naphthoic acid, m.p. 161°, m.m.p. 160–161° with an authentic sample. The infrared spectra of both compounds were identical.

Fraction B, which appeared as a brown zone (0.56 g.), was rechromatographed on alumina using benzene–chloroform (6:1 v./v.) as developer. Most of fraction B fluoresced and was identical to fraction C. The slow moving fraction called B (recrystallized from ethanol to yield 0.030 g., m.p. 225–226°) is possibly the N-carboxyanilide derivative of 2-phenylbenz[*e*] isoindolin-1-one.

Anal. Calcd. for $C_{19}H_{14}N_2O_2$: C, 75.52; H, 4.64; N, 9.28. Found: C, 75.77; H, 5.14; N, 8.87.

Infrared spectrum of substance B (KBr): 3200 (w), 3030 (w), 2900 (w), 1700 (s), 1680 (m), 1645 (w), 1590 (s), 1548 (s), 1500 (m), 1447 (s), 1395 (w), 1359 (s), 1310 (w), 1275 (m), 1237 (s), 1178 (w), 1156 (m) cm.$^{-1}$.

Fraction C (0.33 g.) was rechromatographed on alumina according to the same procedure used for fraction B, yield 0.30 g. Recrystallization from ethanol gave pure material, m.p. 177°. The literature melting point of 2-phenylbenz[*e*]isoindolin-1-one[19] is 177°.

Anal. Calcd. for $C_{18}H_{13}NO$: C, 83.20; H, 5.02; N, 5.40. Found: C, 82.89; H, 5.32; N, 5.66.

Infrared spectrum of 2-phenylbenz[*e*] isoindolin-1-one in KBr: 3030 (w), 2900 (w), 1682 (s), 1643 (w), 1593 (m), 1550 (m), 1500 (m), 1444 (m), 1375 (s), 1294 (w), 1273 (w), 1245 (w), 1148 (m) cm.$^{-1}$.

Crossed Carbonylation Experiment of 1-Naphthaldehyde Phenylhydrazone and Benzaldehyde *m*-Tolylhydrazone to Yield 2-Phenylbenz[*e*]isoindolin-1-one and N-*m*-Tolylphthalimidine.—A mixture of 1-naphthaldehyde phenylhydrazone (0.32 g., 0.0013 mole) and benzaldehyde *m*-tolylphenylhydrazone (0.27 g., 0.0013 mole) was carbonylated as described previously in the Experimental section.

The product consisted of an organocobalt complex (0.066 g.) and a mixture of products which were separated by chromatography as described previously.

Benzaldehyde (0.032 g.), benzonitrile (about 0.020 g.), and 1-naphthonitrile were obtained from the first fraction. The second fraction was rechromatographed on alumina using benzene–petroleum ether (b.p. 30–65°) (6:1 v./v.) as developer. The product, 0.24 g., was recrystallized from ethanol, m.p. 177°, m.m.p. 177° with a sample of 2-phenylbenz[*e*]isoindolin-1-one prepared as described in the Experimental. The infrared spectra of both substances were identical.

The third fraction (0.14 g.), rechromatographed on alumina using benzene–chloroform (1:1 v./v.) as developer, was recrystallized from ethanol, m.p. 148–149°, m.m.p. 148–149° with an authentic sample of N-*m*-tolylphthalimidine. The infrared spectra of both compounds were identical.

Acknowledgment.—Grateful acknowledgment is made to the National Research Council of Canada for financial support of this work.

This research also was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

The authors also wish to express their gratitude to Dr. P. Kebarle of the University of Alberta, Edmonton, Canada, for the mass spectrometric analysis.

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Aldehyde Hemihydrates

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Received May 23, 1963

A reinvestigation of the dry codistillation of barium *n*-dodecanoate and barium formate has shown that Krafft's *n*-dodecanal, which was first reported in 1880, is *n*-dodecanal hemihydrate. *n*-Dodecanal, *n*-decanal, and *n*-heptanal on treatment with water form isolable hemihydrates in which the carbonyl groups and water are chemically combined. Hemihydrate formation appears to be a general reaction for normal aliphatic aldehydes. The experimental evidence indicates that the structures of the addition products are α,α'-dihydroxy ether derivatives.

In 1880, Krafft reported the synthesis of *n*-dodecanal and other higher aldehydes by the dry codistillation of the barium salts of the corresponding acids and barium formate.[2] The C_{12} aldehyde was characterized as a solid, melting at 44.5°. Subsequent investigators, however, characterized *n*-dodecanal, obtained by numerous synthetic methods[3–8] and from natural products,[9,10] as a high boiling liquid with a melting point of about 11°.

Krafft's *n*-dodecanal has been the subject of periodic conjecture since its isolation. The product has been postulated to be *n*-dodecanal polymer,[11,12] a hydrogen bonded complex of *n*-dodecanal and *n*-dodecanol,[7] the hemiacetal of *n*-dodecanal and *n*-dodecanol,[13] and *n*-dodecanal enol.[5] The polymeric structure does not appear to be the correct structure of Krafft's *n*-dodecanal because polymers of *n*-dodecanal have been prepared, and they have properties inconsistent with the properties of Krafft's material.[8,12] The hydrogen bonded structure and the hemiacetal are not satisfactory because Krafft's *n*-dodecanal has been prepared from liquid *n*-dodecanal purified through the bisulfite addition product[5] and the semicarbazone derivative,[10] thereby precluding the presence of *n*-dodecanol. The enolic structure postulated by Zaar[5] seemed to be the correct structure even though enols of simple aldehydes generally cannot be isolated.[14] This investigation was undertaken to confirm the enolic structure of Krafft's *n*-dodecanal.

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(1) To whom requests for reprints should be sent in care of The Pure Oil Company, Research Center, Crystal Lake, Ill.

(2) F. Krafft, *Ber.*, **13**, 1413 (1880).

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(14) *Cf.* P. H. Hermans, "Theoretical Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1954, Chap. XII.

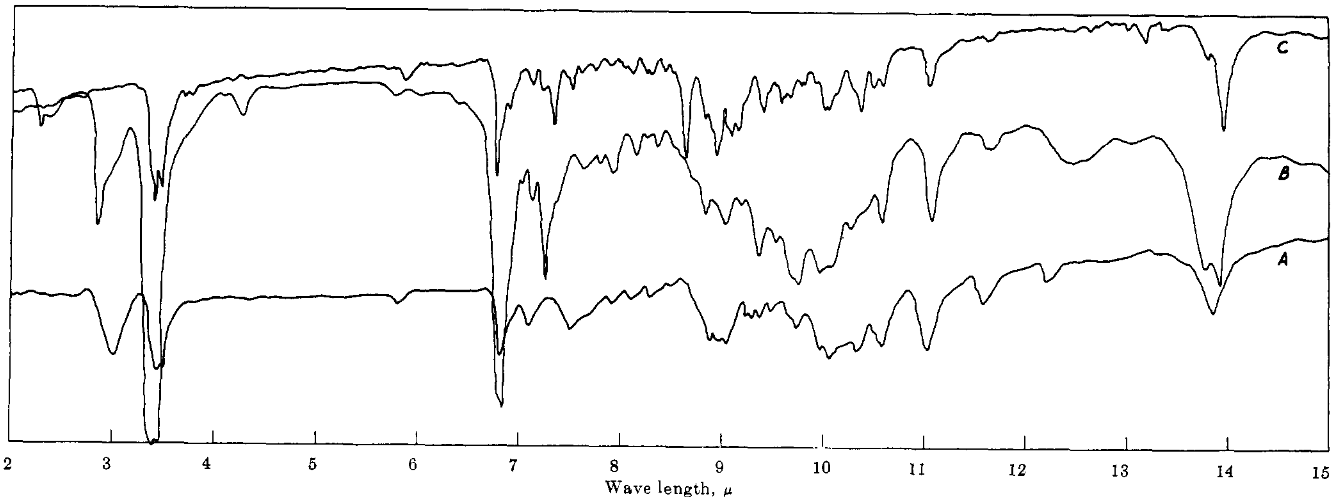


Fig. 1.—Infrared spectra of Krafft's *n*-dodecanal and *n*-dodecanal hemihydrate, solid (A); *n*-dodecanal-*n*-dodecanol hemiacetal, Nujol mull (B); and *n*-dodecanal trimer, Nujol mull (C).

Discussion

Krafft's procedure[2] was repeated to isolate his *n*-dodecanal for characterization by infrared analysis. Several experiments were carried out, but in each case, by-products were formed along with the desired product. Liquid *n*-dodecanal, *n*-dodecanal–*n*-dodecanol hemiacetal, and *n*-dodecanol were isolated by fractional distillation of the product mixture obtained from the dry co-distillation of barium *n*-dodecanoate and barium formate. A white, crystalline, odorless solid was isolated in low yields from the initial fractions and was characterized as Krafft's *n*-dodecanal by melting point and other properties. When the product was melted, decomposition occurred to yield liquid *n*-dodecanal. A direct comparison of the infrared spectra, shown in Fig. 1, of the solid product and the hemiacetal established the nonidentity of the compounds. These facts are in agreement with Zaar's earlier observations that Krafft's *n*-dodecanal affords liquid *n*-dodecanal on distillation, that the same carbonyl derivatives are formed from both products, and that Krafft's *n*-dodecanal and the hemiacetal are different.[4,5] The nonidentity of the solid and *n*-dodecanal trimer also was established in this work by direct comparison of the infrared spectra shown in Fig. 1.

Since several chemical reactions occurred when the mixture of the barium salts of *n*-dodecanoic and formic acids was thermally decomposed, attempts were made to develop a better preparative procedure to facilitate further characterization. Commercial stocks of liquid *n*-dodecanal purified through the bisulfite addition product and maintained under an inert atmosphere at a temperature slightly above the melting point of the aldehyde gave Krafft's *n*-dodecanal in low yields. Samples of liquid *n*-dodecanal that had been purified through the bisulfite addition product and also fractionally distilled formed the crystalline solid very slowly and in low yields on prolonged storage. Attempts to recrystallize the solid from most solvents resulted in decomposition to liquid aldehyde. On storage at room temperature, Krafft's *n*-dodecanal gradually reverted to liquid aldehyde as shown by infrared analysis and odor. Storage at lower temperatures reduced the rate of decomposition.

The properties of Krafft's *n*-dodecanal and the spectral evidence supported the enolic structure. The compound exhibits hydroxyl group absorption, and it has no carbonyl absorption as shown in Fig. 1. The absence of carbonyl absorption also tended to rule out the hydrogen bonded complex as a possible structure. However, additional evidence indicated that the enol could also be eliminated as a possible structure. Krafft's product did not give positive results in tests which are usually characteristic of enols, and it was found that liquid *n*-dodecanal from which Krafft's product had been removed did not form additional solid on storage. This latter observation was unexpected because the keto–enol equilibrium should of course be maintained.

The composition of Krafft's *n*-dodecanal was ultimately established as *n*-dodecanal hemihydrate by careful elemental analysis. Confirmatory evidence was obtained by the Karl Fischer and Zerewitinoff determinations, and by treatment of *n*-dodecanal, which had previously been separated from the hemihydrate, with trace amounts of water; the hemihydrate formed again on cool storage of the aldehyde. Conclusive evidence was obtained by treatment of liquid *n*-dodecanal with stoichiometric amounts of water; *n*-dodecanal hemihydrate identical with Krafft's *n*-dodecanal formed quantitatively. Pure anhydrous liquid *n*-dodecanal which cannot form the hemihydrate is thus difficult to prepare by the dry codistillation of the mixture of salts, by fractional distillation of the liquid aldehyde, or by use of conventional drying agents. The hemihydrate separates when samples of the liquid aldehyde containing trace amounts of water are stored.

To our knowledge, this investigation is the first characterization of a hemihydrate of a simple carbonyl compound, and it became of interest to examine the behavior of other aldehydes. It was found that both *n*-decanal and *n*-heptanal afford isolable hemihydrates. The infrared spectra of *n*-decanal hemihydrate and pure *n*-decanal reproduced in Fig. 2 show that the hemihydrate gradually decomposes to *n*-decanal in the infrared beam. The hemihydrate of *n*-heptanal was too unstable under ambient conditions to obtain the spectra in the usual manner. No further work was done with other aldehydes, but it seems probable that

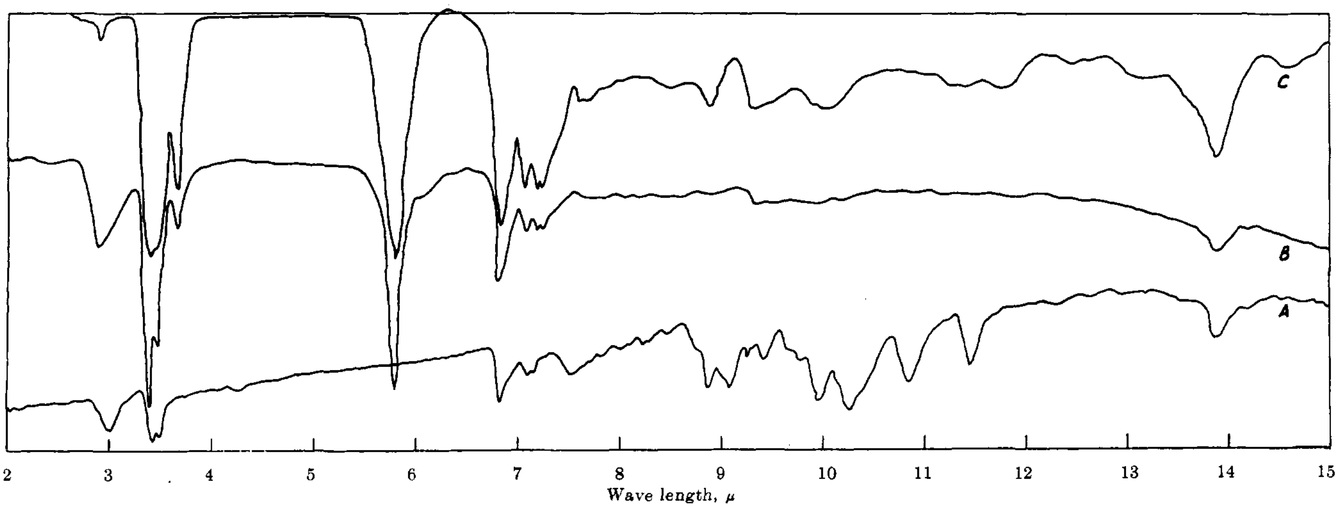


Fig. 2.—Infrared spectra of *n*-decanal hemihydrate, solid (A); *n*-decanal hemihydrate after 30 min. in infrared beam (B); and *n*-decanal, liquid (C).

hemihydrate formation is general for normal aliphatic aldehydes.

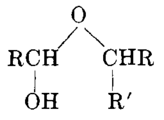
A few hydrates of simple aldehydes have been reported by other workers. In 1845, Bussy isolated a hydrate of *n*-heptanal,[15,16] and Noorduyn was later able to prepare a monohydrate and a dihydrate of the same aldehyde.[17] Colles reported several hydrates of acetaldehyde but the products were characterized only by analysis for acetaldehyde.[18] It is probable that one of Colles' hydrates which formed at −95° from a 2:1 molar mixture of acetaldehyde and water is acetaldehyde hemihydrate. Attempts were made in this investigation to prepare monohydrates by treatment of the aldehydes with equimolar quantities of water in both homogeneous and heterogeneous systems, but in each case, only the hemihydrate could be isolated. The melting points of each product prepared in this work are shown in Table I.

Table I

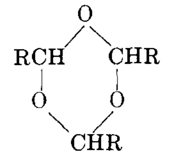
Melting Points[a]

	n-Heptanal	*n*-Decanal	*n*-Dodecanal
Free aldehyde	−43.2 to −42.2	−5 to −3.2	11–12.5
Hemihydrate[b]	54–59 dec.[c]	58.5–63 dec.[c]	56–60 dec.[c]
		41–42 dec.	41–44 dec.
Hemiacetal	Not prepared	Not prepared	46–48
Trimer	Not prepared	Not prepared	55–57

[a] Unless stated otherwise, melting points were taken at atmospheric pressure and are reported without stem corrections. [b] Heating rate of 2°/min. [c] Evacuated capillary tubes.



I, R = Alkyl
R′ = Hydroxyl
Ia, R = *n*-Undecyl
R′ = Hydroxyl
II, R = *n*-Undecyl
R′ = Hydrogen



III, R = *n*-Undecyl

The structures of the hemihydrates have not been rigorously established in this investigation, but it is probable that they are α,α′-dihydroxy ethers as shown in structure I. Compounds of structure I could form by simple addition of one molecule of the aldehyde monohydrate to the carbonyl group of another molecule of free aldehyde. Apparently, the equilibria are shifted to the hemihydrate, and its solubility characteristics and relatively high stability result in isolation of the hemihydrate and not the monohydrate. Some evidence in support of structure I has been collected during this work. The infrared data indicate that carbonyl groups are absent in the hemihydrates because carbonyl absorption[19a] is absent as shown in Fig. 1 and 2. It is possible that carbonyl absorption is obliterated in the spectra of the hemihydrates by strong hydrogen bonding of water of crystallization with the carbonyl groups. We consider this possibility to be unlikely however because infrared spectra of solutions of the hemihydrates in various solvents exhibit increasingly greater carbonyl group absorption with time, without the simultaneous appearance of the 6.0-6.2-μ peak characteristic of molecular water[19b] (see next paragraph). The absence of the 6.0–6.2-μ peak in the spectra of the pure hemihydrates is also partial support for structure I. Other tentative conclusions can be reached by comparing the spectrum of *n*-dodecanal hemihydrate (Ia) with spectra of *n*-dodecanal-*n*-dodecanol hemiacetal (II) and *n*-dodecanal trimer (III) shown in Fig. 1. The hemiacetal (Nujol mull) has a sharp peak at 2.85 μ which corresponds to an unassociated hydroxyl group while the hemihydrate (solid) has a broad band at 3.0 μ. This latter peak may be caused by associated hydroxyl groups, although the difference in the physical states of Ia and II during measurement of the spectra could result in frequency shifts of the hydroxyl absorption bands.[20] The hydroxyl groups of structure I would be expected to absorb at longer wave lengths because the positions of these groups favor intramolecular associa-

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(15) M. Bussy, *J. Pharm. Chim.*, **8**, 321 (1845).

(16) In 1845, water was considered to be HO, and the atomic weights of C, H, and O were 6, 1, and 8, respectively. By modern atomic weights, the formula calculable from Bussy's analysis for *n*-heptanal is $C_7H_{14}O$, the correct empirical formula. Bussy's hydrate would then correspond to the hemihydrate.

(17) A. C. Noorduyn, *Rec. trav. chim.*, **38**, 344 (1919).

(18) W. M. Colles, Jr., *J. Chem. Soc.*, **89**, 1246 (1906).

(19) *Cf.* (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chap. 9; (b) H. M. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand Company, Inc., New York, N. Y., 1949.

(20) See ref. 19a, Chap. 6.

tion.[21] Attempts to confirm experimentally the presence of two hydroxyl groups in the hemihydrates by the Zerewitinoff determination failed, presumably because the compounds decomposed in the solvent. The liberated water resulted in the detection of only one active hydrogen atom per mole of hemihydrate.[22] Dietherification with diazomethane also failed. Further examination of the spectra in Fig. 1 suggests the presence of ethereal oxygen atoms because of absorption in the 9-μ region. Absorption in this region arising from the C–O– stretching vibrations is characteristic of ethers.[19] The remainder of the "fingerprint" region is a complex series of bands which are similar in many respects. The peaks which occur at 10.6 μ and slightly greater than 11 μ appear to be characteristic of the ethereal oxygen atoms in structures Ia, II, and III.

Two inconsistencies remain. Zaar determined the molecular weight of Krafft's *n*-dodecanal in benzene by the freezing point technique, and he found that the molecular weight was about the same as that of *n*-dodecanal.[5] The origin of the water required to form *n*-dodecanal hemihydrate by Krafft's process also requires explanation. If Krafft's *n*-dodecanal decomposed in benzene to afford *n*-dodecanal and *n*-dodecanal monohydrate, the molecular weight determination would be very close to the molecular weight of *n*-dodecanal. Experimental evidence to support this hypothesis was obtained by infrared examination of benzene solutions of the hemihydrate. The hemihydrate was found to decompose in benzene solutions to yield *n*-dodecanal as shown by the appearance of the carbonyl peak immediately after solution occurred. Molecular water as measured by the 6.0–6.2-μ peak appeared only slowly in benzene solution. The pure hemihydrates also appear to decompose in a similar manner as illustrated by curves A and B in Fig. 2.

The formation of the necessary water during the dry co-distillation of the barium salts is difficult to explain because the salts were thoroughly dried before use. In later experiments, after Krafft's *n*-dodecanal had been characterized as the hemihydrate, it was established that water is evolved during the dry distillation when the temperature of the salt mixture is considerably above the boiling point of water. Water is apparently formed from the salts themselves during the high temperature decomposition. Krafft and Zaar probably did not observe product water because it combined with the aldehyde or because only small amounts of water were produced. Relatively small amounts of water are required to convert quantitatively the higher aldehydes to the hemihydrates.

Additional work is in progress on the mechanism of formation and decomposition of aldehyde hemihydrates.

Experimental[23]

Preparation of Acid Salts.—A solution of 100.2 g. *n*-dodecanoic acid, (0.50 mole), and 20.4 g. (0.51 mole) of sodium hydroxide in 1.1 l. of water was treated with 63.5 g. (0.26 mole) of barium chloride dihydrate in 150 ml. of hot water. The mixture was stirred vigorously during the addition and then cooled to 5°. Filtration, successive washing with water, Formula 30 alcohol (90.9 vol. % ethanol, 9.1 vol. % methanol), and ether, and drying at 60° (0.1 mm.) for 16 hr. gave barium *n*-dodecanoate.

Anal. Calcd. for $(C_{12}H_{23}O_2)_2Ba$ (535.97): Ba, 25.63. Found: Ba, 25.30.

A solution of 138.9 g. (3.02 moles) of formic acid, and 120.6 g. (3.01 moles) of sodium hydroxide in 500 ml. of water was treated with 366.5 g. (1.50 moles) of barium chloride dihydrate in 700 ml. of hot water. Formula 30 alcohol (4 l.) was then added with agitation to the cooled solution. Filtration, washing with Formula 30 alcohol, and drying at 105° for 5 days gave barium formate.

Anal. Calcd. for $(CHO_2)_2Ba$ (227.40): Ba, 60.44. Found: Ba, 59.60.

Similar procedures were used to prepare the calcium salts.

Krafft's *n*-Dodecanal.—Krafft's procedure was followed. A mixture of 75.0 g. of barium formate, 50.0 g. of barium *n*-dodecanoate, and 15.2 g. of barium carbonate (C.P. Baker's Analyzed) was thoroughly dispersed with a mortar and pestle. The mixture, 138 g., in a 500-ml. round-bottom flask equipped with a heating mantle, thermometer, and condensing apparatus was heated over 5.5 hr. (20 mm.). Distillation commenced when the pot temperature was about 248°. Slow distillation over a 2.5-hr. period at pot temperatures from 248 to 289° gave 14.0 g. of light yellow distillate which solidified to a semisolid mass in the cooled receiver. The product was fractionally distilled at 0.37 mm., and the distillation data are summarized in Table II.

TABLE II

Fraction	B.p., °C.	Wt., g.
1	60–62°	0.8
2	60–62°	2.0
3	60–75°	1.2
Trap	...	0.8
Not Distilled	...	8.9

Fraction 1 gave about 0.4 g. of a white crystalline, odorless solid after standing at 14° for a few hours. The product was collected by filtration, washed with cold anhydrous ether, and dried in the funnel. The product was characterized as Krafft's *n*-dodecanal by melting point, its reversion to liquid *n*-dodecanal on melting, and by infrared analysis.

After Krafft's *n*-dodecanal had been identified as *n*-dodecanal hemihydrate by comparison with hemihydrate prepared from liquid *n*-dodecanal, water was identified as a product of the dry distillation by infrared analysis and the anhydrous copper sulfate test. Water was found to distil from the reaction mixture at pot temperatures between 115 and 160° over the pressure range, 2–20 mm. Significant quantities of water, about 0.5–1.0 wt. % of the total salt mixture, were liberated from carefully dried salts; so water is probably a product of the reaction. Most of the water can be separated from the initial fractions of liquid *n*-dodecanal by use of reduced pressure and a cold trap.

Other experiments were carried out using modifications of this technique. Calcium salts and the barium and calcium salts together were also tried. In all experiments, liquid *n*-dodecanal, *n*-dodecanol, *n*-dodecanal-*n*-dodecanol hemiacetal, and water were isolated and identified by infrared analysis. In several experiments, it was difficult to obtain *n*-dodecanal hemihydrate uncontaminated with the hemiacetal by-product unless the aldehyde was further purified. Other products also formed during the dry distillation but they were not identified. An example of the fractional distillation at 0.11 mm. of 4.1 g. of product obtained from the dry distillation of 69.9 g. of barium formate, 27.1 g. of calcium *n*-dodecanoate, and 5.2 g. of calcium carbonate is shown in Table III.

Purification of Aldehydes.—*n*-Decanal[24] and *n*-dodecanal[25] were obtained from commercial stocks and converted to the bisulfite addition products which were stored under nitrogen in a desiccator. As needed, each aldehyde was recovered by steam distillation of the addition product from aqueous solutions of sodium bicarbonate, and the recovered aldehyde was fractionated,

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[21] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

[22] D. L. Klass and W. N. Jensen, *J. Org. Chem.*, **26**, 2110 (1961).

[23] Elemental analyses were performed by the Analytical Research and Services Division of The Pure Oil Company, Crystal Lake, Ill., and Micro-Tech Laboratories, Skokie, Ill. Karl Fischer analyses were performed by Colburn Laboratories, Chicago, Ill., and by Prof. K. A. Connors of the School of Pharmacy, University of Wisconsin. All melting points are uncorrected.

[24] Aldrich Chemical Company, Inc., Milwaukee, Wis.

[25] Kindly supplied by the Research Division, Armour and Company, Chicago, Ill.

TABLE III

Fraction	B.p., °C.	Wt., g.	Product
1	62–65	0.52	*n*-Dodecanal
2	62–65	0.68	*n*-Dodecanal
3	57–65	0.48	Impure *n*-dodecanal
4	65–67	0.78	*n*-Dodecanal-*n*-dodecanol hemiacetal
5	65–75	0.11	*n*-Dodecanal-*n*-dodecanol hemiacetal
6	76–86	0.33	Impure *n*-dodecanol
Trap	...	0.84	Impure water
Residue	...	0.28	Not identified

stored under nitrogen, and used within 24 hr. A sample procedure was the following.

n-Decanal, 420 g., was added to a solution of 440 g. of sodium bisulfite in 950 ml. of water. The mixture was agitated overnight on a rolling mill and the addition product was collected by filtration, washed successively with water, alcohol, and ether, and dried. The addition product, 225 g., was added to 2 l. of preboiled water containing 225 g. of sodium bicarbonate, and the resulting mixture was steam-distilled. The distillate was washed with water and dried with sodium sulfate; yield, 65.9 g. Fractionation through a Vigreux column gave a major fraction or pure *n*-decanal; yield, 52.7 g.; b.p. 58–60° (1.5 mm.); n^{19}D 1.4275.

Anal. Calcd. for $C_{10}H_{20}O$ (156.26): C, 76.71; H, 12.87. Found: C, 76.92; H, 12.78.

The oxime derivative was prepared in the usual manner and recrystallized from alcohol and benzene, m.p. 68–69°.

n-Dodecanal purified by this procedure exhibited b.p. 119–120° (10 mm.), n^{25}D 1.4302.

Anal. Calcd. for $C_{12}H_{24}O$ (184.31): C, 78.19; H, 13.13. Found: C, 78.10, 78.00; H, 13.00, 13.03.

The oxime derivative was prepared in the usual manner and recrystallized three times from alcohol, m.p. 77–78°.

n-Heptanal was used as received.[26]

The purity of the aldehydes was determined by titration with hydroxylamine in the usual manner and from plots of the melting "plateaus." Four grams of the aldehyde was placed in a Pyrex test tube of 10-mm. i.d. carrying a calibrated thermometer, and the aldehyde was "quick frozen" to avoid polymerization; the C_{10} and C_{12} aldehydes were solidified at −29°, and *n*-heptanal was solidified at −49°. The tube containing the frozen aldehyde was then enclosed in a larger test tube of 20-mm. i.d. and the apparatus was transferred to a room maintained at a constant temperature, 22° for *n*-dodecanal and 7° for *n*-decanal and *n*-heptanal. The time and temperature variations were measured and plotted in the usual manner. The flatness of the "plateaus" was considered to be the best criterion of purity. The melting points are listed in Table I.

Hydration of *n*-Dodecanal.—The hemihydrate was prepared by treatment of 5.0 g. of *n*-dodecanal with 0.24 g. of water (1:0.5 molar ratio), and the resulting mixture was placed under nitrogen in a refrigerator at 15°. The entire reaction mixture solidified to yield the waxy hemihydrate quantitatively. The odorless, white crystalline product was transferred to a funnel, washed with cold anhydrous ether, and dried in an evacuated desiccator; all of these operations were carried out in a room maintained at 4–5°. The product was insoluble at room temperature in nitrobenzene, cyclohexanol, and diphenyl ether; partially soluble in dioxane, ether, benzene, and cyclohexane; and soluble in pyridine and tetrahydrofuran. An infrared examination of benzene, ether, and tetrahydrofuran solutions of the product showed that the hemihydrate slowly decomposes with the regeneration of *n*-dodecanal. Qualitative tests including the bromine and ferric chloride tests in different solvents were carried out for *n*-dodecanal enol under a variety of conditions and all tests were negative.[27] The hemihydrate was identical with Krafft's *n*-dodecanal. The hemihydrate was stored for about 1 hr. in a Dry Ice–acetone cooling bath before elemental analysis was performed.

Anal. Calcd. for $(C_{12}H_{24}O)_2H_2O$ (386.64): C, 74.55; H, 13.03. Found: C, 74.88; H, 13.01.

Numerous attempts were made to detect two active hydrogen atoms per molecule of *n*-dodecanal hemihydrate by the Zerewitinoff determination using a previously developed technique.[22] One active hydrogen atom was detected in pyridine solvent.

The Karl Fischer determinations for water were carried out with 0.25-g. samples of the product.

Anal. Calcd. for $(C_{12}H_{24}O)_2H_2O$ (386.64): H_2O, 4.66. Found: H_2O, 4.0, 3.9, 3.9.

Attempts were made to isolate *n*-dodecanal monohydrate by conducting a similar experiment with a 1:1 molar mixture of *n*-dodecanal and water. Only the hemihydrate could be isolated.

Anal. Calcd. for $(C_{12}H_{24}O)_2H_2O$ (386.64): C, 74.55; H, 13.03. Found: C, 74.57; H, 12.70.

Attempts also were made to prepare *n*-dodecanal monohydrate in homogeneous aqueous solutions of tetrahydrofuran and pyridine; the hemihydrate was isolated. On numerous occasions, small amounts of the hemihydrate formed on storage of "pure" aldehyde at temperatures slightly above 12°. Removal of the hemihydrate gave filtrates which did not yield additional product on storage until trace amounts of water were added.

n-Dodecanal hemihydrate decomposed slowly on storage under nitrogen at room temperature. Repurification was accomplished by washing the aged samples with chilled anhydrous ether followed by drying in an evacuated desiccator. Recrystallization from ether gave reduced yields of the hemihydrate. Low temperature recrystallization without excessive decomposition may be possible, but this technique was not tried.

Freshly prepared samples of the hemihydrate decomposed when heated in open capillary tubes to slightly turbid liquid aldehyde which appeared to contain minute droplets of suspended water, and the decomposition point varied with the rate of heating. The decomposition points listed in Table I were obtained at a heating rate of about 2°/min.

The instrument used for measurement of the infrared spectra was a Perkin-Elmer Model No. 21 recording spectrophotometer installed in a room maintained at 21°. The spectra of *n*-dodecanal hemihydrate shown in Fig. 1 were obtained by pressing a few crystals of the compound between the sodium chloride plates of the sample holder in a room maintained at 4–5°. The sample holder was then immediately transferred to the spectrophotometer and the spectra were recorded in the usual manner. This technique was found to be the best procedure for recording reproducible spectra of the hemihydrate.

Hydration of *n*-Decanal.—The hemihydrate was prepared by the procedure used for *n*-dodecanal hemihydrate. *n*-Decanal hemihydrate was isolated as odorless, white crystals when the mixture of aldehyde and water was stored at 0°.

Anal Calcd. for $(C_{10}H_{20}O)_2H_2O$ (330.54); C, 72.68; H, 12.81; H_2O, 5.45. Found: C, 72.74, 72.56: H, 13.00, 12.83; H_2O, 5.6, 5.3, 5.8.

Attempts to isolate *n*-decanal monohydrate from equimolar mixtures of water and *n*-decanal afforded only hemihydrate. At room temperature, the hemihydrate was insoluble in *sym*-tetrabromoethane, slightly soluble in ether, and soluble in acetic acid and pyridine. Methylation with diazomethane in ether failed. Small amounts of the hemihydrate deposited on several occasions when supposedly dry *n*-decanal was stored in the refrigerator. Removal of the precipitate gave filtrates which did not form hemihydrate until small amounts of water were added. The decomposition points listed in Table I were measured at a heating rate of about 2°/min. The infrared spectra of the hemihydrate shown in Fig. 2 were obtained by the technique used with *n*-dodecanal hemihydrate.

Hydration of *n*-Heptanal.—*n*-Heptanal hemihydrate was isolated by the procedure used for *n*-dodecanal hemihydrate when the mixture of aldehyde and water was stored at −40°. The white crystalline product was odorless.

Anal. Calcd. for $(C_7H_{14}O)_2H_2O$ (246.38): C, 68.24; H, 12.27; H_2O, 7.31. Found: C, 67.93: H, 12.12; H_2O, 8.0, 8.9, 8.9.

Attempts to prepare *n*-heptanal monohydrate using equimolar mixtures of aldehyde and water gave hemihydrate only. Attempts to obtain the infrared spectra of *n*-heptanal hemihydrate failed because the compound decomposed too rapidly under ambient conditions. The decomposition point shown in Table I was measured at a heating rate of about 2°/min.

***n*-Dodecanol-*n*-dodecanol Hemiacetal.**—The hemiacetal was prepared according to the procedure of Erickson and Campbell.[13] Recrystallization from acetone gave pure hemiacetal, m.p.

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[26] Distillation Products Industries, Eastman Organic Chemicals, Rochester, N. Y.

[27] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 93, 98.

46–48°. The infrared spectrum of a Nujol mull of the hemiacetal is reproduced in Fig. 1.

n-**Dodecanal Trimer.**—Four grams of *n*-dodecanal was placed in a stoppered test tube under nitrogen. The test tube contained a side arm in which 1 drop of concentrated hydrochloric acid was placed to promote the polymerization. The aldehyde was frozen and kept in the refrigerator at 4–5° for 1 month. The product was then transferred to an erlenmeyer flask and 25 ml. of alcohol, 3.1 ml. of 0.5 *N* sodium hydroxide solution, and 40 ml. of 3.0 *N* hydroxylamine hydrochloride reagent were added. The mixture was stored at room temperature for 2 weeks to convert all unchanged aldehyde to the oxime, and the insoluble polymer was then filtered, washed with water, and air-dried; yield, 3.5 g. Recrystallization from alcohol afforded pure *n*-dodecanal trimer, m.p. 55–57° (lit.[8] m.p. 57°). Molecular weight determinations in benzene by the freezing point technique gave values of 526 and 529, calcd. 553. The infrared spectrum of a Nujol mull is reproduced in Fig. 1.

The Addition of Aromatic Nitroso Compounds to Conjugated Dienes

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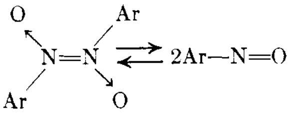
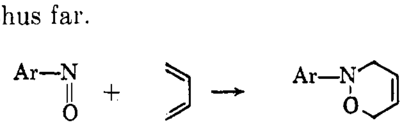
Received May 27, 1963

The addition of aromatic nitroso compounds to 2,3-dimethyl-1,3-butadiene was found to be a first-order reaction in respect to the nitroso compound and to the diene. The energies of activation of the reaction betweeen the conjugated diene and nitrosobenzene or *p*-bromonitrosobenzene were found to be, respectively, 14.23 and 12.46 kcal./mole. Nitrosobenzene failed to react with anthracene, but yielded an adduct with 1,3-cyclooctadiene.

Reactions involving the aromatic nitroso group lend themselves well to kinetic studies, since the nitroso group exhibits specific absorption bands in the visible, ultraviolet, and infrared spectra. Complications may arise from the fact that for many aromatic nitroso compounds in solution an equilibrium exists between the monomeric and dimeric forms. This complication may be avoided by the selection of aromatic nitroso compounds known to be monomeric in solution, *e.g.*, nitrosobenzene, *p*-halonitrosobenzenes, and *p*-nitroso-N,N-dimethylaniline.[1]



The addition of aromatic nitroso compounds to conjugated dienes is commonly considered a Diels–Alder reaction of heteroatomic compounds.[2] The reaction generally proceeds smoothly at moderate temperatures. With few exceptions the sole reaction product has been found to be a substituted 3,6-dihydro-1,2-oxazine.[2–4] Kinetic studies of the addition of aromatic nitroso compounds to conjugated dienes have not been reported thus far.



The dissociation of a 3,6-dihydro-1,2-oxazine into conjugated diene and nitroso compound normally requires considerably higher temperatures than the addition. The formation of an aromatic nitroso compound by the dissociation of the Diels–Alder adduct of various aromatic nitroso compounds and 2,3-dimethyl-1,3-butadiene could not be detected at temperatures below 35°. The rate of this reverse reaction at temperatures below 35° is, therefore, negligible, facilitating the determination of the rate of the addition of aromatic nitroso compounds to 2,3-dimethyl-1,3-butadiene.

Nitrosobenzene when treated with 2,3-dimethyl-1,3-butadiene has been reported to yield small quantities of a side product of unknown structure in addition to the expected N-phenyl-3,6-dihydro-4,5-dimethyl-1,2-oxazine.[5] When a large excess of diene was employed the sole product of the reaction was the oxazine. The side product is believed to be derived from the reaction of nitrosobenzene and the oxazine derivative.[6] For *p*-bromonitrosobenzene, on the other hand, only one product, the expected oxazine, was observed in the addition reaction, employing various concentrations of 2,3-dimethyl-1,3-butadiene.

Results

In order to suppress the formation of a side product, the reaction of nitrosobenzene and 2,3-dimethyl-1,3-butadiene was studied in dichloromethane with a fiftyfold excess of diene. Several Guggenheim plots were constructed at 2° and 25°. The reaction was found to be a first-order reaction in respect to nitrosobenzene, with a specific rate constant at 2° and 25° of 2.84×10^{-4} and 2.10×10^{-3} l. moles^{-1} sec.$^{-1}$. The energy of activation was found to be 14.23 kcal./mole, and the frequency factor, 6.2×10^{6} l. moles^{-1} sec.$^{-1}$.

Nitrosobenzene did not form an adduct with anthracene, even after prolonged reflux in chloroform. An adduct between nitrosobenzene and 1,3-cyclooctadiene was obtained, but the yield was less than 5%, and the reaction was too slow to permit observation.

The reaction between *p*-bromonitrosobenzene and a fiftyfold excess of 2,3-dimethyl-1,3-butadiene also was found to be a first-order reaction (see Fig. 1). It was found to be first order in respect to *p*-bromonitrosobenzene and first order in respect to 2,3-dimethyl-1,3-butadiene when the concentrations of the reactants were of the same magnitude. The specific rate constants were found to be 1.10×10^{-3}, 3.84×10^{-3}, 7.60×10^{-3}, and 8.29×10^{-3} l. moles^{-1} sec.$^{-1}$ at 2,

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