the acid chloride in 10 ml. of benzene, a white precipitate formed immediately. After 20 minutes of refluxing, the solution was washed with dilute hydrochloric acid, dried and evaporated. The residual oil separated as a gum from petroleum ether. It was purified by crystallization from ethanol; white crystals, m.p. 175°.

Anal. Calcd. for $C_{31}H_{29}NO_2$: C, 83.19; H, 6.53. Found: C, 83.39; H, 6.83.

α-Methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyramide.—A stream of gaseous ammonia was bubbled through a solution of 0.40 g. of the β-keto acid chloride in 15 ml. of benzene for 40 minutes. The precipitated ammonium chloride was filtered; the oil left by evaporation of the solvent solidified when triturated with petroleum ether (b.p. 30–60°) but separated as a gelatinous mass from warm petroleum ether; 0.32 g. (84%). The amide was crystallized from ethanol–petroleum ether (b.p. 90–110°); m.p. 161°.

Anal. Calcd. for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78. Found: C, 80.70; H, 6.92.

Methyl α-Methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyrate.—Treatment of 2 g. of pure α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid or the benzene solvate in 25 ml. of ether with approximately 1 g. of diazomethane in 70 ml. of ether resulted in partial decolorization during the first fifth of the addition and complete decolorization after 2 days. After filtration and evaporation of the solvent, the residual oil was stirred with 25 ml. of petroleum ether (b.p. 90–110°). The crystals were purified from methanol–methyl acetate to give 1.67 g. (80%), m.p. 113–114°. A melting point of a mixture of the compound and the ester prepared by the reaction of the β-keto acid chloride with methanol showed no depression.

Refluxing of 0.40 g. of α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid chloride in 15 ml. of methanol for 3 hours and subsequent evaporation of the solvent gave an oil which crystallized; 0.30 g. (69%). Recrystallization from methanol was used for purification, m.p. 113–114°.

Anal. Calcd. for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.38; H, 7.09.

β-Keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric Acid.—The carbonation of the methyl phenyl-di-*o*-tolylcarbinyl ketone was carried out as described for the corresponding ethyl ketone. The acid was obtained in 31% yield. It was purified from petroleum ether (b.p. 30–60°), m.p. 158–159° (dec.). When heated above the melting point, decarboxylation to the original ketone occurred. This β-keto acid did not form a solvate with benzene.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.24; H, 6.19. Found: C, 80.35; H, 6.87.

The formation of α-methyl-β-keto-γ,γ,γ-triphenylbutyric acid from ethyl triphenylcarbinyl ketone and the formation of β-keto-γ,γ-diphenyl-γ-*o*-tolylbutyric acid from methyl diphenyl-*o*-tolylcarbinyl ketone by this procedure of carbonylation were unsuccessful.

URBANA, ILLINOIS

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, PHILLIPS PETROLEUM CO.]

Condensation of 1-Alkanols to Dialkylcarbinols

BY EDWARD E. BURGOYNE AND FRANCIS E. CONDON

RECEIVED JANUARY 14, 1952

1-Alkanols were converted, by passage over soda lime at 400° and 40 atmospheres, into dialkylcarbinols, apparently in accordance with equation (1). Mixtures of 1-alkanols gave corresponding intercondensation products. Minor amounts of a by-product were formed in accordance with the Guerbet reaction, equation (2). The yield of product alcohols was in many cases about 40–60% by weight of the 1-alkanol consumed, or about 55–67% of theoretical. When calcium oxide was used, products resulting from both reactions, $RCH_2CH_2CHRCH(OH)CH_2R$, were observed. Of several solids tested, soda lime appeared the most effective.

Introduction

In a study of base-induced reactions of alcohols, an apparently novel synthesis of dialkylcarbinols was effected by the action of soda lime on 1-alkanols. The reaction requires both elevated temperature and pressure, and takes place apparently in accordance with the equation

$$2RCH_2CH_2OH + Ca(OH)_2 \longrightarrow RCH_2CH(OH)CH_2R + CaCO_3 + 3H_2 \quad (1)$$

In a preliminary study of some aspects of this reaction, a variety of 1-alkanols and mixtures of 1-alkanols were subjected to the action of soda lime at 400° and 40 atmospheres and several solids other than soda lime were tested as condensing agents with 1-propanol.

Results

When 1-propanol was distilled over soda lime at atmospheric pressure, little change occurred until the temperature was increased to about 400°, whereupon copious evolution of gas set in with the formation of a complex liquid mixture of aldehydes, ketones, alcohols, water, propyl ether and possibly other compounds; 3-pentanone and 3-pentanol were identified, and together made up 40% of the weight of 1-propanol converted. Ethanol gave a large amount of acetaldehyde and an amount of 2-propanol corresponding to 21% of the weight of ethanol converted.

When the product from such an experiment with 1-propanol was hydrogenated over Raney nickel at 150° before distillation, the number of components was advantageously reduced, and the 3-pentanol amounted to 44% of the 1-propanol converted (60% of theory).

Data for several experiments at 40 atmospheres are presented in Table I. Under these conditions, the liquid product was relatively saturated, and 3-pentanol was the major product from 1-propanol. Some 2-methyl-1-pentanol was also formed, evidently by Guerbet's condensation[1]

$$2RCH_2CH_2OH \longrightarrow RCH_2CH_2CHRCH_2OH + H_2O \quad (2)$$

Straight-chain 1-alkanols, especially 1-propanol, 1-octanol and a mixture of these, gave good yields of dialkylcarbinols (Expts. 1–5). Branched-chain 1-alkanols did not give good yields. This is shown not only by Expt. 6 with 2-methyl-1-propanol, but also by experiments with 3-methyl-1-butanol and benzyl alcohol described in the Experimental part. In admixture with 1-propanol, 2-methyl-1-

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(1) M. Guerbet, *Compt. rend.*, **133**, 1220 (1901); **134**, 467 (1902); **146**, 298, 1407 (1908); **149**, 129 (1909); **150**, 183 (1910); **155**, 1156 (1913); C. Weizmann and S. F. Garrard, *J. Chem. Soc.*, **117**, 324 (1920).

TABLE I

CONDENSATION OF 1-ALKANOLS TO DIALKYLCARBINOLS AT 400° AND 40 ATMOSPHERES

Expt.	1	2	3	4	5	6	7	8	9	10	11	12
Condensing agent[a]	S-1							S-2	$Ca(OH)_2$	CaO	CaO	MgO
Wt., g.	103	107	103	100	104	105	106	134	102	178	117	149
Charge composition, wt. %												
Ethanol	....	....	....	....	....	....	....	....	....	....	100	....
1-Propanol	100	100	....	....	32	....	45	100	100	100	....	100
1-Butanol	....	....	100	....	....	....	....	....	....	....	....	....
1-Octanol	....	....	....	100	68	....	....	....	....	....	....	....
2-Methyl-1-propanol	....	....	....	....	....	100	55	....	....	....	....	....
Charge rate, mole/kg. solid/hour	7.0	7.0	5.4	2.8	3.3	4.7	8.6	7.3	9.4	3.7	9.2	6.8
Total time, hours	5.7	7.8	7.9	10.0	8.0	7.5	7.5	7.2	4.8	4.8	7.9	6.0
Product												
Gas, mole/mole charge	0.69[h]	0.40	0.50	0.77	0.53	0.61	0.47	0.39	0.51	0.88	0.31	0.07
Liquid, wt. % charge	83	82	79	91	80	74	87	87	61	58	51	94
Liquid composition, wt. %												
Water	4.8	2.5	9.0	4.6	1.8	3.0	2.9	4.6	1.9	....	....	3.2
Light ends	2.4	2.8	10.5	5.1	10.6	5.3	2.3	3.7	6.6	4.2	2.8	13.5[i]
1-Alkanol charged	60.9	73.2	68.4	59.0	45.0[j]	81.4	77.3[k]	73.2	59.3	24.7	67.0	74.4
2-Propanol	....	....	....	....	....	....	....	....	....	....	9.2[l]	....
3-Pentanol[b]	23.2	17.1	....	....	5.5	....	7.3	12.7	15.8	24.4	7.2[m]	2.3
2-Methyl-1-pentanol[c]	3.9	3.2	....	....	2.8	....	....	4.2	9.2	9.7	....	2.9
2-Methyl-3-pentanol[d]	....	....	....	....	....	....	6.5	....	....	....	....	....
4-Heptanol	....	....	5.4[n]	....	....	....	....	....	....	....	3.6[o]	....
3-Decanol[e]	....	....	....	....	14.6	....	....	....	....	....	....	....
8-Pentadecanol[f]	....	....	....	29.9	17.4	....	....	....	....	....	....	....
Other	4.8	1.2	6.7	1.4	2.3	10.3[p]	3.7	1.6	7.2	37.0[q]	10.2	3.7
Ultimate yield, wt. %[g]	44	42	9	59	50	....	37	41	24	36[r]	15	16

[a] Described in Experimental part. [b] B.p. 115°, n^{25}D 1.4079; α-naphthylurethan, m.p. 93–94°; 3,5-dinitrobenzoate, m.p. 99° (J. F. Norris and F. Cortese, THIS JOURNAL, **49,** 2645 (1927); B. T. Brooks, *ibid.*, **56,** 1998 (1934); V. Grignard, *Compt. rend.*, **132,** 336 (1901)). [c] B.p. 145–147°, n^{25}D 1.4148; α-naphthylurethan, m.p. 73–74.5° (A. Magnani and S. M. McElvain, THIS JOURNAL, **60,** 818 (1938)). [d] B.p. 126°, n^{20}D 1.4158; 3,5-dinitrobenzoate, m.p. 61–62°; 3-nitrophthalate, m.p. 147–149° (F. Hovorka, H. P. Lankelma and A. E. Axelrod, *ibid.*, **62,** 188 (1940); P. Sutter, *Helv. Chim. Acta*, **21,** 1270 (1938); A. Pukirev, *Trans. Inst. Pure Chem. Reagents* (*U.S.S.R.*), No. 16, 73 (1939); *C. A.*, **37,** 4686 (1943)). [e] B.p. about 215°, n^{20}D 1.4348; chromic acid oxidation gave 3-decanone which gave a semicarbazone m.p. 99–101° (R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103,** 1923 (1913)). [f] M.p. 43–46°; recrystallized from *n*-pentane, m.p. 49–50°; chromic acid oxidation gave 8-pentadecanone, m.p. 39–40° alone and 37–39° in admixture with 8-pentadecanol (P. Baumgarten, *Ber.*, **76B,** 213 (1943); M. Tut and M. Guyard, *Bull. soc. chim. France*, 1086 (1947); *C. A.*, **42,** 5833 (1948)). [g] Total of all product alcohols listed. [h] Analysis by mass spectrometry: H_2, 87.6; N_2 + CO, 6.6; O_2, 1.7; CO_2, 0.1; C_1, 0.6; C_2, 0.9 mole per cent. [i] Apparently contained propylene, propionaldehyde, methylpentenes and other olefins, and propyl ether. [j] 1-Propanol 10.9, 1-octanol 34.1. [k] 1-Propanol 23.7, 2-methyl-1-propanol 53.6. [l] Estimated from boiling range and refractive index of ethanol-2-propanol fraction. [m] 2-Pentanol, b.p. 117°, n^{20}D 1.4072; 3,5-dinitrobenzoate, m.p. 56–59° (G. B. Malone and E. E. Reid, THIS JOURNAL, **51,** 3426 (1939)). [n] Identity uncertain; b.p. about 150°, n^{20}D 1.4117. [o] Identity uncertain; b.p. 152–155°, n^{20}D 1.4220 (R. T. Dillon and H. J. Lucas, THIS JOURNAL, **50,** 1712 (1928)). [p] The expected 2,4-dimethyl-3-pentanol appeared to be negligible. [q] Apparently 19.6% 4-methyl-3-heptanol: b.p. 175°, n^{20}D 1.4263. Attempts to prepare solid derivatives were unsuccessful; but comparison of the infrared spectrum with that of synthetic 4-methyl-3-heptanol, and of the spectra of the corresponding ketones obtained by chromic acid oxidations, showed qualitative correlation. [r] Includes the 4-methyl-3-heptanol (note *q*).

propanol gave a fair yield of the intercondensation product, 2-methyl-3-pentanol (Expt. 7), and benzyl alcohol gave some of the Guerbet product, 2-benzyl-1-propanol (Experimental part).

With the branched-chain 1-alkanols, there was an annoying tendency for the reaction tube to become clogged, apparently by calcium salts of the corresponding acids, for the unmistakable odor of these acids became very evident when the tube was being cleaned with hydrochloric acid following these experiments.

Because the soda lime used in Expt. 1–7 was found by analysis to comprise over 90% calcium hydroxide, pure calcium hydroxide and calcium oxide were tested as condensing agents. Data for these tests are included in Table I. These bases were less satisfactory condensing agents than soda lime and promoted relatively more of the Guerbet reaction (Expts. 9–11). Small amounts of magnesium hydroxide, sodium hydroxide, silica and/or other substances present in the soda lime used in Expts. 1–7 apparently had a beneficial effect in promoting (1) and excluding (2) to some extent.

With calcium oxide in Expt. 10, the conversion of 1-propanol was very high, and higher condensation products were formed to a considerable extent. One of these in particular, 4-methyl-3-heptanol, identified by means of infrared spectrophotometry, conceivably was produced either by a condensation of 1-propanol with 2-methyl-1-pentanol analogous to equation (1), or by a condensation of 1-propanol with 3-pentanol analogous to equation (2). In either case, in order for such a product to be formed, it appears that the condensing agent must promote extensive reaction according to both (1) and (2). Analogous to the formation of 4-methyl-3-heptanol from 1-propanol, 2-pentanol was produced from ethanol by calcium oxide (Expt. 11).

A second sample of soda lime (S-2), with relatively high magnesium and water contents, was a less satisfactory condensing agent than the low-magnesium soda lime (S-1), and promoted relatively more of the Guerbet reaction (2) (Expt. 8). Magnesium oxide itself gave condensation products from 1-propanol, but the yields were low, much of the alcohol being consumed in side reactions (Expt. 12).

Equation (1) is supported by the presence of hydrogen and absence of carbon monoxide in the exit gases and by the presence of bound carbon dioxide in the spent soda lime. The latter is therefore properly considered a reagent rather than a catalyst.

Several other substances were tested with 1-propanol at 400° and 40 atmospheres in the hope that they would function as catalysts. These were: chromium oxide, thorium oxide, a commercial copper–chromium oxide hydrogenation catalyst (57% chromia–43% cupric oxide), sodium silicate, calcium silicate, a calcium borosilicate precipitated with calcium chloride solution from a solution of sodium metasilicate and borax, and a calcium phosphatosilicate precipitated with calcium chloride solution from a solution of sodium metasilicate and dibasic sodium phosphate.

None of these substances was as effective as soda lime for the condensation of 1-propanol to 3-pentanol. But copper–chromium oxide, at 350° and with about two moles of hydrogen added per mole of alcohol, effectively catalyzed the condensation of 1-propanol to the Guerbet product, 2-methyl-1-pentanol. The yield was 27% by weight of the 1-propanol consumed (32%).

Discussion

The transformation corresponding to equation (1) conceivably occurs by either of the following mechanisms which make use of simpler known reactions

Mechanism I[2]

$$\text{(a)}\quad 2RCH_2CH_2OH \longrightarrow 2RCH_2CHO + 2H_2 \quad \text{(dehydrogenation)}$$

$$\text{(b)}\quad 2RCH_2CHO \longrightarrow RCH_2CH(OH)CHRCHO \quad \text{(aldol condensation)}$$

$$\text{(c)}\quad RCH_2CH(OH)CHRCHO \longrightarrow RCH_2CH(OH)CH_2R + CO \quad \text{(decarbonylation)}$$

$$\text{(d)}\quad CO + H_2O \longrightarrow CO_2 + H_2$$

$$\text{(e)}\quad Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \quad \text{(neutralization)}$$

Mechanism II

$$\text{(a)}\quad 2RCH_2CH_2OH + 2H_2O \longrightarrow 2RCH_2COOH + 4H_2 \quad \text{(oxidation by water)}^{3}$$

$$\text{(b)}\quad 2RCH_2COOH \longrightarrow RCH_2COCH_2R + CO_2 + H_2O \quad \text{(ketonic decomposition)}^{4}$$

$$\text{(c)}\quad RCH_2COCH_2R + H_2 \longrightarrow RCH_2CH(OH)CH_2R \quad \text{(hydrogenation)}$$

$$\text{(d)}\quad Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \quad \text{(neutralization)}$$

The data do not permit an unequivocal choice between these mechanisms. Mechanism I accounts in part for the Guerbet by-product sometimes found in small amounts, for such a by-product could be formed from the aldol condensation product of reaction Ib *via* dehydration followed by hydrogenation[5]; and if reaction Ic is understood as a combination of (A) dehydrogenation of the aldol to an aldehydic ketone, (B) decarbonylation of the aldehydic ketone to a dialkyl ketone, and (C) hydrogenation of the dialkyl ketone to a dialkylcarbinol, this mechanism accounts for the dialkyl ketone found in the product obtained at atmospheric pressure, and the effect of higher pressure is understood as favoring the hydrogenation of the dialkyl ketone.

While Mechanism II does not allow for the Guerbet by-product, it accounts for the above-mentioned formation of alkanoic acids in the experiments with 2-methyl-1-propanol and 3-methyl-1-butanol, which gave poor yields of condensation products. That is, with these alcohols, it appeared that the process was aborted at the stage of reaction IIa.

Experimental

Materials.—The alcohols were commercial products having the following refractive indices: ethanol, $n^{25}D$ 1.3629; 1-propanol, $n^{25}D$ 1.3842; 1-butanol, $n^{25}D$ 1.3967; 1-octanol, $n^{18}D$ 1.4301; 2-methyl-1-propanol, $n^{25}D$ 1.3935; 3-methyl-1-butanol, $n^{25}D$ 1.4047; benzyl alcohol, $n^{20}D$ 1.5373.

The condensing agents are identified as follows: S-1: Eimer and Amend 4–8 mesh, low moisture, "Wilson" type soda lime, total basicity, 25.22 milliequivalents OH^-/g. *Anal.* Ca (as calcium hydroxide), 91.5; Mg (as magnesium hydroxide), 1.0; Na (as sodium hydroxide), 0.7; silica, 0.6; water, 2.1; other, 4.1. S-2: Eimer and Amend 4–8 mesh, high moisture, "Wilson" type soda lime, total basicity, 22.47 milliequivalents OH^-/g. *Anal.* Ca (as calcium hydroxide), 64.2; Mg (as magnesium hydroxide), 19.4; Na (as sodium hydroxide), 0.9; water, 13.4; other, 2.1. $Ca(OH)_2$ and CaO were J. T. Baker C.P. grade, and were pilled with Sterotex to $^1/_8$-inch pills. MgO was a commercial magnesia catalyst, $^5/_{32}$-inch pills.

Procedure.—In preliminary experiments at atmospheric pressure, 1-propanol was distilled from a 125-ml. flask through a glass tube, 20 mm. × 40 cm., the first 10 cm. comprising a preheating section wrapped with resistance wire and packed with glass wool, the last 30 cm. being packed with soda lime (S-1) and heated in a tube furnace. The effluent from the catalyst tube passed through a condenser to a receiver, thence through a Dry-Ice trap and a wet test meter.

For experiments at elevated pressure, the alcohol was pumped by a Bosch Diesel injector pump into the top of a 1-inch stainless steel tube, 1 m. long, enclosing a centrally positioned $^1/_4$-inch steel tube extending its entire length, which served as a thermocouple well, and containing about 65 cm. (about 167 cc.) of condensing agent heated in a four-section tube furnace about 76 cm. long. The product was released from the bottom of the tube through a motor valve controlled by a Taylor Fulscope pressure controller and was passed through a water-cooled condenser to a receiver, thence through an ice-cooled trap, a Dry-Ice trap, and a wet test meter. Temperature in the reaction tube was measured by means of four about equally spaced thermocouples and was controlled by means of four Variacs regulating the four independent heating sections of the tube furnace.

Product Analysis.—The liquid product was distilled in a Podbielniak Hypercal column, 1 m. × 13 mm. inside diameter. Components were identified by means of boiling point, refractive index and the preparation of solid derivatives.

Attempted Condensation of 3-Methyl-1-butanol to 2,6-Dimethyl-4-heptanol at 400° and 40 Atmospheres.—3-Methyl-1-butanol, charged at a rate of 4.3 mole/kg. soda lime/hr., produced gas amounting to 0.63 mole/mole and 68% of liquid product with the composition:

Water	3.4% by weight
Light ends	6.3
3-Methyl-1-butanol	82.9
2,6-Dimethyl-4-heptanol[a]	5.8[b]
Other	2.5

[a] Identity uncertain; b.p. 167–198°, $n^{20}D$ 1.423. [b] Ultimate yield 9%.

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[2] *Cf.* V. I. Komarewsky and J. R. Coley, THIS JOURNAL, **63**, 700, 3269 (1941).

[3] *Cf.* M. Guerbet, *Compt. rend.*, **153**, 1487 (1912); E. E. Reid, H. Worthington and A. W. Larchar, THIS JOURNAL, **61**, 99 (1939).

[4] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, pp. 200–202.

[5] C. Weizmann, E. Bergmann and L. Haskelberg, *Chemistry & Industry*, **56**, 587 (1937).

Attempted Condensation of 1-Propanol with Benzyl Alcohol to 1-Phenyl-1-propanol at 400° and 40 Atmospheres.—A mixture of benzyl alcohol (64% by weight) and 1-propanol (36%), charged at a rate of 5.5 mole/kg. soda lime/hr., produced gas amounting to 0.41 mole/mole and 83% of a complex liquid product containing

Water	8.7% by weight
Benzene[a]	4.3
1-Propanol	19.3
3-Pentanol	2.5
2-Methyl-1-pentanol	1.1
Toluene[b]	4.8
Benzyl alcohol	21.6
Benzaldehyde[c]	4.9
2-Benzyl-1-propanol[d]	8.9
Other	23.9

[a] Azeotrope with water; b.p. 67°, $n^{20}\mathrm{D}$ 1.4712 after separation from water. [b] Azeotrope with 1-propanol; b.p. 97°, $n^{20}\mathrm{D}$ 1.4942 after washing with water and drying. [c] B.p. 177–179°, $n^{20}\mathrm{D}$ 1.5454; by Cannizzaro reaction with concentrated aqueous KOH gave benzoic acid, m.p. 120.5–122°. [d] B.p. 91° (2 mm.), $n^{20}\mathrm{D}$ 1.5296; oxidation with acidic potassium permanganate, followed by treatment with thionyl chloride, then ammonia, gave 2-benzylpropanamide,[6] m.p. 105–106.5°.

Acknowledgments.—Chemical analyses were performed by Miss Dottie Carter, Mr. B. B. Buchanan and Mr. J. F. Eberle. Spectrometric analyses were performed by Mr. J. A. Favre, Mr. H. A. Price and Mr. H. W. Rollmann. Phillips Petroleum Company granted permission to publish the data.

(6) L. Edeleanu, *Ber.*, **20**, 618 (1887).

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

α,β-Unsaturated Sulfonyl Compounds in the Diels–Alder Reaction. II

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RECEIVED MARCH 20, 1952

β-Benzoylvinyl phenyl sulfone is found to be an active dienophile, giving adducts with cyclopentadiene, 2,3-dimethylbutadiene, isoprene and butadiene in excellent yields. These adducts have been obtained only as high-boiling viscous oils, but crystalline dibromides or dinitrophenylhydrazones are readily formed from them. Anthracene gives a crystalline adduct; furan does not react under any conditions tried. 1,2-Di-*p*-toluenesulfonylethylene also is an active dienophile; crystalline adducts are formed in almost quantitative yield from the simple diolefins, but none has been obtained from furan. Anthracene gives two crystalline adducts, presumably the *meso* and racemic forms.

Previous work in this Laboratory[1] has indicated that a single sulfonyl group imparts a significant dienophilic activity to a double bond on which it resides. The purpose of the present work was to extend this study to compounds in which the double bond is activated by both a sulfonyl and a carbonyl group, and by two sulfonyl groups. The addition of butadiene to a compound in which the double bond was activated by both a sulfonyl and a carbonyl group, 1,4-thiapyrone-1-dioxide was reported by Fehnel and Carmack,[2] but no further investigations of the dienophilic properties of this compound were made.

trans-β-Benzoylvinyl phenyl sulfone was prepared by the method of Kohler and Larsen.[3] β-Chloropropiophenone was condensed with sodium benzenesulfinate to give β-benzoylethyl phenyl sulfone. Treatment with bromine in chloroform converted this material to β-bromo-β-benzoylethyl phenyl sulfone, and dehydrobromination was effected by methanolic potassium acetate. The product was the pure *trans* isomer; it was treated with the same dienes that Adams and Gold[4] used with *trans*-dibenzoylethylene.

trans-β-Benzoylvinyl phenyl sulfone was found to be a very reactive dienophile. The reactions with cyclopentadiene and 2,3-dimethylbutadiene were essentially complete in about five minutes at room temperature in benzene solution. Isoprene and butadiene reacted somewhat more slowly, but gave comparable yields of the adducts (*ca.* 95%). Furan did not form an adduct in refluxing benzene solution, but the possibility of reaction under more vigorous conditions is not excluded. Anthracene did not form an adduct in refluxing benzene solution, but fusion of the reactants resulted in the formation of the adduct. The anthracene adduct was a solid, but all the others were viscous, high-boiling oils; they were analyzed as the crystalline dibromides or dinitrophenylhydrazones.

The Diels–Alder reaction always involves *cis*-addition of the diene to the multiple bond of the dienophile. Since the diene reactions were carried out only with the pure *trans*-β-benzoylvinyl phenyl sulfone, the *trans* relationship of the benzoyl and benzenesulfonyl groups must be retained in the adducts. Each adduct derived from a symmetrical diene therefore should consist of a single racemate. In the case of the unsymmetrical diene, isoprene, addition could occur in either one of two directions or in both directions simultaneously. Either of, or a mixture of, two racemates could be produced. It seems unlikely that a single, apparently pure (sharp-melting) dibromide could have been isolated if the adduct were a mixture of racemates, and hence it is believed that the diene addition proceeded in one direction almost exclusively. The direction of addition has not been determined.

1,2-Di-*p*-toluenesulfonylethylene (probably *trans*) was prepared by a modification of the method of Fromm and Seibert.[5] The first step in the synthesis involves the condensation of *p*-thiocresol

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(1) H. R. Snyder, H. V. Anderson and D. P. Hallada, THIS JOURNAL, **73**, 3258 (1951); see also C. S. Rondestvedt and J. C. Wygant, *ibid.*, **73**, 5785 (1951).

(2) E. Fehnel and M. Carmack, *ibid.*, **70**, 1813 (1948).

(3) E. P. Kohler and R. G. Larsen, *ibid.*, **57**, 1448 (1935).

(4) R. Adams and M. Gold, *ibid.*, **62**, 56 (1940).

(5) E. Fromm and E. Seibert, *Ber.*, **55**, 1014 (1922).