[21] NOTE ADDED IN PROOF.—The paper of J. D. Roberts and G. R. Coraor, THIS JOURNAL **74**, 3586 (1952) has just appeared. From their study of the exchange between 2-methylbutane-1-C^{14} and *t*-butyl bromide, the isolation of an optically active product from this type of reaction seems to be almost hopeless of accomplishment because of the very high rate of isomerization by methyl migration along the chain of the hydrocarbon fragment.

[22] B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **43**, 1820 (1951).

[23] Professor Burwell's students have obtained similar results with heptanes and octanes in the presence of sulfuric acid at elevated temperatures (private communication from Professor Burwell).

[24] ADDED IN PROOF.—Similar results have been found by D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, THIS JOURNAL, **74**, 3269 (1952).

measure of the rate of carbonium ion formation. On a purely chance basis, therefore, isomerization might be expected to be greater in 19 than in 17. Actually, isomerization in 17 is about twice as great as in 19. Thus, the behavior of the postulated carbonium ion intermediate shows some environment dependence.

The very low degree of cracking occurring in these reaction mixtures attained through extreme purification of the materials used suggests that the cracking activity attributed to aluminum bromide in reactions with hydrocarbons of chain length greater than four[25] may more reasonably be attributed, at least in part, to the presence of trace impurities which operate as catalyst promoters in much the same way as in the isomerization reactions studied by Pines and Wackher.[15]

The purity of the 3-methylhexane requires comment. If natural 2-methyl-1-butanol is assumed to be optically pure, then, from its low rotation,[17] the sample employed here contained 1–2% of isoamyl alcohol. While this would lead to about the same proportion of 2-methylhexane in the final hydrocarbon, such quantity could not be detected by boiling point, refractive index, or density determinations, and probably not by the infrared technique used here. Further impurities entered during the conversion of active amyl alcohol to the bromide since the rotation of the bromide was about 25% low.[17] Presumably racemization and formation of *t*-amyl bromide and possibly 2-methyl-3-bromobutane were involved as reported by Brokaw and Brode.[26] Hydrocarbons derived from the isomeric bromides must have been largely removed by the preparative and purification procedures, since a maximum of about 2% impurities in the final product was indicated by infrared analysis.

The impurity shown by the ultraviolet absorption spectrum to persist through the purification processes probably was partly responsible for the inability of this worker to produce 3-methylhexane which was stable in the presence of aluminum bromide. However, its effect should have been more or less constant from reaction to reaction in contrast to the erratic behavior observed. As affairs stand, the writer would not care to attempt to evaluate its effect quantitatively.

It is a pleasure to acknowledge the writer's indebtedness to Professor W. G. Brown, who suggested the problem and guided the work, to the Naval Research Laboratory, who supplied the funds supporting most of this work, and to Mr. Jay Burns, who performed the infrared analyses.

CHICAGO, ILLINOIS

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(25) Discussion with Dr. D. P. Stevenson.

(26) G. Y. Brokaw and W. R. Brode, *J. Org. Chem.*, **13**, 194 (1948).

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

The Acyloin Condensation of Aralkyl Esters

BY EARLE VAN HEYNINGEN

RECEIVED MARCH 3, 1952

The acyloin condensation was carried out on several aralkyl esters and the products of the reaction indicate that it proceeds by a free radical mechanism.

It has been proposed by several authors that the acyloin condensation proceeds by a free radical mechanism.[1,2] Kharasch and co-workers, by studying the reaction of esters with sodium in liquid ammonia, have substantiated the initial formation of a sodium ketyl under these conditions and have postulated that the acyloin condensation in an inert solvent goes in a like manner. The work of Lynn and English on the reaction of dialkylamides of aromatic acids with sodium in inert solvent, further corroborates the free radical mechanism.[3] An investigation of the acyloin condensation of aralkyl esters has yielded additional evidence that a sodium ketyl is first formed in this reaction.

The acyloin condensation of 1-phenyl-1-carbethoxycyclopentane yields a solid, bi-(1-phenylcyclopentyl) (V), which is not the expected acyloin.

To account for the formation of this hydrocarbon (V), the following mechanism has been assumed (Fig. 1). Sodium adds to the carbonyl of the ester to form the sodium ketyl, which splits to the phenylcyclopentyl free radical (III), and the elements of sodium ethyl formate (IV). The free radical (III) then dimerizes to bi-(1-phenylcyclopentyl) (V).

Should the foregoing explanation be correct, one would also expect as a result of the production of the radicals II and III, the formation of the products of their reduction (VI, XI), disproportionation (VI, VII), and interaction with themselves (IX, X) and each other (VIII). Since the isolation of such compounds would substantiate the postulated mechanism, a thorough investigation of the reaction product was undertaken.

The oily residue from the separation of V was separated into three main fractions by distillation. The lowest boiling fraction proved to be mainly phenylcyclopentane (VI) containing some phenylcyclopentene (VII). The second fraction consisted of the starting ester. The highest boiling fraction yielded the monoketone (VIII) whose structure was established by analysis and by its infrared spectrum, and the colorless acyloin (IX) whose identity was established by analysis and the presence of hydroxyl and carbonyl absorption in its

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(1) F. F. Blicke, THIS JOURNAL, **47**, 229 (1925).

(2) M. Kharasch, E. Sternfeld and F. R. Mayo, *J. Org. Chem.*, **5**, 362 (1940).

(3) J. Lynn and J. English, *ibid.*, **16**, 1546 (1951).