THE JOURNAL OF Organic Chemistry®

VOLUME 29, NUMBER 5 | MAY 12, 1964

Pyrolytic and Photolytic Decomposition of Trityl β-Naphthoate[1]

K. DARRELL BERLIN AND BRIJRAJ S. RATHORE[2]

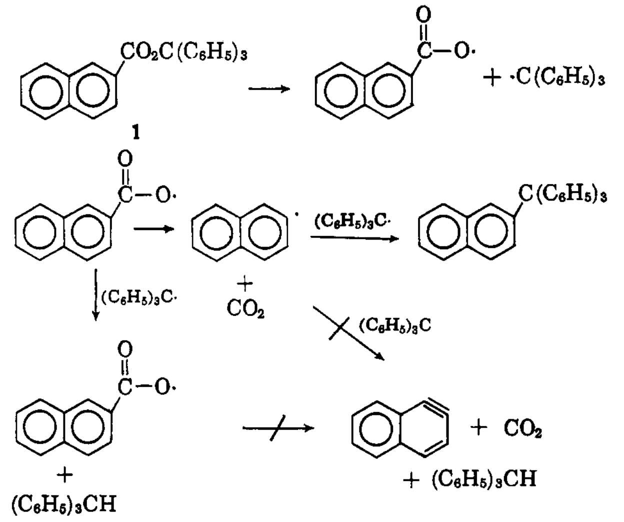
Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma

Received November 19, 1963

Pyrolysis of trityl β-naphthoate was investigated over the range 250–350° in a static system. Although the decomposition was examined after long time intervals, the process was essentially complete within an interval of 1.5 hr. Both acyl–oxygen and alkyl–oxygen bond severance occurred as evidenced by the major products, β-naphthoic acid, β-naphthoic anhydride, triphenylmethane (tritane), and two polymers, one a hydrocarbon and the other a polyester. Minor products observed were carbon dioxide, carbon monoxide, water, naphthalene, benzophenone, 9-phenylfluorene, and an unknown gas. Oxidation of the melt resulted in a marked increase in benzophenone. Although photolysis of the ester in an oxygen atmosphere resulted in limited decomposition, benzophenone was identified in the photolysate. A radical mechanism is postulated to explain the data.

As part of a program to elucidate the chemistry of aroyloxy radicals generated under pyrolytic conditions, trityl β-naphthoate was considered important since little has been published on β-naphthoxyloxy radicals. In view of the preference of trityl radical to abstract hydrogen rapidly at elevated temperatures,[3] naphthyne was envisioned as a possible intermediate *via* removal of the α-hydrogen and loss of carbon dioxide.[4,5] Moreover, trityl β-naphthalene is a conceivable product since the homolog, trityl benzoate, is recorded to decompose at 235° with tetraphenylmethane formed in moderate yields.[6,7] The simplicity of decomposition as depicted in Scheme I was not observed, however.

SCHEME I



Trityl β-naphthoate (1) was prepared by an extension of the method described previously.[8] Recently we reported the pyrolysis of several trityl alkyl carboxylates from which acyl-oxygen and alkyl-oxygen bond cleavages were observed.[3] Thermal decomposition of 1 was conducted in a static system over the range 250–350° under nitrogen. It was discovered that the ester decomposed completely within 1.5 hr. near 350°. Major products were β-naphthoic acid, β-naphthoic anhydride, tritane, and two polymers (A and B). Small amounts of several other compounds also were observed as shown in Table I.

Molecular models indicate the ester to be quite hindered with carbonyl oxygen atom in close proximity to an orthohydrogen on the phenyl ring of the trityl moiety. High yields of β-naphthoic acid suggest cleavage of ester in such a manner that the acid is formed rapidly. A concerted mechanism for the decomposition is conceivable as shown, although initial homolytic alkyl–oxygen fission is possible perhaps to give radical pairs. β-Naphthoyloxy radical has been reported as unstable in boiling carbon tetrachloride.[6] In regard to the thermal stability of β-naphthoyloxy radical, pyrolysis of β-naphthoyl peroxide occurred vigorously at

---

[1] (a) We gratefully acknowledge the generous support of the National Science Foundation, Grant 19733; (b) the paper was presented in part at the Southwest Regional Meeting of the American Chemical Society, Dec., 1963, Houston, Tex.

[2] Dow Chemical Company Predoctoral Fellow, 1963-1964.

[3] K. D. Berlin, L. H. Gower, B. S. Rathore, G. P. Sturm, J. W. White, J. B. Richards, and M. Peterson, *J. Org. Chem.*, **28**, 2039 (1963).

[4] A discussion of possible benzyne-type intermediates in ester pyrolysis can be found in the literature [P. E. Reininger and P. D. Ritchie, *J. Chem. Soc.*, 2678 (1963)].

[5] It is recorded that β-naphthoyl peroxide decomposes in carbon tetrachloride to give several decarboxylated naphthalene derivatives [see M. S. Kharasch and R. L. Dannley, *J. Org. Chem.*, **10**, 406 (1945)].

[6] E. Jones and P. D. Ritchie, *J. Chem. Soc.*, 4141 (1960).

[7] Noteworthy is the isolation of tetraphenylmethane (20-30%) from the reaction of trityl radical with benzoyl peroxide [see G. S. Hammond, J. T. Rudesill, and F. J. Modic, *J. Am. Chem. Soc.*, **73**, 3929 (1951)].

[8] K. D. Berlin, L. H. Gower, J. W. White, D. E. Gibbs, and G. P. Sturm, *J. Org. Chem.*, **27**, 3595 (1962).

TABLE I

PYROLYSIS OF TRITYL β-NAPHTHOATE (UNDER NITROGEN)[a]

Products	Wt., g.	Mole % of ester
Carbon dioxide	0.0799	3.63
Carbon monoxide Naphthalene Water Unknown gas	0.1723	
β-Naphthoic acid	5.8795	68.4
β-Naphthoic anhydride	0.865	10.6
Tritane	4.6672	38.2
9-Phenylfluorene	0.1938	1.6
Benzophenone	0.0073	0.008
Polymer A	2.137	17.4
Polymer B	4.80	
Tar	0.683	
	19.485	
Wt. of ester	20.700	

[a] Temperature, 345–350°; time, 1.5 hr.

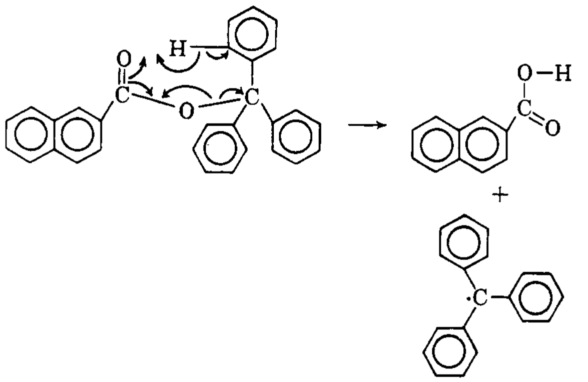
TABLE II

PYROLYSIS OF β-NAPHTHOYL PEROXIDE[a]

Products	Wt., g.	Mole % of peroxide
Carbon dioxide	0.1225	27.8
β-Naphthoic acid	0.768	44.6
Naphthalene	Traces	
Residue	0.510	
	1.4005	
Wt. of peroxide	1.710	

[a] Temperature, 107–109°; time, 10 min.

109° to yield β-naphthoic acid and carbon dioxide (Table II). Apparently β-naphthoyloxy radicals decay by removing a hydrogen from the naphthalene ring in a fast reaction. Consequently, the reactivity of this aroyloxy radical would be enhanced at pyrolysis temperature as would the rate of decarboxylation. Since very little carbon dioxide is evolved, it is doubtful that naphthoyloxy radicals are entirely free, and hence formation of a biradical and naphthoic acid is proposed as the mechanism rather than the cleavage of the ester into β-naphthoyloxy and trityl radicals. A biradical intermediate has been postulated previously from the decay of trityl radical.[9] It is suggested that a similar highly reactive biradical **2** is formed which rearranges to another biradical **3**. Intramolecular coupling of this biradical would give 9-phenylfluorene or the former could polymerize to polymer A. Scheme II is proposed to account for most of the products. Tar also is obtained, and very probably its precursor may furnish hydrogen for trityl radicals to give tritane. Formation of naphthoic anhydride, naphthalene, carbon dioxide, and water is thought to result from secondary pyrolysis of β-naphthoic acid.[10] This conclusion is supported by the fact that pyrolysis of β-naphthoic acid gave identical products in nearly proportionate mole ratios with 69% recovery of the acid (Table III).



SCHEME II

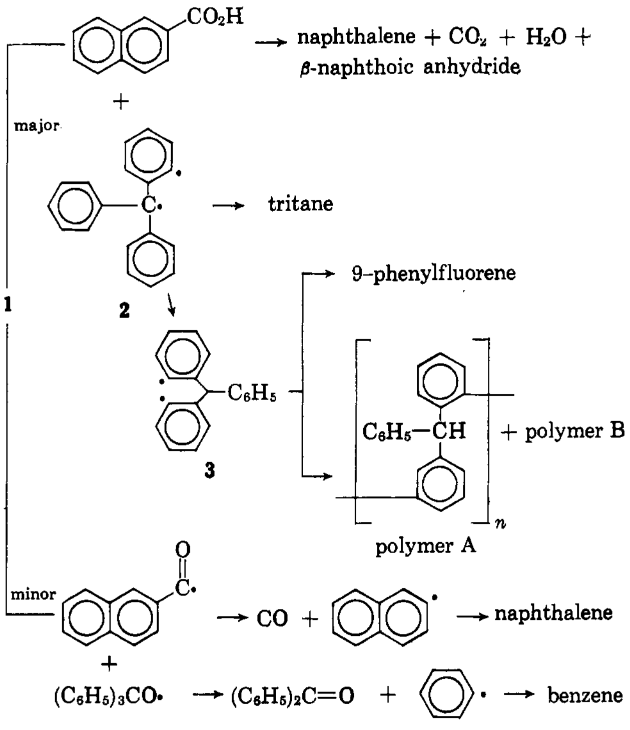


TABLE III

PYROLYSIS OF β-NAPHTHOIC ACID[a]

Products	Wt., g.	Mole % of acid
Naphthalene Carbon dioxide Water	0.146	
β-Naphthoic anhydride	1.040	24.4
β-Naphthoic acid	3.106	69.0
	4.292	
Wt. of acid	4.502	

[a] Temperature, 345–355°; time, 1.5 hr.

Elemental analysis of polymer A confirmed its hydrocarbon skeleton with an empirical formula of $C_{19}H_{14}$. Strong absorption in the infrared at 700 and 745 cm.$^{-1}$ implies the presence of mono- and *ortho*-substituted phenyl groups.

A comparison of the ultraviolet spectrum of polymer A with that of 9-phenylfluorene and 2,2′-dimethylbiphenyl showed remarkable similarities as might be expected (Table IV). Additional support for the postulated structure of polymer A was gained by examination of the n.m.r. spectrogram which displayed a complex multiplet at δ 7.18 and a singlet at 5.46. The latter is nearly identical with the field position of the tertiary hydrogen in tritane.

---

(9) R. L. Letsinger, R. Collat, and M. Magnusson, *J. Am. Chem. Soc.*, **76**, 4185 (1945).

(10) Decarboxylation of β-naphthoic acid by distillation with barium hydroxide has been reported by M. Merz [*Z. Chem.*, **12**, 72 (1869)]. However, a survey of the literature revealed that pyrolysis of β-naphthoic acid by itself or its esters has not been studied previously.

TABLE IV

A COMPARISON OF ULTRAVIOLET SPECTRA[a]

Polymer A	9-Phenylfluorene	2,2′-Dimethylbiphenyl
240	236	230.9
269	268	264
280	276	273

[a] Values are given in mμ.

Polymer B did not give consistent analytical results even with samples that had been fractionated repeatedly. Infrared absorption at 1739 cm.$^{-1}$ suggests a carbonyl group, but it is apparently hindered since the polymer resisted boiling alkali, Girard T reagent, and boiling alkaline potassium permanganate. Certainly, if it is an ester function it is not on a terminal position, since **1** is saponified rapidly by dilute base.

In an effort to learn the fate of tritane in the presence of β-naphthoyloxy radical, the hydrocarbon was heated at 145° in the presence of β-naphthoyl peroxide.[11] Although decarboxylation and formation of naphthoic acid were recorded, nearly 90% tritane could be recovered. Minor products detected were tritanol, β-naphthyl β-naphthoate, and trityl peroxide (Table V).

TABLE V

PYROLYSIS OF β-NAPHTHOYL PEROXIDE WITH TRITANE[a]

Products	Wt., g.	Mole % of peroxide
Carbon dioxide	0.136	30.9
β-Naphthoic acid	0.525	30.5
Tritanol	0.05	
Trityl peroxide	Traces	
β-Naphthyl β-naphthoate	0.05	
Benzophenone	Trace	
Naphthalene	Trace	
Tritane	2.14	87.7%
Residue	0.08	(Recovered)
Wt. of peroxide	1.71	
Wt. of tritane	2.44	

[a] Temperature, 142–145°; time, 60 min.

Formation of peroxide probably occurs through oxidation of trityl radical. The infrared spectrum of the small residue was identical in nearly all respects with the residue obtained from static pyrolysis of β-naphthoyl peroxide. It was noted that this residue possessed a different structure from that of polymer A or B. However, the data indicate that tritane is attacked by the β-naphthoyloxy radical which may account to a small extent for the product distribution in the pyrolysate of **1**.

Photolysis of **1** in boiling benzene with an oxygen stream directed into the solution resulted in partial decomposition of the ester to give tritanol, benzophenone, and β-naphthoic acid. Oxidation of the ester **1** at 350° resulted in a remarkable increase in the yield of benzophenone compared to the static pyrolysis under nitrogen. Clearly these products suggest initial homolytic fission in the ester.

Both polymer A and 9-phenylfluorene were conspicuously absent from the oxidation at high temperature. However, a new material, polymer C, was isolated from the pyrolysate. Formation of polymer C *via* oxidation of polymer B determined the origin of the former (Table VI). The similarities between the photolytic and pyrolytic decompositions of **1** suggest a radical pathway of decay following initial homolysis of the alkyl–oxygen bond.

TABLE VI

PYROLYSIS OF TRITYL β-NAPHTHOATE (IN OXYGEN)[a]

Products	Wt., g.	Mole % of ester
Carbon dioxide	0.075	7.35
Naphthalene Water	0.065	
β-Naphthoic acid	2.601	65.3
β-Naphthoic anhydride	0.380	10.0
Tritane	1.620	28.9
Benzophenone	0.445	10.55
Polymer C	2.601	
Insoluble residues	0.310	
	8.097	
Wt. of ester	9.5795	

[a] Temperature, 345–355°; time, 1.5 hr.

Experimental[12]

Preparation of Trityl β-Naphthoate (1).—Trityl bromide (16.1 g., 0.05 mole) and sodium β-naphthoate (10.9 g., 0.056 mole) in 70 ml. of benzene were boiled for 39 hr. The contents were filtered while hot, and the filtrate was concentrated to an oil. About 15 ml. of isopropyl ether was added and the contents were concentrated again. A pale yellow solid was obtained which was washed with about 25 ml. of isopropyl ether containing 2 ml. of triethylamine; yield 17.7 g. (86.7%), m.p. 146–149°. Recrystallization from isopropyl ether raised the melting point to 149–150°; infrared spectrum (KBr): 3030, 1724, 1282, 781, 763, 743, and 714–689 cm.$^{-1}$ (broad).

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.95; H, 5.31. Found: C, 86.59; H, 5.39.

Pyrolysis of Trityl β-Naphthoate in Nitrogen.—The pyrolysis was studied in a static system using a salt bath (potassium nitrate, sodium nitrate mixture) preheated to 350° and which was removed at the end of the heating period (1.5 hr.). On cooling, the contents set to a hard solid mass which was dissolved in 200–300 ml. of carbon tetrachloride, and the solution was poured into 500 ml. of Skelly F. The contents were then concentrated to dryness. The yellow mass obtained was extracted with Skelly F in a Soxhlet extractor.

The Skelly F extract contained tritane, benzophenone, 9-phenylfluorene, and polymer A, all of which were separated by chromatography on acid-washed alumina. 9-Phenyfluorene was identified by its infrared spectrum.[13] Extraction of the residue with sodium bicarbonate removed the free acid. The new residue obtained was essentially polymer B and β-naphthoic anhydride with small amounts of tritane, benzophenone, 9-phenylfluorene, and polymer A. This residue was further fractionated by extraction with Skelly B. The Skelly B insoluble solid softens at 260° and turns brown near 270–280° with no sharp melting point. Extraction of this residue with methanol gave only a tar that was absorbed by charcoal. Reprecipitation of this solid from a carbon tetrachloride solution with ethanol gave fractions which melted above 300°. Concentration of the Skelly B extract gave lower melting fractions of polymer B (identical infrared spectra), which were filtered. The filtrate was then evaporated to dryness and the residue was extracted with methanol. Evaporation of the methanolic extract to dryness gave a semi-

---

(11) Wieland has studied the pyrolysis of benzoyl peroxide in the presence of tritane and observed the formation of benzoic acid, trityl benzoate, and carbon dioxide in high yield [see H. Wieland, T. Ploetz, and H. Indest, *Ann.*, **532**, 179 (1937)].

(12) Carbon dioxide was determined by absorption in an ascarite tube. Vapor phase chromatographic (v.p.c.) analyses were done on a Wilkens Model A-550 Hy Fi hydrogen flame unit using a column of silicone rubber, 10% on Chromosorb W., 80–100 mesh, 8 ft. × 1/8 in. Infrared spectra were recorded on a Beckman IR-5 instrument. N.m.r. spectra were recorded on a Varian A-60 high resolution spectrometer. Tetramethylsilane was used as an internal standard with its scale as 0 in δ units. Skelly F is petroleum ether, b.p. 35–45°. Skelly B is petroleum ether, b.p. 60–70°. Microanalyses were done by Midwest Microlab, Inc., Indianapolis, Ind.

(13) An authentic sample was kindly supplied by Mr. James Rea, Department of Chemistry, University of Missouri, Columbia, Mo.

solid residue. This was treated with Girard T reagent to remove benzophenone. The residual material was refluxed with aqueous sodium hydroxide (25 ml. of 10% solution) to hydrolyze the anhydride or any ethyl or methyl ester that might have formed during the work-up. Acidification with concentrated hydrochloric acid gave β-naphthoic acid. The base-insoluble portion was chromatographed over alumina to yield tritane, 9-phenylfluorene, and polymer A. The products are listed in Table I.

Polymer A.—This material was soluble in ethanol and could be separated into different fractions by fractional precipitation from an ethanolic solution with water. Melting ranges of fractions varied from 80–144°. The polymer softened to a glassy bead which could be tapped from the melting point capillary tube. Molecular weight determination[14] on a fraction with melting range of 132–144° gave values of 598–600 in benzene solution; infrared spectrum (KBr): 3030, 1600, 1492, 1449, 1034, 744, and 700 cm.$^{-1}$.

Anal. Calcd. for an empirical formula $C_{19}H_{14}$: C, 94.01; H, 5.78. Found: C, 93.66; H, 5.78.

Polymer B.—Fractions with melting ranges varying from 150–300° were isolated during the work-up; infrared spectrum (KBr): 3030, 1739, 1600, 1492, 1449, 1279, 1187, 1034, 744, and 700 cm.$^{-1}$.

Anal. Found for fraction melting at 233–252°: C, 88.96; H, 5.18. Found for fraction melting above 300°: C, 91.75; H 5.25.

Pyrolysis of Trityl β-Naphthoate Using Oxygen.—Pyrolysis was effected in the same system as above with the exception that oxygen was bubbled into the melt. Traces of naphthalene were detected as sublimate in the condenser. After cooling, the residue was dissolved in benzene and extracted with cold sodium bicarbonate to remove the free acid. The anhydride was hydrolyzed and removed by boiling the solution with aqueous sodium hydroxide solution. V.p.c. analysis of the solution showed only benzophenone and tritane as the volatile components. Benzophenone was leached by treatment with Girard T reagent, and tritane was isolated by chromatography on alumina. The final residue was chiefly polymer C. Table VI contains all products.

Pyrolysis of β-Naphthoic Acid.—β-Naphthoic acid was pyrolyzed in the same system. After removal of the free acid by extraction with cold sodium bicarbonate, the residue was characterized and shown to be β-naphthoic anhydride, m.p. 136–137°, lit.[15] m.p. 133–134°.

Pyrolysis of β-Naphthoyl Peroxide.[16]—The flask containing the peroxide was heated cautiously to 107° in an oil bath. The contents softened slightly and decomposed vigorously after heating at 107–109° for 10 min. Heating was stopped and the oil bath was removed. β-Naphthoic acid was extracted with base and left an orange solid containing a trace of naphthalene and an unknown substance which showed carbonyl absorption at 1724 and 1695 cm.$^{-1}$ in the infrared spectrum. This material resisted all attempts at purification by recrystallization or sublimation. Table II shows all products.

Pyrolysis of β-Naphthoyl Peroxide with Tritane.—The two components in the molar ratio 1:2 were carefully powdered and transferred to the pyrolysis flask. The contents slowly were heated to 142° over a period of 1 hr. during which time some effervescence was observed. Further heating for 1 hr. was done at 142–145°. After removal of the acid, the base-insoluble residue was chromatographed over alumina. The various products are listed in Table V.

Photolysis of Trityl β-Naphthoate.—Photolysis of the ester in benzene with oxygen bubbling into the solution was studied over a period of 72–93 hr. A type 30620 Hanovia lamp (140 watts) was used. The infrared spectrum of the crude photolysate indicated β-naphthoic acid. The contents then were refluxed with a solution of 5 g. of sodium hydroxide in 50 ml. of water. The nonacid portion was found to be tritanol containing a small quantity of benzophenone as identified by v.p.c.

---

[14] We acknowledge our thanks to Dr. Paul O. McCoy, Department of Chemistry, University of Oklahoma, Norman, Okla., for the molecular weight determination.

[15] O. Hausamann, *Ber.*, **9**, 1515 (1876).

[16] Crude peroxide melting at 120–125° was used. Pure peroxide decomposes explosively at 138°.

Multinuclear Ferrocenes. III. Acetylation of Biferrocenyl[1-3]

STANLEY I. GOLDBERG AND JAMES S. CROWELL

Department of Chemistry, University of South Carolina, Columbia, South Carolina

Received October 16, 1963

Acetylation of biferrocenyl with acetic anhydride in the presence of polyphosphoric acid provides all three possible monoacetylbiferrocenyl position isomers as well as three isomeric diacetylbiferrocenyls. Structure assignments for all products are made on the basis of n.m.r. analysis, while previous infrared and ultraviolet spectral correlations for disubstituted ferrocenes are examined. In spite of the fact that the ferrocenyl group has been established as a strong electron donator, competitive acetylation of ferrocene and biferrocenyl in the present work shows that biferrocenyl is less susceptible to electrophilic substitution than is ferrocene. This apparent inconsistency is explicable in terms of a rapid equilibrium in which the iron atom of one ferrocene nucleus in biferrocenyl is bonded to electrophile, thus deactivating the molecule.

With the availability of methods of synthesis much better than that used in its initial preparation,[4] notably the Ullmann-type coupling of iodoferrocene,[5,6] study of biferrocenyl became a practical undertaking, and we began investigations into the chemistry of this molecule. Since the biferrocenyl molecule may be viewed as a ferrocene nucleus bearing a ferrocenyl substituent, we were interested initially in learning its reactivity relative to ferrocene itself as well as the possibility of obtaining information regarding the existence of any preferred pattern of orientation during electrophilic substitution.

Results and Discussion

A. Relative Reactivity.—In several instances the ferrocenyl group has been shown to possess strong electron-donating ability. Thus, ferrocenylbenzoic acids and ferrocenylphenols are weaker acids than benzoic acid and phenols, respectively, and *m*- and *p*-ferrocenylanilines are stronger bases than aniline itself.[7] The remarkable stability of a ferrocenylcarbinyl

---

[1] Previous paper: S. I. Goldberg and R. L. Matteson, *J. Org. Chem.*, **29**, 323 (1964).

[2] We are pleased to acknowledge generous support of this work by the National Science Foundation, Grant G-24083. We also wish to express additional thanks to that agency for the institutional grant which made possible the purchase of the n.m.r. spectrometer used in this work.

[3] Taken in part from the M.S. thesis of J. S. Crowell, University of South Carolina, 1963.

[4] S. I. Goldberg and D. W. Mayo, *Chem. Ind.* (London), 671 (1959).

[5] E. G. Perevalova and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **132**, 1093 (1960).

[6] M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

[7] A. N. Nesmeyanov, E. G. Perevalova, and R. V. Golovnya, *Dokl. Akad. Nauk SSSR*, **103**, 81 (1958); *cf.* A. N. Nesmeyanov, *Proc. Roy. Soc.* (London), **246**, 495 (1958).