The Synthesis of Secondary Organoaluminum Compounds

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The displacement reaction of triisobutylaluminum or diisobutylaluminum hydride with various straight-chain internal olefins and the reaction of aluminum with hydrogen and internal olefins were investigated. Contrary to prior belief both processes were found to be preparatively useful and to result, under proper conditions of temperature and pressure, in the formation of open-chain di-*sec*-alkylaluminum hydrides, a new class of organoaluminum compounds. Yields of approximately 95% were realized in the preparation of di-*sec*-tridecylaluminum hydride and di-*sec*-dodecylaluminum hydride *via* the displacement route, and aluminum conversions of between 65% with cyclohexene and 82% with 3-heptene, 4-nonene, and 6-dodecene were achieved in the total synthesis of the respective di-*sec*-alkylaluminum hydrides. The optimum reaction conditions were determined for both processes. The secondary organoaluminum hydrides were isolated and identified in these six cases, and the thermal stability of these compounds was determined. Only partial displacement could be effected in the reaction of diisobutylaluminum hydride with the trialkylethylene 6-*n*-amyl-5-undecene. No evidence for the presence of tertiary aluminum alkyl in the reaction product could be detected. Difficulty of displacement was also encountered in the case of 2-methyl-7-ethyl-3- (and 4-) nonene.

In 1954 K. Ziegler and co-workers discovered two fundamentally new processes for the synthesis of aluminum trialkyls and dialkylaluminum hydrides. One of these is known as the so-called "direct" (total) synthesis[2] and in the newer literature usually is represented by eq. 1 and 2. The other process is referred to as

$$2\mathrm{Al}(\mathrm{C}_n\mathrm{H}_{2n+1})_3 + \mathrm{Al} + 1.5\mathrm{H}_2 \longrightarrow 3\mathrm{HAl}(\mathrm{C}_n\mathrm{H}_{2n+1})_2 \quad (1)$$

$$3\mathrm{HAl}(\mathrm{C}_n\mathrm{H}_{2n+1})_2 + 3\mathrm{C}_n\mathrm{H}_{2n} \longrightarrow 3\mathrm{Al}(\mathrm{C}_n\mathrm{H}_{2n+1})_3 \quad (2)$$

the "displacement reaction"[3] and can be conducted so as to yield either aluminum trialkyls or dialkylaluminum hydrides according to eq. 3 and 4. Diisobutylaluminum hydride is often used in reaction 3 or 4 in place of triisobutyl aluminum and, although these reactions are principally not restricted to the use of isobutylaluminum compounds, their practical value in the preparation of defined organoaluminum compounds is based on the special ease of formation of triisobutylaluminum and diisobutylaluminum hydride *via* reactions 1 and 2, respectively. As olefins, $\mathrm{C}_n\mathrm{H}_{2n}$, α-olefins of the types $\mathrm{CH}_2{=}\mathrm{CH}_2$, $\mathrm{CH}_2{=}\mathrm{CHR}$, and $\mathrm{CH}_2{=}\mathrm{CRR'}$ have been utilized in the overwhelming majority of all cases reported in the literature. The reaction products of these synthetic routes are organoaluminum compounds of the type AlR_3 or HAlR_2 in which the aluminum is attached to a primary carbon atom.

$$\mathrm{Al}(i\text{-}\mathrm{C}_4\mathrm{H}_9)_3 + 3\mathrm{C}_n\mathrm{H}_{2n} \longrightarrow \mathrm{Al}(\mathrm{C}_n\mathrm{H}_{2n+1})_3 + 3\ i\text{-}\mathrm{C}_4\mathrm{H}_8 \quad (3)$$

$$\mathrm{Al}(i\text{-}\mathrm{C}_4\mathrm{H}_9)_3 + 2\mathrm{C}_n\mathrm{H}_{2n} \longrightarrow \mathrm{HAl}(\mathrm{C}_n\mathrm{H}_{2n+1})_2 + 3\ i\text{-}\mathrm{C}_4\mathrm{H}_8 \quad (4)$$

Since the discovery of these two new reactions, the opinion of those familiar with the art has prevailed in the pertinent literature: (a) that the utilization of α-olefins (containing the group $=\mathrm{CH}_2$) would be a necessary prerequisite for their feasibility; (b) that olefins with a nonterminal double bond would essentially not react or react only slightly in either process 2, 3, or 4, respectively, and that the results obtained with such olefins in these reactions were practically useless; or (c) that secondary organoaluminum compounds would be unstable, not accessible from internal olefins, or that they, if accessible at all, would spontaneously rearrange or be prone to rearrange to primary organoaluminum compounds.[4-25]

The utilization of 2-alkenes in both of these processes has, however, been described in a few cases in the patent literature.[24,26-29] From the description of the experimental results it must be assumed that the reaction products consisted of mixtures of primary and secondary aluminum trialkyls, primary and secondary dialkylaluminum hydrides, and substantial amounts of starting materials.

Results and Discussion

We have undertaken a rather extensive study of the synthesis of secondary organoaluminum compounds *via* both of the mentioned routes (and also of the isomerization of these compounds[30]) between the middle of 1959 and the early part of 1961.[31] In this study the

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(1) (a) Presented before the Division of Organic Chemistry at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964. (b) Inquiries should be sent to 744 Mine Road, Somerville, N. J. 08876

(2) K. Ziegler, H. G. Gellert, H. Lehmkuhl, W. Pfohl, and K. Zosel, *Ann. Chem.*, **629**, 1 (1960), and earlier publications cited there.

(3) K. Ziegler, H. Martin, and F. Krupp, *ibid.*, **629**, 14 (1960), and earlier literature cited there.

(4) K. Ziegler, H. G. Gellert, E. Holzkamp, and G. Wilke, *Brennstoff-Chem.*, **35**, 321 (1954).

(5) K. Ziegler, F. Krupp, and K. Zosel, *Angew. Chem.*, **67**, 425 (1955).

(6) K. Ziegler, *Experientia, Suppl. II*, 282 (1955).

(7) F. Krupp, Ph.D. Thesis, Technische Hochschule Aachen, 1955, pp. 4, 26, 39, 42, 43, 76, 107.

(8) K. Ziegler, *Angew. Chem.*, **68**, 725 (1956).

(9) K. Ziegler, "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 198.

(10) K. Weyer, Ph.D. Thesis, Technische Hochschule Aachen, 1956, p. 1.

(11) R. Koester, paper presented before the German and Austrian Chemical Society, April 26, 1956, Salzburg, Austria; Abstract, *Angew. Chem.*, **68**, 383 (1956).

(12) W. Pfohl, Ph.D. Thesis, Technische Hochschule Aachen, 1957, pp. 1, 3, 4.

(13) K. Ziegler, *Suomen Kemistilehti*, **A30**, 110 (1957).

(14) K. Ziegler, *Usp. Khim.*, **26**, 1187 (1957).

(15) R. Koester, *Ann. Chem.*, **618**, 34 (1958).

(16) K. Reinert, Ph.D. Thesis, Technische Hochschule Aachen, 1958, p. 1.

(17) K. Ziegler, H. Lehmkuhl, W. Pfohl, and K. Zosel, German Patent (East) 14808 (June 6, 1958), example no. 8.

(18) K. Ziegler, U. S. Patent 2,892,858 (June 30, 1959), example no. 3.

(19) A. C. McKinnis, U. S. Patent 2,906,763 (Sept. 29, 1959).

(20) See ref. 2, p. 8.

(21) See ref. 3, p. 19.

(22) K. Ziegler, H. G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Soell, and W. R. Kroll, *Ann. Chem.*, **629**, 144 (1960).

(23) K. Zosel and E. Holzkamp, South African Patent Specification 60/3629 (Dec. 28, 1960), p. 12.

(24) R. A. Walde, U. S. Patent 3,048,612 (Aug. 7, 1962).

(25) *Chem. Eng. News*, **41**, No. 15, 72 (1963).

(26) H. B. Fernald, Belgian Patent 559,404 (Jan. 22, 1958); U .S. Patent 3,100,786 (Aug. 13, 1963).

(27) J. T. Balhoff, U. S. Patent 2,943,102 (June 28, 1960).

(28) R. A. Walde, U. S. Patent 2,976,306 (March 21, 1961).

(29) F. X. Werber and F. A. Mirabile, French Patent 1,285,405 (Feb. 23, 1962).

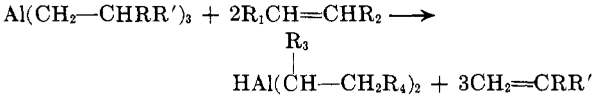
(30) G. Bruno, manuscript in preparation.

(31) British Patent 913,358 (Dec. 19, 1962), and 914,053 (Dec. 28, 1962); French Patent 1,285,405 (Feb. 23, 1962), and Addition 79,807(Feb. 1, 1963).

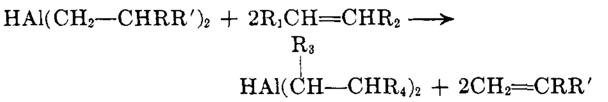
lower internal olefins from C_4 to C_8 were omitted, as far as the investigation of the displacement reaction was concerned, because of technical reasons. An early experiment with triisobutyl aluminum and 3-heptene was not very successful. Displacement reactions with such comparatively low-boiling olefins must very obviously be conducted in a pressure column. Special techniques like the creation of an autogeneous decomposition pressure of the organoaluminum compound as reported by Walde,[28] or the utilization of complexing agents like amines for the starting aluminum alkyl as described by the same author[24] should then be unnecessary.

Furthermore all 2-alkenes were excluded from the study. The situation must be complicated in these cases because of the possible partial catalytic isomerization of the 2-alkene to the corresponding α-olefin in contact with the organoaluminum compound at elevated temperature,[32] the isomerization of the initially formed secondary organoaluminum compound, and the difficulty of distinguishing and differentiating between these two reactions.

As a first result, it was found that internal straight-chain olefins react with suitable aluminum trialkyls or dialkylaluminum hydrides (triisobutylaluminum and diisobutylaluminum hydride were utilized) practically quantitatively under conventional conditions with formation of open-chain di-*sec*-alkylaluminum hydrides, a new class of organoaluminum compounds, according to eq. 5 and 6. In these equations R denotes an alkyl group, R′ is alkyl or H, and R_1 and R_2 are straight-chain alkyl groups which may or may not be identical with R_3 and R_4, which are also straight-chain alkyl groups.



$$Al(CH_2{-}CHRR')_3 + 2R_1CH{=}CHR_2 \longrightarrow HAl(\overset{R_3}{\overset{|}{C}}H{-}CH_2R_4)_2 + 3CH_2{=}CRR' \quad (5)$$

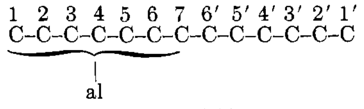


$$HAl(CH_2{-}CHRR')_2 + 2R_1CH{=}CHR_2 \longrightarrow HAl(\overset{R_3}{\overset{|}{C}}H{-}CHR_4)_2 + 2CH_2{=}CRR' \quad (6)$$

The optimum reaction temperatures are somewhat higher than those recommended by Ziegler and coworkers for α-olefins.[3] The temperature range between 120 and 170°, especially between 135 and 150°, seems to be most suitable. Between 100 and 120° the reaction proceeds sluggishly. Between 120 and 135° the rate is still comparatively slow, although this range may be most useful for the preparation of defined di-*sec*-alkylaluminum hydrides, *e.g.*, 2- and 3-isomers from 2-alkenes with only very minor portions of primary isomers. Above 150° and especially above 170° the displacement reaction encounters competition to an increasing degree with the isomerization of the originally formed di-*sec*-alkylaluminum hydrides to *n*-alkylaluminum compounds,[30] and then furthermore with the well-known dimerization of α-olefins.[32] The extent of the latter reactions in overlap with the pure displacement is, however, decisively determined by the position of the double bond of the internal olefin. The time–temperature relationships which one has to consider in order to obtain clear results vary for internal olefins with different positions of the double bond in relation to the respective nearest end of the carbon chain. These aspects will be discussed in detail in a following publication.[36]

It is essential that the reaction mixture be maintained at the reflux temperature of the internal olefin so that it can act as a carrier for the α-olefin displaced from the starting aluminum compound.[3] The same effect can of course be achieved (without reflux) by passing a slow stream of inert gas such as nitrogen or argon through the liquid reaction mixture at the chosen reaction temperature. The latter measure in conjunction with the aforementioned low temperature range (100–135°) would appear to be a good way to effect displacement with internal olefins with little or no isomerization of the original reaction products, *i.e.*, the di-*sec*-alkylaluminum hydrides.

We have further determined that the displacement reaction with internal olefins proceeds considerably faster and can be conducted at lower temperatures (thereby avoiding secondary reactions, especially partial isomerization during the displacement), and/or can be driven to higher degrees of completion if it is possible to obtain reflux of the displacing olefin at the reaction temperature by a reduction of pressure in the apparatus. Since the optimum temperature range for the reaction is approximately 135–150°, this can be done without much difficulty in the case of all internal olefins from C_{10} on. Finally, in order to drive the reaction to completion it is necessary to employ the internal olefin in an excess, although conversions up to approximately 80–90% of the theory can be obtained at a useful and practical reaction rate without any olefin excess. Under the above outlined conditions the displacement reaction of aluminum tri-*n*-alkyls or di-*n*-alkylaluminum hydrides with internal straight-chain olefins then proceeds comparably with respect to yields, reaction rates, and purity of the initial reaction products with the results which have been obtained by Ziegler and co-workers for α-olefins of the types $CH_2{=}CH_2$, $CH_2{=}CHR$, and $CH_2{=}CRR'$.[3] In a typical experiment di-*sec*-tridecylaluminum hydride of 90+% purity was synthesized by displacement reaction of triisobutylaluminum with 6-tridecene at reaction temperatures between 138 and 151° and pressures between 13 and 50 mm. (see Experimental). No evidence was found of an isomerization of the initial reaction product, *i.e.*, the *sec*-tridecylaluminum compound, to the corresponding *n*-tridecyl isomer during a total reaction time of 21 hr. It is, however, very likely that rearrangement of the initially formed 6- (and 7-) tridecylaluminum hydride to isomers other than the 1-tridecylaluminum compound did indeed occur in overlap with the pure displacement reaction. This would lead to a mixture of possibly six different isomeric positional species and a much larger number of different compositions of the type HAlRR′. Our analytical 1 method excluded only components of the al–C type. This method was an infrared analysis of the products obtained upon addition of 1-decene across the al–H



al = ¹/₃Al

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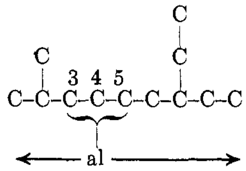
(32) See ref. 22, pp. 138–147.

bond of the crude di-*sec*-tridecylaluminum hydride, oxidation with oxygen, and hydrolysis of the resulting aluminum alkoxide. A systematic investigation of whether complete displacement with internal olefins is possible without simultaneous isomerization would preferably be based on the use of a 2-alkene of higher molecular weight, for instance 2-tridecene. This was not done in this project because the emphasis was on the isomerization of the di-*sec*-alkylaluminum hydrides. Moreover, even in the case of a straight-chain 2-alkene, the formation of two different positional species, *viz.*, 2- and 3-alkylaluminum, would presumably be inevitable.

Other di-*sec*-alkylaluminum hydrides of similar purity were also obtained by displacement reaction and occasionally isolated, for instance, the compound synthesized from 6-dodecene. The compounds are in general oily to highly viscous liquids. Further investigation of the properties and chemical behavior of these substances was not carried out. One property which we did have reason to test in connection with this project was the thermal stability. We found that di-*sec*-dodecylaluminum hydride decomposes immediately upon the heating of a 33% solution in decalin to 170° with precipitation of aluminum metal and evolution of hydrogen. On the other hand we did not encounter this instability when di-*sec*-tridecylaluminum hydride was synthesized by the procedure described in the Experimental part. A sample which was withdrawn from this mixture after the reaction was 90% complete started to decompose only after further heating to about 160° at 25 mm. for a period of 2 hr. Comparison of these two results suggested the presence of a stabilizing agent in the latter experiment. This was indeed the case. The reaction product of the last mentioned experiment contained at this stage approximately 10% unchanged 6-tridecene, and it was later determined that internal olefins act as stabilizers for internal organoaluminum compounds at higher temperatures. It seems obvious, on the other hand, on the basis of the experiment with decalin that such stabilizing properties are not inherent in inert solvents which are commonly used in organoaluminum chemistry. We have verified these results on other occasions.

We furthermore attempted, in a displacement reaction with triisobutylaluminum and 4-nonene, to make use of the known catalytic activity of a colloidal nickel catalyst.[3] Although we made no kinetic measurements we did not detect any catalytic activity of the nickel which would have been useful from a preparative viewpoint. Whereas a mixture of triisobutylaluminum and 1-dodecene evolves isobutene upon addition of nickel acetylacetonate at room temperature,[3] we observed no isobutene evolution below 120° with 4-nonene in place of 1-dodecene. At higher temperatures the per cents of evolved isobutene were approximately equal in experiments with the system triisobutylaluminum–4-nonene with or without the addition of nickel acetylacetonate.

We have further investigated the displacement reaction of diisobutylaluminum hydride with a mixture of 2-methyl-7-ethyl-3- (and 4-) nonene. Although the reaction was found to proceed only with much difficulty, compared with the straight-chain internal olefins, an over-all yield of 77% of the theory of isobutene was obtained. The analytical data of the reaction product were also consistent with the approximate composition $HAl(C_{12}H_{25})_{1.5}(i\text{-}C_4H_9)_{0.5}$. Upon saturation of al–H with excess 1-heptene, oxidation, hydrolysis, etc., there were obtained in mole %, based on the formula $(n\text{-}C_7H_{15})Al(C_{12}H_{25})_{1.5}(i\text{-}C_4H_9)_{0.5}$ 37.1% of 1-heptanol; 17.1% of 2-methyl-7-ethyl-*X*-nonene, *X* = 3 and/or 4 and/or 5, infrared spectrum and refractive index identical with that of the starting olefin; and 25.0% of branched C_{12} ketone and C_{12} alcohols. With respect to the latter, the infrared spectrum pointed to the presence of both primary and secondary alcohols. The presence of a primary alcohol would indeed indicate a partial migration of the aluminum across a tertiary carbon atom during the displacement. The appearance of a substantial amount of 2-methyl-7-ethyl-*X*-nonene (17.1 mole %) as one of the major products of oxidation and hydrolysis of the organoaluminum compound as well as the fact that the amount of 1-heptanol exceeds 33.3% (actually one should not expect more than approximately 85% of this amount, *i.e.*, approximately 28%) can now be explained on the basis of a recent patent[33] in which the preparation of, for example, substantial amounts of 1-dodecanol and 1-octene by oxidation of tri-*n*-octylaluminum in presence of 1-dodecene and subsequent hydrolysis of the resulting aluminum alkoxide are disclosed. Since the oxidation of our displacement product (from 2-methyl-7-ethyl-*X*-nonene) was also conducted in presence of an α-olefin, *i.e.*, excess 1-heptene from the saturation of al–H before oxidation, the same reaction has obviously occurred.



The presence of a substantial amount of ketones (also obtained on other occasions as one of the major products of oxidation and hydrolysis of internal organoaluminum compounds, where only a secondary alcohol should be expected) is, on the other hand, not readily explainable. The oxidation of secondary organoaluminum compounds obviously does not take the simple course as does the oxidation of primary aluminum alkyls, which is well known to give, after hydrolysis of the resulting aluminum alkoxide, primary alcohols in yields of approximately 80% of the theory.[34] We have not investigated this aspect, and further work is required for its clarification.

We have also briefly investigated the possibility of the utilization of a trialkylethylene in a displacement reaction. The combination diisobutylaluminum hydride–6-*n*-pentyl-5-undecene, $(n\text{-}C_5H_{11})_2C{=}CH\text{-}C_4H_9\text{-}n$, was used. Displacement was found to proceed with even greater difficulty than in the case of the 2-methyl-7-ethyl-3- (and 4-) nonene. Under the reaction conditions which had proved to be optimum for 1,2-dialkylethylenes a yield of only approximately 55% of evolved isobutene was obtained.

Results of the work-up and analysis of the initial reaction product were essentially similar to those which

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(33) D. M. Coyne, P. A. Lobo, and B. J. Williams, British Patent 890,307 (Feb. 28, 1962).

(34) K. Ziegler, F. Krupp, and K. Zosel, *Ann. Chem.*, **629**, 241 (1960).

were obtained in the preceding experiment. No primary or tertiary C_{16} alcohol was detected in the products of oxidation and hydrolysis.

After the accessibility and thermal stability of secondary organoaluminum compounds had been established *via* the displacement reaction, we began to investigate the possibility of the total synthesis of these compounds from aluminum, hydrogen, and internal olefins. A somewhat difficult and complex situation was to be expected in this case because of the possibility of one or more of the previously known side reactions: catalytic olefin dimerization, olefin hydrogenation, aluminum alkyl isomerization, or olefinic double-bond migration.

One of the major difficulties of the "total synthesis" of organoaluminum compounds is the preparation of a sufficiently active aluminum metal. Throughout our runs we used an aluminum shot which had been activated by the known wet-milling procedure[35] in the presence of an organoaluminum compound and, in some cases, in the additional presence of aluminum stearate.[36] We found the reaction to proceed somewhat slowly with the metal, at least under the comparatively mild conditions which we used in order to avoid the aforementioned side reactions.

After the termination of our project, reports[37] became known of a very substantial acceleration of the "total synthesis" by alloying the aluminum metal with up to 2% of "positive catalytic elements" such as Ti, Zr, Hf, Nb, or V, and by exclusion of "negative catalytic elements" such as Cu, Si, and/or Pb. We have little doubt that much improved results in the synthesis of secondary organoaluminum compounds from aluminum, hydrogen, and internal olefins would be obtained if the experiments discussed here were to be repeated using aluminum alloys of the abovementioned compositions.

Another (undesirable) aspect of the present total synthesis is the loss of olefin by hydrogenation to the corresponding paraffin,[2] at least partially by hydrogenation of the organoaluminum compound which is being formed,[38] but presumably also under the catalytic influence of the formed aluminum alkyl.[39] This effect is, of course, also correlated to a considerable extent to the activity of the aluminum metal. We have found this side reaction to be tolerable, although not negligible, in our runs with internal olefins; the loss of the latter due to hydrogenation amounted on the average to approximately 5% of the total amount of olefin used over the whole period of the respective experiment, with exception of cyclohexene which was hydrogenated during the run to a much larger extent.

The reaction conditions which we used constituted a compromise between rate on one hand and the desire to avoid side reactions on the other hand; approximately 120° and 150–350 atm. of hydrogen pressure proved to be the optimum, at least under our specific circumstances, *i.e.*, the aluminum activity, the available means of agitation (rocker bomb), olefin feed (discontinuously), etc. When we, on occasion, increased the reaction temperature to 140°, we started to experience some of the above-mentioned side reactions; in this case (with 2-pentene), these were, especially, aluminum alkyl isomerization followed by olefin dimerization, and increased olefin hydrogenation.

At a reaction temperature of approximately 120°, however, it was possible to synthesize the di-*sec*-alkylaluminum hydrides derived from cyclohexene, 3-heptene, 4-nonene, and 6-dodecene with conversions of aluminum of between 70 and 80% and essentially no isomerization of the initially formed secondary organoaluminum compounds.

Di-*sec*-alkylaluminum hydrides undergo, as reported earlier,[40] an interesting addition and rearrangement reaction, predominantly with the formation of high yields of aluminum tri-*n*-alkyls, when heated to elevated temperatures between 170 and 220° in the presence of excess internal olefin. Straight-chain aliphatic compounds with terminal functional groups are thus accessible from nonterminal olefins *via* di-*sec*-alkylaluminum hydrides and aluminum tri-*n*-alkyls by further reaction of the latter in accordance with known procedures, *e.g.*, primary alcohols by oxidation with air and hydrolysis of the resulting aluminum alcoholates with dilute acid, or terminal olefins by direct pyrolysis of the aluminum tri-*n*-alkyls.

Experimental

Starting Materials.—Commercially available triisobutylaluminum and diisobutylaluminum hydride were purified by distillation at 10^{-4} mm. and were analyzed for aluminum according to the method of Glemser and Thelen[41] and by measuring the volume and determining the composition of the volatile gases upon hydrolytic decomposition of samples.[35]

3-Heptene, 4-nonene, and 6-tridecene were prepared from the carboxylic acids (*n*-butyric, *n*-valeric, and *n*-heptanoic acid, respectively) by ketonization according to the method described by Cowan, *et al.*,[42] hydrogenation of the fractionated ketones with a prereduced nickel formate catalyst in mineral oil suspension, fractionation of the secondary alcohols on a 60-cm. Stedman column, esterification with stearic acid, and pyrolysis of the esters. Finally, the olefins were purified by distillation under argon from sodium or sodium–potassium alloy. Physical constants and analytical data of the olefins follow: for 3-heptene, $n^{20}{}_D$ 1.4053, iodine number 257 and 258 (calcd., 258), about 98% purity according to infrared analysis, practically all *trans;* for 4-nonene, b.p. 148° (760 mm.), $n^{20}{}_D$ 1.4195, practically pure internal olefin according to infrared analysis with only traces of other olefinic structures present; and for 6-tridecene, b.p. 109° (13 mm.), $n^{20}{}_D$ 1.4352, iodine number 137 and 136 (calcd., 139), practically pure internal, almost all *trans* olefin by infrared analysis.

6-Dodecene was synthesized by "addition" alkylation of butadiene with *n*-butyllithium and *n*-butyl chloride according to Ziegler, *et al.*,[43] and purified by fractionation on a 60-cm. Stedman column: b.p. 99° (18 mm.), $n^{20}{}_D$ 1.4328, iodine number 150 and 151 (calcd., 150), approximately 96–97% purity according to infrared analysis (*cis* and *trans*).

A mixture of 2-methyl-7-ethyl-3-(and 4-)nonene was prepared from 2-methyl-7-ethyl-4-nonanol (Chemische Werke Huels A.G., Marl-Huels, West Germany, b.p. 117.5° (13 mm.), $n^{20}{}_D$ 1.4400, hydroxyl number 299, 300) by pyrolysis of its stearic acid ester and subsequent purification by distillation from sodium: $n^{20}{}_D$

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[35] K. Ziegler, H. G. Gellert, H. Martin, K. Nagel, and J. Schneider' *Ann. Chem.*, **589**, 91 (1954).

[36] G. Schaeffer, German Patent 1,092,916 (Nov. 17, 1960); corresponds to U. S. Patent 3,068,181 (Dec. 11, 1962).

[37] F. J. Radd and W. W. Woods, French Patent 1,287,742 (March 16, 1962); corresponds to U. S. Patent 3,104,252 (Sept. 17, 1963).

[38] R. Koester, G. Bruno, and H. Lehmkuhl, German Patent (East) 16,560 (Feb. 5, 1957).

[39] A. P. Stuart and J. L. Jezl, U. S. Patent 2,983,770 (May 9, 1961).

[40] G. Bruno, Abstracts, Division of Organic Chemistry at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 24C; see also *Chem. Eng. News*, **42**, No. 4, 47 (1964); see also ref. 30.

[41] O. Glemser and L. Thelen, *Angew. Chem.*, **62**, 269 (1950).

[42] D. M. Cowan, G. H. Jeffery, and A. I. Vogel, *J. Chem. Soc.*, 171 (1940).

[43] K. Ziegler, E. Eimers, W. Hechelhammer, and H. Wilms, *Ann. Chem.*, **567**, 43 (1950).

TABLE I

DISPLACEMENT REACTION OF TRIISOBUTYLALUMINUM[a] WITH 6-TRIDECENE[b]

Reaction period, hr.	Internal temp., °C.	Pressure, mm.	Evolved i-C_4H_8		Remarks
			Wt., g.	% yield	
0–6	138	50	434	65.4	Isobutene evolution started at 100° (internal)
6–12	136	14	573	86.3	
12–15	149	14	598	90	Practically no more isobutene evolution, experiment interrupted,[c] 982 g. (5.39 moles) of 6-tridecene added[d]
15–21	137–147	36–50	653	99[e]	

[a] Original charge, 784 g. (3.95 moles). [b] Original charge, 1445 g. (7.92 moles). [c] A sample of the reaction product (142.5 g., corresponding to 0.34 mole of aluminum alkyl compound) was withdrawn; an attempt to drive the reaction to completion simply by further variation of temperatures and pressures, *i.e.*, without addition of excess 6-tridecene, was unsuccessful. Only traces of isobutene were obtained, and thermal decomposition of the organoaluminum compound, noticeable as a milky turbidity, started to occur after the latter had been heated to an internal temperature of 159–162° (25 mm.) for a period of 2 hr. The sample was discarded. [d] Arbitrarily chosen excess and much more than would have really been necessary. [e] Taking into consideration the withdrawn sample.[c] The isobutene condensate in the overhead trap was allowed to evaporate without prior analysis. It is evident on the basis of the analytical data of the organoaluminum reaction product (see further below) that this isobutene condensate must have contained a few per cent of tridecene carried over into the overhead trap during the reaction.

TABLE II

ANALYTICAL FRACTIONATION OF THE REACTION MIXTURE OBTAINED FROM DI-*sec*-TRIDECYLALUMINUM HYDRIDE BY SUCCESSIVE ADDITION OF 1-DECENE, OXIDATION, AND HYDROLYSIS

Fraction	Wt., g.	B.p., °C. (mm.)	$n^{20}D$	OH no.	CO no.	Iodine no.	Major components[a]
1	1	Up to 61 (12)	1.4143				
2	9	62 (12)	1.4153	6.8		43.5	~30% internal olefin; rest probably paraffins
3	0.6	62–107 (12)	1.4253				
4	22.4	108 (12)	1.4332	78		80.2	~25% 1-decanol; 58% 6-tridecene
5	2	108–119 (12)	1.4330				
6	38.4	120 (12)	1.4368	350			1-Decanol
7	4.2	120–136.5 (13)	1.4352				~50% $R-CH_2-CH_2OH$; approx. 50% RCOR′
8	36.7	136.5 (13)	1.4345	26	255		Predominantly ketone; rest secondary alcohol
9	2	136.5–142 (13)	1.4364				
10	51.7	142–144 (13)	1.4409	262	16		Secondary alcohol; small amounts of ketone
11	8.2	144–145.3 (14)	1.4414				Practically pure secondary alcohol; little ketone

[a] By infrared analysis.

1.4328, iodine number 150 (calcd., 150), practically pure internal, predominantly *trans* olefin by infrared analysis.

The trialkylethylene, 6-*n*-pentyl-5-undecene, was synthesized by Grignard reaction of *n*-pentylmagnesium chloride with di-*n*-pentyl ketone (from *n*-hexanoic acid[42]) and dehydration of the resulting tertiary alcohol, after fractionation, by distillation with iodine.[44] Purification of the olefin was effected by distillation from sodium and fractionation on a 60-cm. Stedman column: b.p. 141° (14 mm.), $n^{20}D$ 1.4455, according to infrared analysis trialkylethylene of 95% minimum purity.

Aluminum shot of the Th. Goldschmidt Co., Essen, West Germany, was used as starting raw metal for the total syntheses.

Solvents were purified by distillation from sodium–potassium alloy and stored over sodium wire.

Displacement Reactions.—All organometallic operations were conducted under inert gas (nitrogen or argon). All boiling points are uncorrected.

The apparatus consisted of a three-neck flask of suitable volume, *i.e.*, of approximately double the total volume of materials to be charged, equipped with a three-way, bottom-outlet stopcock as a nitrogen inlet, a magnetic stirrer bar, a thermometer, and a reflux condenser. The following accessories were connected in series at the top of the reflux condenser: a bubbler with ground joint, a liquid-air cold trap of suitable size (depending upon the isobutene volume to be expected), another bubbler, a manometer, and a tee. A nitrogen source, controlled by a needle valve, was attached to one end of the tee and a water jet pump, also controlled by a needle valve, was connected to the other. The pressure in the apparatus was regulated by "tuning" of the two needle valves, and measured at the intermediate manometer.

6-Tridecene.—A mixture of this olefin with triisobutylaluminum (mole ratio approximately 2:1) was heated in the above-described apparatus under reflux, with stirring, at various temperatures and pressures. The pressure in the apparatus was adjusted in such a way that a good reflux rate of the tridecene in the condenser was obtained at each chosen internal temperature. The results are summarized in Table I.

After completion of the reaction, 459 g. of the clear, colorless tridecene solution of the reaction product, representing 19 wt. % of the total, was transferred to a distillation apparatus. All volatile material was distilled from the organoaluminum compound under a vacuum of 10^{-4} mm. at external temperatures up to 120°; the distillation was finished by increasing the external temperature to 130° for no more than 40 min. There was obtained 200 g. of distillate whose refractive index and infrared spectrum were practically identical with that of the starting 6-tridecene. The residue, a clear, colorless oil of high viscosity, amounted to 256 g. [calcd., 0.683 mole (sec-$C_{13}H_{27})_2AlH$, 270 g.].

Anal. Calcd. for $C_{26}H_{55}Al$: Al, 6.8. Found: Al, 6.95.

Upon hydrolysis with isopropyl alcohol, 1.9763 g. of this distillation residue yielded 5.6 mmoles of gas (0°, 760 mm.) containing 92.6% hydrogen and 7.4% isobutane [calcd. for $(C_{13}H_{27})_2AlH$, 5.0 mmoles of H_2].

The weight of the reaction product and the results of the aluminum determination and hydrolysis indicate the composition of the reaction product to be approximately $(C_{13}H_{27})_{1.9}(i\text{-}C_4H_9)_{0.1}$-AlH, corresponding to a purity of the ditridecylaluminum hydride of approximately 95 mole %.

A 136.5-g. portion of the tridecene-free reaction product (0.358 mole based on the last mentioned formula) was mixed with 55.1 g. (0.396 mole) of pure 1-decene. The mixture was heated, with stirring, overnight at 70°, diluted with 2.5 l. of dry hexane, and oxidized by introduction of oxygen into the solution which was maintained at temperatures of 20–30°. After the exothermic reaction had been completed the mixture was further stirred and heated to 40° for a period of 20 min. with continued introduction of oxygen. Subsequently, the solvent was distilled from the reaction mixture at 12 mm. and internal temperatures up to 50°. The residue, 214.5 g., was taken up with ether and the ethereal solution was hydrolyzed by pouring it onto a stirred mixture of 53 g. sulfuric acid and 370 g. of ice. After the usual work-up, 193.5 g. of product was obtained. This material was vacuum fractionated on a 1-m. spinning-band column (model of the E. Haage Co., Mülheim-Ruhr, West Germany) to obtain the fractions given in Table II. The total weight of the fractions was

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(44) J. M. Church, F. C. Whitmore, and R. V. McGrew, *J. Am. Chem. Soc.*, **56**, 176 (1934).

TABLE III

ANALYTICAL FRACTIONATION OF REACTION MIXTURE OBTAINED FROM $(sec\text{-}C_{16}H_{33})(i\text{-}C_4H_9)AlH$ BY SUCCESSIVE ADDITION OF 1-HEPTENE, OXIDATION, AND HYDROLYSIS

Fraction	Wt., g.	B.p., °C. (12 mm.)	$n^{20}D$	OH no.	CO·no.	Iodine no.	Major components[a]
1	3.8	27.5	1.3960				Isobutyl alcohol
2	1	27.5–77.5					
3	26.1	77.5–78.5	1.4232	481			1-Heptanol
4	2.7	78.5–135.5	1.4371				
5	19.4	136.5–137.5	1.4435	3	0	120	*trans* olefins and (presumably) considerable amounts of $R_1R_2C{=}CHR_3$ (~850 cm.$^{-1}$)
6	1.9	137.5–161.0	1.4420				
7	22.1	161–164	1.4461	181	59	1.7	Secondary alcohol, considerable ketone

[a] By infrared analysis.

176.2 g. The residue (12 g.) had iodine number of 22; saponification number, 25; hydroxyl number, 40; and acid number, 3.5.

Addition of the amounts of major components of the individual main fractions results in the following compilation: 46.1 g. of 1-decanol (0.291 mole), corresponding to 81.3% of theory; 13.0 g. of internal tridecenes (0.071 mole); 38.2 g. of tridecanones (0.192 mole), corresponding to 28.2% of theory; and 60.5 g. of *sec*-tridecanols (0.302 mole), corresponding to 44.4% of theory. The per cents calculated above are based on a molar amount of 0.358 aluminum trialkyl of the net composition $(sec\text{-}C_{13}H_{27})_{1.9}(i\text{-}C_4H_9)_{0.1}Al(n\text{-}C_{10}H_{21})_{1.0}$ as starting material for the over-all analysis. The calculation is further based on the assumption that not only the *sec*-tridecanols but also the tridecanones are formed by oxidation and hydrolysis of *sec*-$C_{13}H_{27}$-al. We also believe that at least some of the internal tridecenes which were obtained in the analytical fractionation can be accounted for by the assumption of a displacement reaction between excess 1-decene, from the addition across al–H, with *sec*-tridecylaluminum during the oxidation step.[33] This would mean that the actual per cent of 1-decanol which was obtained in the above fractionation is somewhat lower than 81.3%, and that the amounts of C_{13} monooxy compounds are correspondingly higher than 72.6%.

No primary C_{13} monooxy compound was detected in any of the fractions or in the residue.

All of the above results are consistent with the mentioned net composition of the original reaction product of 6-tridecene with triisobutylaluminum, *i.e.*, $(sec\text{-}C_{13}H_{27})_{1.9}(i\text{-}C_4H_9)_{0.1}AlH$, or, in other words, with a purity of the di-*sec*-tridecylaluminum hydride of ~95 mole % considering the limitations of the employed analytical procedures in organoaluminum chemistry.

2-Methyl-7-ethyl-3- (and 4-) nonene.—This olefin (522.1 g., 3.1 moles) was mixed with 110.1 g. (0.774 mole) of diisobutylaluminum hydride. The mixture was stirred vigorously and heated to reflux at 90–130 mm. and internal temperatures of 130–143° for a period of 3.33 hr. Thereafter, 54 g. of isobutene condensate (62.1% of theory) had accumulated in the overhead receiver. Further heating of the mixture at internal temperatures of 150–160° and pressures of 150 mm. and above for 2.5 hr. yielded only an additional 6 g. of isobutene. A slight milky turbidity of the mixture was observed during this latter operation. Addition of 260.8 g. of 2-methyl-7-ethyl-3- (and 4-) nonene (1.55 moles) to the mixture and continued heating at 120–140° internal temperature and 85–125 mm. for 5.5 hr. did not improve the results. An additional 7 g. of isobutene was obtained. The total quantity of displaced isobutene amounted to 67 g. (77% of theory). All volatile material was distilled from the organoaluminum compound at external temperatures up to 80° and at 10^{-4} mm. to obtain 582 g. (3.46 moles) of distillate whose refractive index and infrared spectrum were practically identical with that of the starting olefin. An opaque, viscous residue of 240.5 g. remained in the distillation flask. The net composition of this product was, on the basis of the above data, assumed to be $(C_{12}H_{25})_{1.54}(i\text{-}C_4H_9)_{0.46}AlH$. Upon hydrolysis with isopropanol, 1.1217 g. (3.56 mmoles), gave 3.56 mmoles of hydrogen and 1.13 mmoles of isobutane (0°, 760 mm.); calculated for $(C_{12}H_{25})_{1.54}(i\text{-}C_4H_9)_{0.46}AlH$, 3.55 mmoles of hydrogen and 1.64 mmoles of isobutane. In view of the known solubility of isobutane in the hydrolysis mixture the agreement with the proposed composition is reasonable.

A 110.9-g. portion of the olefin-free reaction product (0.352 mole, calculated for the above formula) was mixed with 52 g. of 1-heptene (0.53 mole) and the mixture was stirred at 70° overnight. Without prior separation of excess 1-heptene, the resulting aluminum trialkyl, diluted with 1.2 l. of dry hexane, was oxidized at 0–10°. After completion of the exothermic reaction, the mixture was heated with continued introduction of oxygen at 50–60° for a period of 20 min. After hydrolysis of the aluminum alkoxide (167.5 g.) and the usual work-up, 151 g. of crude product was obtained. This material was fractionated under vacuum on a 1-m. spinning-band column. A series of fractions, similar to that in Table II, was obtained. The individual fractions were analyzed by the aforementioned methods. Addition of the major components of the main fractions resulted in the following compilation [all listed % yields are based on 0.352 mole $(C_{12}H_{25})_{1.54}(i\text{-}C_4H_9)_{0.46}Al(n\text{-}C_7H_{15})_{1.0}$ as starting material]: 5 g. of isobutyl alcohol; 45.6 g. of 1-heptanol (0.392 mole), corresponding to 110.1% yield; 30.5 g. of 2-methyl-7-ethyl-*X*-nonene (0.181 mole, the infrared spectrum showed only *trans* C=C, thus X = 3 and/or 4 and/or 5); 14.8 g. of C_{12} ketones (0.08 mole), corresponding to 14.8% yield; and 34.3 g. of C_{12} alcohols (0.184 mole), corresponding to 33.9% yield. According to infrared analysis this mixture contained secondary and primary alcohols, the latter presumably of structure, RCH_2CH_2OH. However, the infrared identification of the primary alcohol, regardless of structure, was somewhat uncertain. The residue amounted to 8.4 g.

6-*n*-Pentyl-5-undecene.—A mixture of 393 g. (1.75 moles) of this olefin and 64 g. (0.45 mole) of diisobutylaluminum hydride was heated at 141–143° (13 mm.) under reflux and stirring for a period of 10.5 hr. Thereafter, 30 g. of isobutene (0.534 mole, 59.4% yield) had accumulated in the overhead trap. All volatile material was distilled from the organoaluminum reaction product with stirring at 10^{-4} mm. and external temperatures up to 120°. A distillate of 288 g. of the starting olefin was obtained. The residue, 135.5 g., was a colorless, viscous oil. A 1.2257-g. portion of this oil yielded, upon hydrolysis with isopropanol, 4.0 mmoles of hydrogen and 3.2 mmoles of isobutane (0°, 760 mm.); calculated for a compound of the composition $(C_{16}H_{33})_{1.0}(i\text{-}C_4H_9)_{1.0}AlH$, 3.94 mmoles of hydrogen and 3.94 mmoles of isobutane.

A 60.7-g. portion of the olefin-free organoaluminum reaction product (0.1955 mole, assuming the last-mentioned composition), was mixed with 33 g. (0.336 mole) of 1-heptene. The mixture was stirred and heated at 70° overnight, and was oxidized as usual, *i.e.*, without prior separation of the excess α-olefin (1-heptene). After the usual work-up (hydrolysis of the aluminum alkoxide, etc.) 87.3 g. of a crude "alcohol" mixture was obtained. Vacuum fractionation of this material on a 1-m. spinning-band column yielded the fractions described in Table III. The residue (4.5 g.) contained predominantly secondary alcohol. The total weight of distillate was 77.0 g.

Evaluation of the results in Table III leads to the following compilation [% yields are minimum numbers based on 0.1955 mole of $(sec\text{-}C_{16}H_{33})(i\text{-}C_4H_9)Al(n\text{-}C_7H_{15})$ as starting material, intermediate fractions and losses not considered]: 26.1 g. of 1-heptanol (0.224 mole), corresponding to 115% yield; 19.4 g. of C_{16} olefin (0.086 mole); 17.3 g. of secondary C_{16} alcohol (0.071 mole, 36.4% yield); and 4.8 g. of C_{16} ketone (0.02 mole, 10.2% yield). The sum of C_{16} ketone, secondary C_{16} alcohol, and internal C_{16} olefin amounts to 0.177 mole, corresponding to 90.5% yield if the origin of the free C_{16} olefin is explained by a displacement reaction of excess 1-heptene with al–$C_{16}H_{33}$ during the oxidation step.[33] This explanation is substantiated by the fact that 115% of the theoretical amount of 1-heptanol was obtained.

Total Syntheses. Aluminum Activation.—A steel ball mill of 0.9-l. volume of the type described by Ziegler, *et al.*,[2,35] filled to 80% of its volume with steel balls of 1.2-cm. diameter (Sieb-

Table IV

Synthesis of Di-*sec*-alkylaluminum Hydrides from Aluminum, Hydrogen, and Nonterminal Olefins

Reactants		Activator compd., g.	Time, hr.	Temp., °C.	Pressure, atm.	Al conversion, %	Olefin recovered, moles	Product, g.
Olefin, moles	Al, g.-atoms							
3-Heptene, 2	1.1	i-Bu_2AlH, 17.5	23	120	200–250	76.7	0	$(sec\text{-}C_7H_{15})_2AlH$, 234
4-Nonene, 3.3	1.48	i-Bu_2AlH, 8 Al stearate, 1.5	22	120	185–330	76.2	0.97[a]	$(sec\text{-}C_9H_{19})_2AlH$, 336
6-Dodecene, 2.16	0.74	n-Dod_3Al, 37	14	120	170–330	82.5	0.88[b]	$(sec\text{-}C_{12}H_{25})_2AlH$,[c] 262
Cyclohexene, 4.4	2	i-Bu_2AlH, 8 Al stearate, 1.5	17	130	180–320	65	0[d]	$(C_6H_{11})_2AlH$,[e] 252

[a] Nonane content, 17.8%. [b] Dodecane content, 9.4%. [c] With consideration of the amount of $Al(n\text{-}C_{12}H_{25})_3$ used for the aluminum activation. [d] 146 g. of cyclohexane (1.7 moles), b.p. 80.5°, $n^{20}D$ 1.4270, was recovered, no cyclohexene. [e] Recrystallization from n-pentane gave 135 g. of colorless, crystalline product, m.p. 136° (uncor.), decomposition range 150–160°.

technik GmbH, Mülheim-Ruhr, West Germany) was employed. Prior attempts to utilize steel balls of other companies were unsuccessful and resulted in plating of the aluminum shot. The mill was charged, under argon, with aluminum shot (Th. Goldschmidt Co., Essen, West Germany), activator, and 150 ml. of a dry, inert diluent such as hexane, heptane, or p-xylene. The charge was ground on a vibrating ball-mill base for a period of 10–12 hr., and then discharged into a glass flask of suitable size. Usually one or two subsequent washings of the mill with 40–50 ml. each of the diluent were sufficient to remove all of the ground aluminum metal from the mill. Thereafter, the whole charge, including the diluent, was transferred from the flask to a stainless steel rocker bomb of 1-l. net capacity.

Olefin Feed.—Hydrogen was introduced into the rocker bomb at room temperature until pressures between 120–140 atm. were obtained, and the reactor was externally heated to the desired temperature. Then the olefins were added at half-hourly or hourly intervals in amounts of 25–65 ml., depending upon the time period necessary for the reactor pressure to become constant. A laboratory piston metering pump of an allowable operating pressure of 500 atm. was used for the feed operation.

Work-Up.—The excess hydrogen was slowly vented from the reaction vessel. The reaction mixture was quantitatively transferred from the autoclave to a glass flask, weighed, and separated from the nonreacted aluminum by filtration under argon. Subsequently, the diluent and nonreacted olefin were distilled from the organoaluminum reaction product at 13 mm. and/or 0.1 mm., respectively.

Characterization.—The methods employed for identification and analyses are described in the section on displacement reactions.

Neither 1-heptanol nor 1-nonanol were isolated from the products of oxidation and subsequent hydrolysis of the organoaluminum reaction products from the runs with 3-heptene and 4-nonene, respectively. The *sec*-dodecanol/dodecanone mixture obtained from the organoaluminum reaction product of the run with 6-dodecene contained, as expected, an amount of 1-dodecanol corresponding to the amount of $Al(n\text{-}C_{12}H_{25})_3$ activator used.

The results are summarized in Table IV.

Acknowledgment.—The author thanks Dr. H. Schirp for a stimulating discussion regarding this problem. All infrared analyses and all interpretations of infrared spectra in conjunction with this project were performed by Dr. H. van Raay, whose assistance and helpful cooperation are gratefully acknowledged.

Fused Aromatic Derivatives of Thiete and Thiete Sulfone[1]

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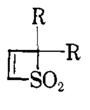
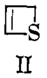
Derivatives of thiete (II), in which the double bond forms part of an aromatic system, have been prepared by the Diels–Alder addition of isobenzofurans to thiete sulfones, followed by dehydration and reduction. Limitations of the process are outlined. The stereochemistry of the Diels–Alder adducts has been elucidated by n.m.r. spectroscopy.

The recent interest in the chemistry of four-membered unsaturated sulfur heterocycles has led to two synthetic approaches to thiete 1,1-dioxides (I).[2,3] Neither thiete (II), the parent of the system, nor any of its derivatives, have been reported; several unsuccessful attempts to prepare II have, however, been documented.[4] The possible increased stability of the thiete anion (III) has already been discussed.[4] In view of our present general interest in the chemistry of unsaturated heterocyclic systems[1] and in an attempt to gain some insight into the chemical and physical properties of the thiete ring system in particular, the preparation of several fused aromatic derivatives of thiete was undertaken.



Ia, R=H
b, R=CH_3



II

III

Synthetic Procedure.—The synthetic scheme selected was based on the excellent diene characteristics of the isobenzofurans and the demonstrated dienophilic properties of thiete 1,1-dioxide (Ia).[4,5] When 1,4-diphenyl-2,3-benzofuran (IV) was condensed with Ib in refluxing xylene solution under a nitrogen atmosphere, there was obtained in 92.5% yield the expected adduct Va. The acid-catalyzed dehydration of Va proceeded

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[1] Part XII of the series on Unsaturated Heterocyclic Systems. For part XI, see L. A. Paquette and L. D. Wise, *J. Org. Chem.*, **30**, 228 (1965).

[2] D. C. Dittmer and M. E. Christy, *ibid.*, **26**, 1324 (1961).

[3] W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Letters*, **No. 25**, 1677 (1963).

[4] D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

[5] A similar independent study has been carried out by D. C. Dittmer, N. Takashina, and F. A. Davis, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 69S.